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Runnerstrom, Evan Lars

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Charge transport in metal oxide nanocrystal-based materials

by

Evan Lars Runnerstrom

A dissertation submitted in partial satisfaction of the

requirements for the degree of

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in

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in the

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of the

University of California, Berkeley

Committee in charge:

Professor Ting Xu, Co-chair

Professor Delia Milliron (Research Advisor), University of Texas, Austin, Co-chair

Professor Fiona Doyle

Professor Nitash Balsara

Summer 2016

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Abstract

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There is probably no class of materials more varied, more widely used, or more ubiquitous than metal oxides. Depending on their composition, metal oxides can exhibit almost any number of properties. Of particular interest are the ways in which charge is transported in metal oxides: devices such as displays, touch screens, and smart windows rely on the ability of certain metal oxides to conduct electricity while maintaining visible transparency. Smart windows, fuel cells, and other electrochemical devices additionally rely on efficient transport of ionic charge in and around metal oxides.

Colloidal synthesis has enabled metal oxide nanocrystals to emerge as a relatively new but highly tunable class of materials. Certain metal oxide nanocrystals, particularly highly doped metal oxides, have been enjoying rapid development in the last decade. As in myriad other materials systems, structure dictates the properties of metal oxide nanocrystals, but a full understanding of how nanocrystal synthesis, the processing of nanocrystal-based materials, and the structure of nanocrystals relate to the resulting properties of nanocrystal-based materials is still nascent. Gaining a fundamental understanding of and control over these structure-property relationships is crucial to developing a holistic understanding of metal oxide nanocrystals. The unique ability to tune metal oxide nanocrystals by changing composition through the introduction of dopants or by changing size and shape affords a way to study the interplay between structure, processing, and properties.

This overall goal of this work is to chemically synthesize colloidal metal oxide nanocrystals, process them into useful materials, characterize charge transport in materials based on colloidal metal oxide nanocrystals, and develop ways to manipulate charge transport. In particular, this dissertation characterizes how the charge transport properties of metal oxide nanocrystal-based materials depend on their processing and structure. Charge transport can obviously be taken to mean the conduction of electrons, but it also refers to the motion of ions, such as lithium ions and protons. In many cases, the transport of ions is married to the motion of electrons as well, either through an external electrical circuit, or within the same material in the case of mixed ionic electronic conductors. The collective motion of electrons

over short length scales, that is, within single nanocrystals, is also a subject of study as it pertains to plasmonic nanocrystals. Finally, charge transport can also be coupled to or result from the formation of defects in metal oxides. All of these modes of charge transport in metal oxides gain further complexity when considered in nanocrystalline systems, where the introduction of numerous surfaces can change the character of charge transport relative to bulk systems, providing opportunities to exploit new physical phenomena.

Part I of this dissertation explores the combination of electronic and ionic transport in electrochromic devices based on nanocrystals. Colloidal chemistry and solution processing are used to fabricate nanocomposites based on electrochromic tin-doped indium oxide (ITO) nanocrystals. The nanocomposites, which are completely synthesized using solution processing, consist of ITO nanocrystals and lithium bis(trifluoromethylsulfonyl)amide (LiTFSI) salt dispersed in a lithium ion-conducting polymer matrix of either poly(ethylene oxide) (PEO) or poly(methyl methacrylate) (PMMA). ITO nanocrystals are prepared by colloidal synthetic methods and the nanocrystal surface chemistry is modified to achieve favorable nanocrystal-polymer interactions. Homogeneous solutions containing polymer, ITO nanocrystals, and lithium salt are thus prepared and deposited by spin casting. Characterization by DC electronic measurements, microscopy, and x-ray scattering techniques show that the ITO nanocrystals form a complete, connected electrode within a polymer electrolyte matrix, and that the morphology and properties of the nanocomposites can be manipulated by changing the chemical composition of the deposition solution. Careful application of AC impedance spectroscopy techniques and DC measurements are used to show that the nanocomposites exhibit mixed ionic and electronic conductivity, where electronic charge is transported through the ITO nanocrystal phase, and ionic charge is transported through the polymer matrix phase. Additionally, systematic changes in ionic and electronic conductivity with morphology are measured. The synthetic methods developed here and understanding of charge transport ultimately lead to the fabrication of a solid state nanocomposite electrochromic device based on nanocrystals of ITO and cerium oxide.

Part II of this dissertation considers electron transport within individual metal oxide nanocrystals themselves. It primarily examines relationships between synthetic chemistry, doping mechanisms in metal oxides, and the accompanying physics of free carrier scattering within the interior of highly doped metal oxide nanocrystals, with particular mind paid to ITO nanocrystals. Additionally, synthetic methods as well as metal oxide defect chemistry influences the balance between activation and compensation of dopants, which limits the nanocrystals' free carrier concentration. Furthermore, because of ionized impurity scattering of the oscillating electrons by dopant ions, scattering must be treated in a fundamentally different way in semiconductor metal oxide materials when compared with conventional metals. Though these effects are well understood in bulk metal oxides, further study is needed to understand their manifestation in nanocrystals and corresponding impact on plasmonic properties, and to develop materials that surpass current limitations in free carrier concentration and mobilities. In particular, efforts to address these limitations by developing new nanocrystal materials (with careful consideration of structure-property relationships) are described. Synthetic control of nanocrystal shape is also explored. Each of these topics have

implications in determining the properties of localized surface plasmon resonances (LSPRs) in these nanocrystals.

Part II culminates as the defect chemistry of metal oxides is identified as a major factor influencing LSPR and charge transport in doped metal oxide nanocrystals. Aliovalent dopants and oxygen vacancies act as centers for ionized impurity scattering of electrons, and this electronic damping leads to lossy, broadband LSPR with low quality factors, limiting applications that require near field concentration of light. However, the appropriate dopant can mitigate ionized impurity scattering. Herein, the synthesis and characterization of a novel doped metal oxide nanocrystal material, cerium-doped indium oxide ($\text{Ce}:\text{In}_2\text{O}_3$) is described. $\text{Ce}:\text{In}_2\text{O}_3$ nanocrystals display tunable mid-infrared LSPR with exceptionally narrow line widths and the highest quality factors observed for nanocrystals in this spectral region. Drude model fits to the spectra indicate that a drastic reduction in ionized impurity scattering is responsible for the enhanced quality factors, and high electronic mobilities reaching $33 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ are measured optically, well above the optical mobility for ITO nanocrystals. The microscopic mechanisms underlying this enhanced mobility are investigated with density functional theory calculations, which suggest that scattering is reduced because cerium orbitals do not hybridize with the In orbitals that dominate the bottom of the conduction band. Ce doping may also reduce the equilibrium oxygen vacancy concentration, further enhancing mobility. Absorption spectra of single $\text{Ce}:\text{In}_2\text{O}_3$ nanocrystals are used to determine the dielectric function, and simulations predict strong near field enhancement of mid-IR light, especially around the vertices of $\text{Ce}:\text{In}_2\text{O}_3$ nanocubes.

Part III examines how the defect chemistry of metal oxides can be used to manipulate not only electronic transport, but also ionic transport in materials that are relevant for high temperature electrochemistry. Over the past few years, the observation of unexpected but significant proton conductivity in porous, nanocrystalline ceramics has generated substantial scientific interest mirroring the excitement surrounding ionic conduction in other nanostructured or porous materials. Numerous studies, to varying degrees of success, have attempted to describe or control the mechanisms that enable proton motion in nanocrystalline ceramics. Here, colloidally synthesized ceramic nanocrystals of cerium oxide (CeO_2) and titanium oxide (TiO_2) are utilized to systematically study how grain size, microporosity, and composition influence proton conduction. By measuring the temperature-dependent impedance of porous thin films of these nanocrystals under dry and wet atmospheres, it was found that both CeO_2 and TiO_2 display significant proton conductivity at intermediate temperatures between 100°C and 350°C . Furthermore, oxygen activity strongly impacts proton transport; using oxygen as a carrier gas drastically reduced the proton conductivity by up to 60 times. Together, these results suggest that the most likely source of mobile protons in these systems is dissociative adsorption of water at surface oxygen vacancies, with composition, nanocrystal size, and oxide defect equilibria influencing the surface activity toward this reaction and hence the proton conductivity.

For my late father, and my mother, who has more than offset his absence.

And when the event, the big change in your life, is simply an insight—isn't that a strange thing? That absolutely nothing changes except that you see things differently and you're less fearful and less anxious and generally stronger as a result: isn't it amazing that a completely invisible thing in your head can feel realer than anything you've experienced before?

—Jonathan Franzen, *The Corrections*

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life interesting and hilarious in and out of lab. Gary: you haven't been my roommate for as long as Rob, but I have been your guardian angel since you joined the group. It's a role I've deeply enjoyed playing over the past four years, not because you really needed it, but because it brought me so much satisfaction to see you succeed while imagining that I may have had a little something to do with it, even if it was really all you. I know that sometimes I can hassle you, but it's more in the way I would hassle a little brother. You've always had my back in lab, at home, and at beam time. Thanks for some great scientific discussions and for teaching me a lot about cooking and GISAXS. Clay: it has been awesome being your roommate, because I know I can always count on you to enjoy and eat my cooking. Eating habits aside, thanks for being the glue that holds Fresh House together. Thank you also for collecting some great XAS data for my projects, and for helping me understand what little I do about XAS. Memo: thanks for convincing me to join Delia's group. With a smile always on your face, your work ethic, intelligence, collaborative spirit, and warmth towards others makes you the prototypical group member that makes DMG great. Thanks for teaching me nearly everything I know about hands-on electrochemistry and for launching the electrochromics projects that kept me busy and funded. Thanks also for showing me how to stay sane as an engineer surrounded by chemists, and for some hard-fought fantasy football match ups. Sebastien: upon joining the group, it didn't take long for us to become good friends and even better collaborators. Our work together on ITO plasmons was truly exhilarating and I hope that together we have established a long lasting and productive research theme for the group. Thanks for being a great guy to talk science with and to grab a beer with. I'll always remember our trip to your cabin in Michigan along with Memo and Anna, after which I still haven't stopped thinking about whitefish pate. Marissa: we didn't get to interact much before you graduated, but thank you for teaching me how to use the Schlenk line and vacuum manifold safely, and for always asking how I'm doing at the holiday party. Ankit (aka Simulator): few people could have simulated the way in which you have become an indispensable member of the group and Team Plasmon. I am so impressed by your ability to understand and model the physics and chemistry of nearly every project in the group. I'm glad I had the distinction of training you three years ago. Corey: your grasp of electron transport in nanocrystals is simply astonishing to me. Thanks for always being available when I wanted to bro out, and for being a valuable LoL teammate. Sungyeon: your work ethic is quite impressive. You have not only taken on a difficult research project and been successful, but you have also dedicated yourself to performing an inordinate number of critical tasks to keep our lab running smoothly. Nothing more reliably gains my respect. Camila: I am so glad I met you during your UT visit weekend back in April of 2014, and that I was able to convince you to not only come to UT, but to join our research group. Since then, you've become a great friend and a star graduate student, and I am consistently impressed with your work in lab and your contributions to our group's science and social dynamic. I think you are the next MVP of the group. Shin: you've made great strides in lab in a pretty short time. I suspect that you are the next nanocrystal synthesis god of DMG. Lauren: when you visited our lab at LBNL, I knew you would make a great DMG member. Thankfully, after helping to convince you to come to UT and join Delia's group, I now know

I was right. I can't wait to see all of the great and exciting work you'll do on VO₂.

I also want to take a moment to thank all of the following visitors to our group: Ilka, Ann-Katrin, Franziska, Ilknur, Luca, Lukas, Susanne, and Anthony. You all never failed to befriend me or anyone else, and made the group more exciting, dynamic, and diverse. Thanks also to those undergraduate visitors who I mentored: Max, Brad, and Vincent. Thanks for giving me the enjoyable experience of mentoring you and helping me out with my research. I hope I was able to teach you something!

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Chapter 1

Introduction, motivation, and background

1.1 Prologue: the ubiquity of metal oxides

Oxygen is the most abundant element on Earth. This simple fact, combined with oxygen's electronegative and reactive nature, means that almost every other element on earth is found as an oxide or hydroxide. It is little surprise then that nearly all of Earth's silicon, the second most abundant element, is sequestered as silica or silicate minerals. Likewise, hydrogen, the tenth most abundant element on Earth, forms what is undoubtedly the most important oxide on our planet. To the uninitiated, oxides may seem to lack technological importance and rather present a barrier to creating interesting and advanced materials; after all, elemental silicon (arguably the most important technological substance on Earth) is literally mined from sand. Solar power would surely be cheaper and more ubiquitous if elemental silicon were easier to come by. Even when we do manage to extract elements from their oxides, which humans have been doing since the Bronze Age, they tend to revert. Owners of automobiles in cities that use salt to melt ice and anyone who has left a cast iron skillet soaking in the sink will attest to this phenomenon. As inconvenient as oxides may seem, they are a fact of life.

Thankfully, humanity has managed to exploit this fact of life, and we have discovered numerous ways to use oxides themselves in technical applications. Oxide materials, particularly metal oxides, present a huge breadth of interesting and useful electronic and electrochemical properties, ranging from insulating behavior to semiconducting properties to excellent electronic conduction, ionic conduction, highly reversible redox properties, and even mixed electronic-ionic conduction. Many transition metal oxides display unique magnetic properties, including ferromagnetism, magnetic-electronic coupling, multiferroicity, and superconductivity. These properties are put to work for enormously important applications, including integrated circuits, where oxides like silicon oxide, zirconium oxide, and hafnium oxide are used as excellent insulators for gate dielectrics in metal oxide semiconductor field effect tran-

sistors. Other important examples include transparent conducting oxides (e.g., tin-doped indium oxide), used in displays, touchscreens, and solar panels, transition metal oxides (e.g., titanium oxide), used for lithium ion batteries and catalysis, rare earth oxides (e.g., cerium oxide), used in solid oxide fuel cells, magnetics, and catalysis, and oxide glasses (e.g., silicon oxide), used for optical lenses, windows, architecture, and to contain beverages. As our understanding of the physical and chemical properties of oxides grows, along with our ability to apply these properties, so too does our ability to synthesize oxides with techniques offering increasingly precise control over size, shape, and composition. Among these techniques are sputtering, chemical vapor deposition (CVD), atomic layer deposition, pulsed laser deposition, molecular beam epitaxy (MBE), spark plasma sintering, hydro- or solvothermal synthesis, and colloidal synthesis, the last of which will be the focus of this dissertation.

In many cases, these synthetic techniques can also be used to create nanostructured metal oxides. For example, MBE can be used to grow well-defined, high quality nanostructured “islands”, while CVD has been leveraged to grow Si and other nanowires, and sintering processes can be manipulated to create engineered nanoporosity. These techniques present a number of disadvantages, however, such as cost and complexity, the need for lithography and other patterning steps, or poor control over nanostructure morphology. By contrast, solution-phase colloidal synthesis has emerged as a robust and straightforward method for synthesizing discrete nanoscale crystallites, hereafter referred to as colloidal nanocrystals, or simply nanocrystals. Control over size and shape, composition, and their colloidal nature means that nanocrystals are easy to work with and remain discrete. The ability to use solution processing and the discrete nature of nanocrystals is useful both for scientific study and eventual applications, as solution-phase synthesis can be scaled up cheaply and solution processing is potentially much cheaper than vacuum-based processes like sputtering. Nanocrystals are particularly interesting from a scientific perspective as their high surface area-to-volume ratio means that a significant portion of the nanocrystal has surface-like character. For example, in a tin-doped indium oxide (ITO) nanocrystal 4 nm in diameter, nearly one third of the atoms in the nanocrystal could be considered to be surface atoms (Figure 1.1). This high specific surface area leads to unique interactions between nanocrystals and their environment. This gives rise to new and unique properties that are not necessarily observed in larger or bulk versions of the same material. Studying these unique nanoscale properties will hopefully lead to greater understanding and the ability to harness nanocrystals not only for new applications, but also to create new paradigms for applications based on bulk materials that may be already established or “stale”.

This dissertation specifically considers colloidal metal oxide nanocrystals that can be used in three different applications with potential real-world impact. These are:

1. Smart windows, or electrochromic windows, which can dynamically change their transmittance and optical properties in response to electricity. Metal oxide nanocrystals are changing the way we think about and design smart windows, and have enabled the invention of a new type of smart window, based on localized surface plasmon resonance, that can selectively block near infrared and visible light.

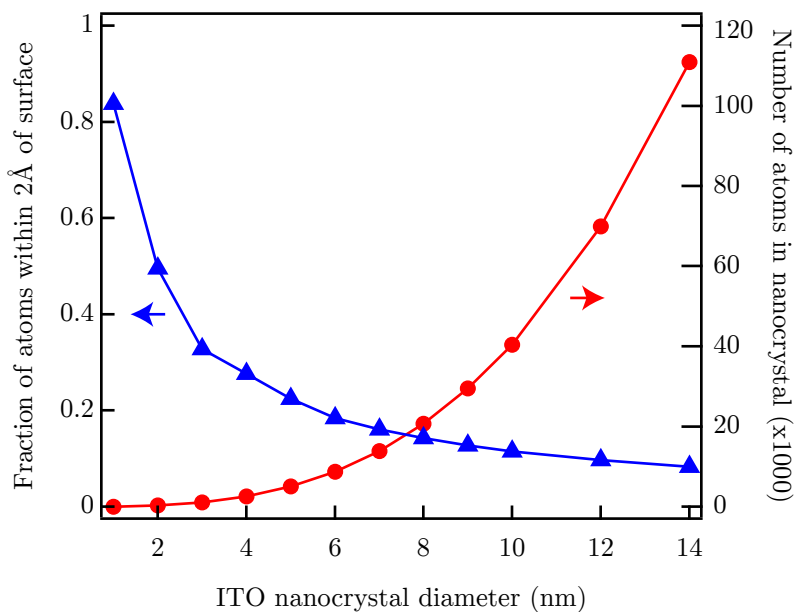


Figure 1.1: The number of atoms in an ITO nanocrystal and the fraction of atoms within 2 Å of the surface vs. nanocrystal diameter.

2. Localized surface plasmon resonance (LSPR), a phenomenon in which all of the conduction electrons in a nanocrystal oscillate collectively in resonance with incident light. Not only can plasmonic nanocrystals be used in smart windows, but they can be used for advanced optics, spectroscopy, and sensors. Metal oxide nanocrystals have emerged as highly tunable routes towards plasmonic materials with optical features in the near infrared and mid infrared spectrum.
3. Proton conducting ceramic materials. Thin films of certain porous metal oxide ceramic nanocrystals have been found to support proton conduction, even though dense versions of the same material exhibit no proton conductivity. This has positive implications for intermediate temperature fuel cell electrolytes and other electrochemical devices.

The common thread among each of these applications is the importance of charge transport. Electrochromic windows rely on the transport of electrons between nanocrystals and the transport of ions to and from nanocrystal surfaces. LSPR relies on the collective transport of all electrons within individual nanocrystals. Proton conducting electrolytes rely on the generation and transport of free protons on nanocrystal surfaces. I have extensively studied the charge transport mechanisms in each of these cases, and how the physical properties of metal oxide nanocrystals and materials based on them influences charge transport. Ultimately, this dissertation develops new understanding of how fundamental materials science principles and nanocrystal processing and chemistry can be utilized to manipulate and tune charge transport in these systems.

1.2 Methodology and selected characterization methods for metal oxide nanocrystals and nanocrystal-based materials

1.2.1 Colloidal nanocrystal synthesis

The synthetic basis for this work is the solution-phase synthesis of colloidal metal oxide nanocrystals. Solution-phase synthesis is a powerful technique that allows production of nanoscale crystals with sizes ranging from 1 to 100 nm, and the surfactants (also referred to as ligands) that are employed in this technique confer colloidal stability to the nanocrystals, a critical advantage. Other advantages include the ability to precisely control size, shape, and monodispersity of colloidal nanocrystals,^{1–3} which is often not easily achieved with other physical (i.e., ball milling) techniques for making nanocrystals. The colloidal stability of nanocrystals makes them amenable to solution processing, flexible and tunable surface functionalization, and easy film deposition and self-assembly complex structures and superlattices.³ Recent synthetic developments in nanocrystal synthesis have increased the chemical versatility of the technique, which can now be used to produce metallic, doped and undoped semiconductor, and doped and undoped metal oxide nanocrystals, among other materials.⁴

A popular method for synthesizing colloidal metal oxide nanocrystals involves standard Schlenk line techniques to maintain an inert atmosphere around the reaction solution, so as to avoid complications from ambient water or air, which can alter reaction pathways and destabilize the colloid. Metal salts, often carboxylates, alkoxides, or halides, are used as the precursors for the desired nanocrystal formulation, and it has recently become possible to create doped and alloyed nanocrystals, thanks to a better understanding of precursor reactivity and decomposition kinetics with the help of fundamental chemical principles and techniques, such as hard-soft acid base theory and nuclear magnetic resonance studies.^{4–9} In a typical synthesis, the metal precursors are mixed with an appropriate solvent and surfactant and heated up to 180–350°C to decompose the precursors and form nanocrystals. Often, a nucleophilic initiating agent is also included in the reaction; since many metal precursors are carboxylates, nucleophiles such as alkyl amines and alkyl alcohols attack the metal carboxylates to decompose them *via* SN₁ or SN₂-type reactions, a reaction mechanism that has been well-observed and characterized in the literature. The use of nucleophilic reactants provides additional control over nanocrystal synthesis, as they can be used to further tune the reactivity and decomposition kinetics of precursors, allowing for lower temperatures than required for thermal decomposition reactions. Generally, the solvents used in nanocrystal synthesis are hydrophobic, while the surfactants and initiating agents are amphiphilic, with coordinating head groups and long aliphatic tails. The resulting nanocrystal surfaces are coordinated by the surfactant head groups while the aliphatic tails extend outwards from the surface, providing the nanocrystals with a hydrophobic ligand shell. This ligand shell affords colloidal stability and allows for nanocrystal dispersion and processing in hydrophobic

organic solvents.

The utility of colloidal synthesis arises from good control over the generation of reactive intermediates that, in turn, nucleate and grow nanocrystals. The use of appropriate organic surfactants is critical to modulate the interfacial interactions between the growing nanocrystal and its surroundings.² Nanocrystal synthesis can be easily understood in the framework of nucleation and growth. As the reaction progresses, reactive intermediates, termed monomers, are generated from the decomposition of the metal salt precursors. Eventually, the reaction solution becomes supersaturated with monomers, and a driving force to nucleate a solid to alleviate this supersaturation arises. The energy associated with forming a nucleus of radius r is:

$$\Delta G(r) = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \quad (1.1)$$

where ΔG_v , is the difference in Gibbs free energy between the monomers in solution and the energy per molar volume of the corresponding solid, and is thus proportional to the degree of supersaturation. The first term of Equation 1.1 drives the energy of the system lower, which favors the formation of a larger volume of solid to alleviate supersaturation. However, this is in competition with the second term, which is the system's energy increase associated with the formation of a new solid-liquid surface, which has an areal surface energy of γ . At small sizes, the second term outweighs the first, leading to a positive $d\Delta G(r)/dr$ and causing the nucleus to shrink. At sufficiently large sizes, however, the volume term will outweigh the surface term, and it will become favorable for nanocrystals to grow. The critical radius at which this occurs, r^* , can be found by setting $d\Delta G(r)/dr = 0$, and is given by the expression:

$$r^* = -2\frac{\gamma}{\Delta G_v} \quad (1.2)$$

The critical activation energy for nucleation, ΔG^* , is the value of $\Delta G(r^*)$. This nucleation and growth behavior, and the critical radius at which growth becomes favorable, are illustrated in Figure 1.2.

LaMer extended nucleation and growth theory to colloidal synthesis in 1950, and the “LaMer” model forms the basis for understanding nanocrystal synthesis today.¹⁰ The LaMer model breaks the synthesis down into three regimes: monomer generation, nucleation, and growth (Figure 1.3). Decomposition of the metal precursors generates monomer intermediates at a given kinetic rate corresponding to the monomer generation slope in Figure 1.3. Monomer concentration quickly increases past the saturation threshold, but nanocrystals do not form yet, because the monomer concentration is still small enough such that ΔG_v is too small, and r^* is too large for stable nuclei to form. As the monomer concentration continues to increase, it eventually crosses the nucleation threshold and stable nanocrystal nuclei form continuously. This nucleation step eventually depletes the monomer concentration so that formation of new nuclei is no longer favorable, and the existing nuclei begin to grow continuously until the reaction is stopped or the monomer concentration passes below the saturation threshold. At longer reaction times, other processes, such as Ostwald ripening, can lead to changes in nanocrystal size and polydispersity.

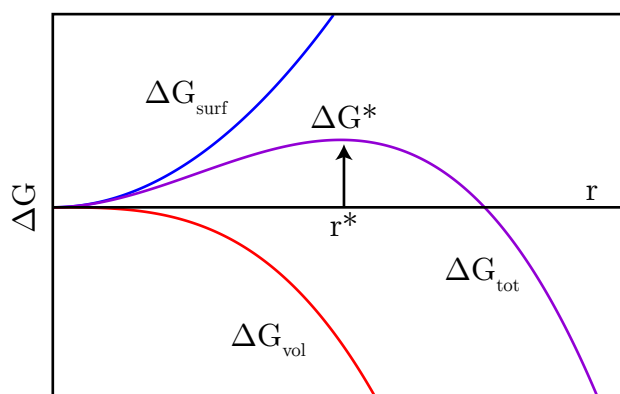


Figure 1.2: Change in Gibbs free energy during nucleation and growth processes of nanocrystals.

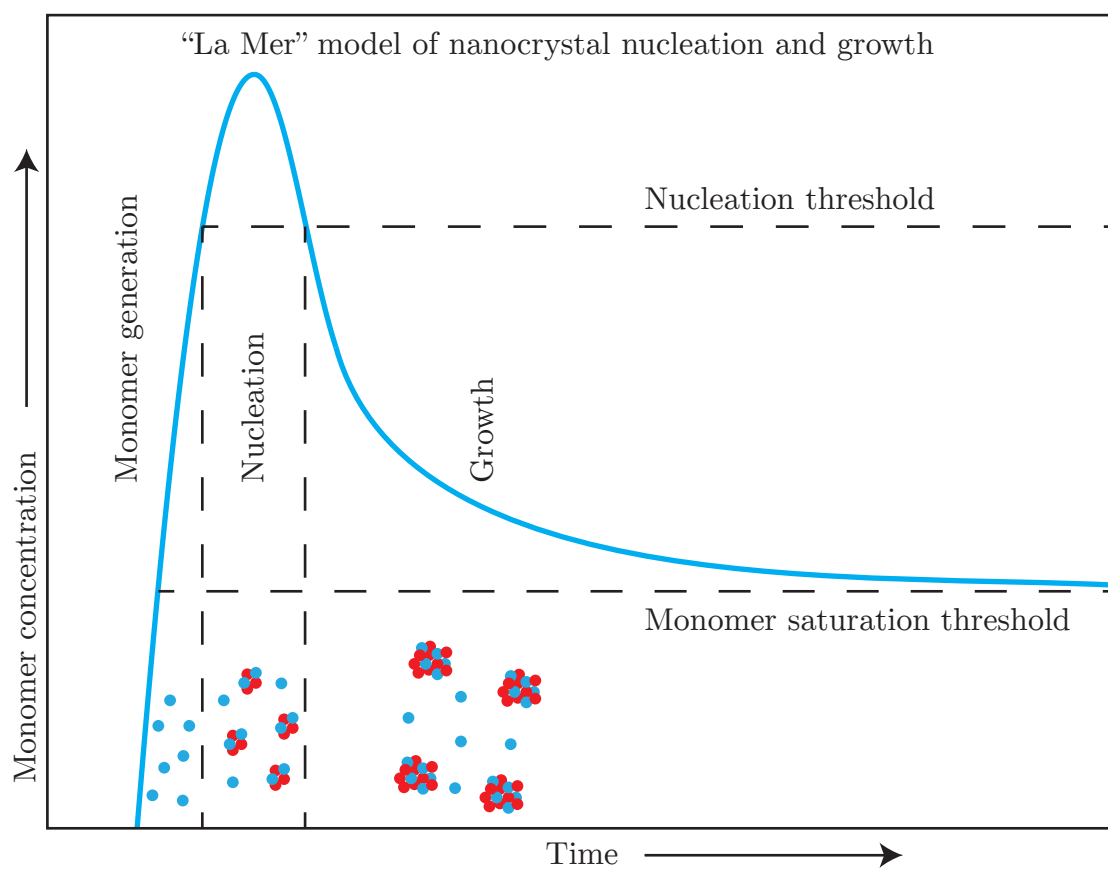


Figure 1.3: Schematic depiction of the LaMer model for colloidal nanocrystal growth, adapted with permission from Reference¹⁰, Copyright 1950 American Chemical Society.

Monodisperse and size controlled nanocrystals are most easily formed when the nucleation step is as short as possible. Because nuclei are continuously formed when the nucleation threshold is exceeded, a long nucleation step will result in many nuclei of different sizes, leading to a broad nanocrystal size distribution after the growth step. Conversely, a “burst” of nucleation on a short time scale quickly depletes the monomer concentration and the reaction transitions to the growth regime with nuclei that are close to equal in size. This model underlines the utility of initiating agents in nanocrystal synthesis, as they can increase the monomer formation rate to encourage a fast nucleation step. It is also possible to artificially create a discrete nucleation step by injecting an initiating agent or injecting precursors into hot solvent to encourage very rapid monomer generation rates. Surfactants and ligands are also critical, as they mediate growth rate by controlling the addition of monomers to growing nanocrystal surfaces, provided that their interaction with the surface is sufficiently labile. This growth process is known as dynamic solvation.^{2;11} Surfactants also modify the surface energy γ , which not only stabilizes nanocrystals at small sizes, but can also be used to generate nanocrystals with controlled shape. Many surfactants adsorbed to nanocrystal surfaces modify surface energy so that the low-index crystal facets are relatively close in energy, which results in spherical nanocrystals as each crystal aims to minimize its surface area.² Other surfactants, especially those that bind selectively to particular crystal facets, sufficiently reduce the growth rate of that facet so that non-spherical nanocrystals can be obtained through kinetic shape control.²

1.2.2 DC electronic measurements: 4-point probe, transmission line method

Both two-point and four-point DC electrical measurements are employed to measure charge transport in this work. Four-point probe measurements in the van der Pauw geometry are particularly useful for straightforward measurements of electronic conductivity of nanocrystal films, because contact resistance effects are eliminated, and samples without precisely defined geometries can be measured. Note that accurate thicknesses are necessary for calculating resistivity using both four-point, and two-point DC methods, as well as with AC methods. Accurate sample thicknesses are measured by a combination of cross-sectional SEM imaging and stylus profilometry.

Two-point electronic measurements are also useful, particularly when a given sample is to be subjected to both DC and AC characterization under controlled environments where van der Pauw measurements are not feasible. Two-point probe DC measurements can be used to calculate the electronic resistance of a sample, and, if the electrode and sample geometry are well defined and known, electronic resistivity can be calculated. Two-point measurements, however, are subject to contact resistance effects, which can be significant in comparison to the resistance of the sample, especially for nanomaterials. In this case, it is necessary to perform a “transmission line” measurement (Figure 1.4), where the resistance of the sample is measured with electrodes of varying spacing. When the resistance is plotted vs. electrode

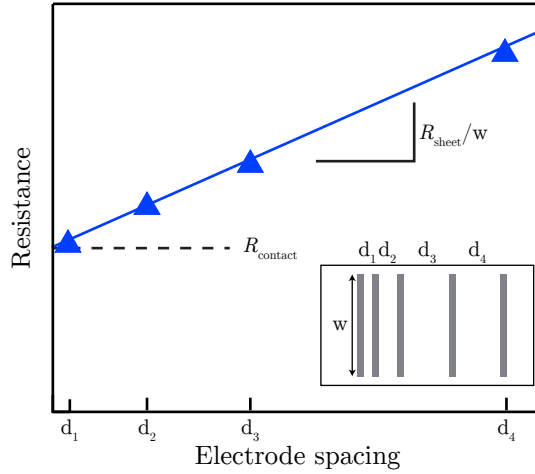


Figure 1.4: Transmission line method for determining electronic resistivity and contact resistance with two-point DC measurements.

spacing, assuming that the sample follows Ohm's law, the slope of the line that is formed is equal to the sheet resistance over the electrode width. The sheet resistance can be used to calculate resistivity if the sample thickness is known. Extrapolating the line to an electrode spacing of zero gives the combined contact resistance of the two electrodes.

1.2.3 Impedance spectroscopy

AC impedance spectroscopy (sometimes referred to as electrochemical impedance spectroscopy, or EIS) is a frequency-dependent electronic/electrochemical characterization technique that can yield valuable information about charge transport that would not easily be accessed with DC techniques. In general terms, impedance spectroscopy is performed by applying a sinusoidal voltage perturbation to the system under study and measuring the resulting current response, shown mathematically below and graphically in Figure 1.5:

$$V(t) = V_0 + V_a \exp(j\omega t) \longrightarrow I(t) = I_0 + I_a \exp(j(\omega t + \phi)) \quad (1.3)$$

where V_0 is the steady-state voltage, V_a is the magnitude of the voltage perturbation, ω is the frequency of the periodic perturbation, I_0 is the steady-state current, I_a is the magnitude of the oscillating current, and ϕ is the phase delay of the current response with respect to the voltage perturbation. The system under study can be modeled as a transfer function that transforms the voltage perturbation into a current:

$$Z(j\omega) = \frac{\Delta V(j\omega)}{\Delta I(j\omega)} \quad (1.4)$$

This complex transfer function $Z(j\omega)$ is called the *impedance* of the system, and is otherwise known as the AC analogue of resistance. Because the impedance is frequency-dependent, an

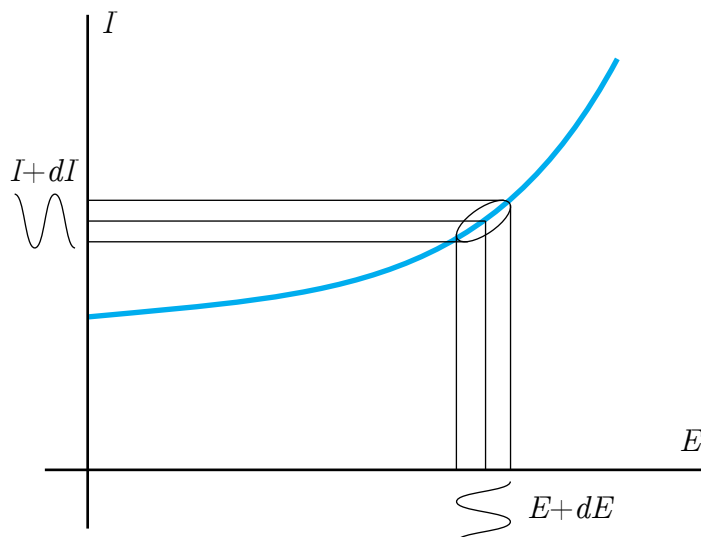


Figure 1.5: Visual representation of impedance spectroscopy, where a sinusoidal voltage (E) induces a current response (I). This representation is also known as a *Lissajous plot*.

impedance spectroscopy experiment measures $Z(j\omega)$ at multiple frequencies spanning from tens of MHz to single μHz , hence the term *spectroscopy*.

As an AC technique, EIS can measure the conductivity associated with all mobile charges, including lithium ions, protons, and oxygen ions in addition to electrons. Furthermore, provided that the perturbing AC voltage is sufficiently small, the system's response is in the linear, small signal regime. As such, EIS measures the properties of a system under equilibrium conditions, whereas other techniques, like cyclic voltammetry and DC methods, often perturb the system significantly out of equilibrium. Finally, perhaps the strongest advantage of EIS is that it allows measurements in the frequency domain, which allows us to decouple different conduction or polarization processes in a way that is impossible in the time domain. Two or more physical processes with different time constants or relaxation times, such as electronic conduction across grain boundaries vs. within grains, or individual events in an electrochemical reaction mechanism, can be independently resolved in an impedance spectroscopy measurement. EIS is becoming particularly important as a tool to evaluate electronic and electrochemical processes in nanomaterials, and to distinguish such behaviors at the nanoscale compared to the bulk.

In many cases, the impedance response of a system can be modeled with familiar circuit elements such as resistors, capacitors, and inductors to generate an *equivalent circuit* to which the data can be fit, and from which physical parameters, like conductivities, can be extracted. The impedances of circuit elements can be added in the same way as resistors. However, EIS is not a chemical spectroscopy and transfer functions are not unique, so care must be exercised when using this approach, as multiple equivalent circuits can give the same impedance response. Provided, however, that we have some physical intuition or

understanding of the system under study, then an appropriate equivalent circuit can be used. The impedance responses of some common circuit elements are described below:

- The relationship between current and voltage in a **resistor** is time-independent ($V = IR$), so its impedance is simply the resistance:

$$Z_{\text{resistor}} = R \quad (1.5)$$

- A **capacitor** resists changing voltage by storing charge; this capacitance is defined as $C = dq(t)/dV(t)$, so that the current can be defined as $I(t) = C dV(t)/dt$. Performing a Laplace transform on the current expression yields the impedance response:

$$Z_{\text{capacitor}} = \frac{1}{j\omega C} \quad (1.6)$$

- An **inductor** resists changing current by storing energy in a magnetic field; this inductance is defined as $L = d\phi/dI(t)$, where ϕ is magnetic flux, so that the voltage can be defined as $V(t) = L dI(t)/dt$. The Laplace transform yields the impedance response:

$$Z_{\text{inductor}} = j\omega L \quad (1.7)$$

- A **constant phase element** is an artificial circuit element that can be thought of as a non-ideal capacitor with independent parameters Q and α . It is used to model the response of real-world systems with a distribution of time constants, due to sample inhomogeneity from surface roughness, porosity, etc. Q is a pseudo capacitance, the exponent α is a measure of this non-ideality, and the impedance response reduces to a capacitor when $\alpha = 1$. The phase angle is given by $\phi = -90^\circ \times \alpha$ and the impedance response is:

$$Z_{\text{CPE}} = \frac{1}{Q(j\omega)^\alpha} \quad (1.8)$$

- A **Warburg element** is similar to a constant phase element with $\alpha = 0.5$ and describes the impedance associated with infinite-length 1D diffusion from a surface. For example, a Warburg element could be used to model the diffusion of ions (after charge transfer) within the active material of a battery. The impedance response is:

$$Z_{\text{Warburg}} = \frac{A_W}{\sqrt{j\omega}} \quad (1.9)$$

$$A_W = \frac{k_B T}{n^2 F^2 A C_0 \sqrt{D}} \quad (1.10)$$

where k_B is Boltzmann's constant, T is temperature, n is the charge of the mobile species, F is Faraday's constant, A is the area of the surface, C_0 is the surface concentration, and D is the diffusion constant.

The impedance response of a system is a complex number, and so the data lend themselves to a number of ways to be displayed, as in Figure 1.6. The most popular is likely the *Nyquist plot*, which displays the imaginary impedance on the ordinate axis, vs. the real impedance on the abscissa. Another popular representation is the *Bode plot*, which plots the absolute magnitude of impedance and the phase angle vs. frequency. These data representations rely on the following relationships:

$$Z = \text{Re}(Z(\omega)) + j\text{Im}(Z(\omega)) \quad (1.11)$$

$$|Z(\omega)| = \sqrt{\text{Re}(Z(\omega))^2 + \text{Im}(Z(\omega))^2} \quad (1.12)$$

$$\tan \phi = \frac{\text{Im}(Z(\omega))}{\text{Re}(Z(\omega))} \quad (1.13)$$

Circuits with (multiple) characteristic time constants appear in the Nyquist plot as a (multiple) semicircle(s) or a portion thereof. The endpoints of the semicircle can be further used for quantitative evaluation of the system. For example, a simple RC circuit, which can be a good representation of the combined electronic and dielectric response of a solid sample, or of the double layer capacitance and charge transfer resistance of an electrochemical system, displays a single semicircle in the Nyquist plot. The width of the semicircle corresponds to the resistance R , while the apex of the Nyquist plot occurs at the characteristic frequency of the system:

$$\omega_c = \frac{1}{RC} \quad (1.14)$$

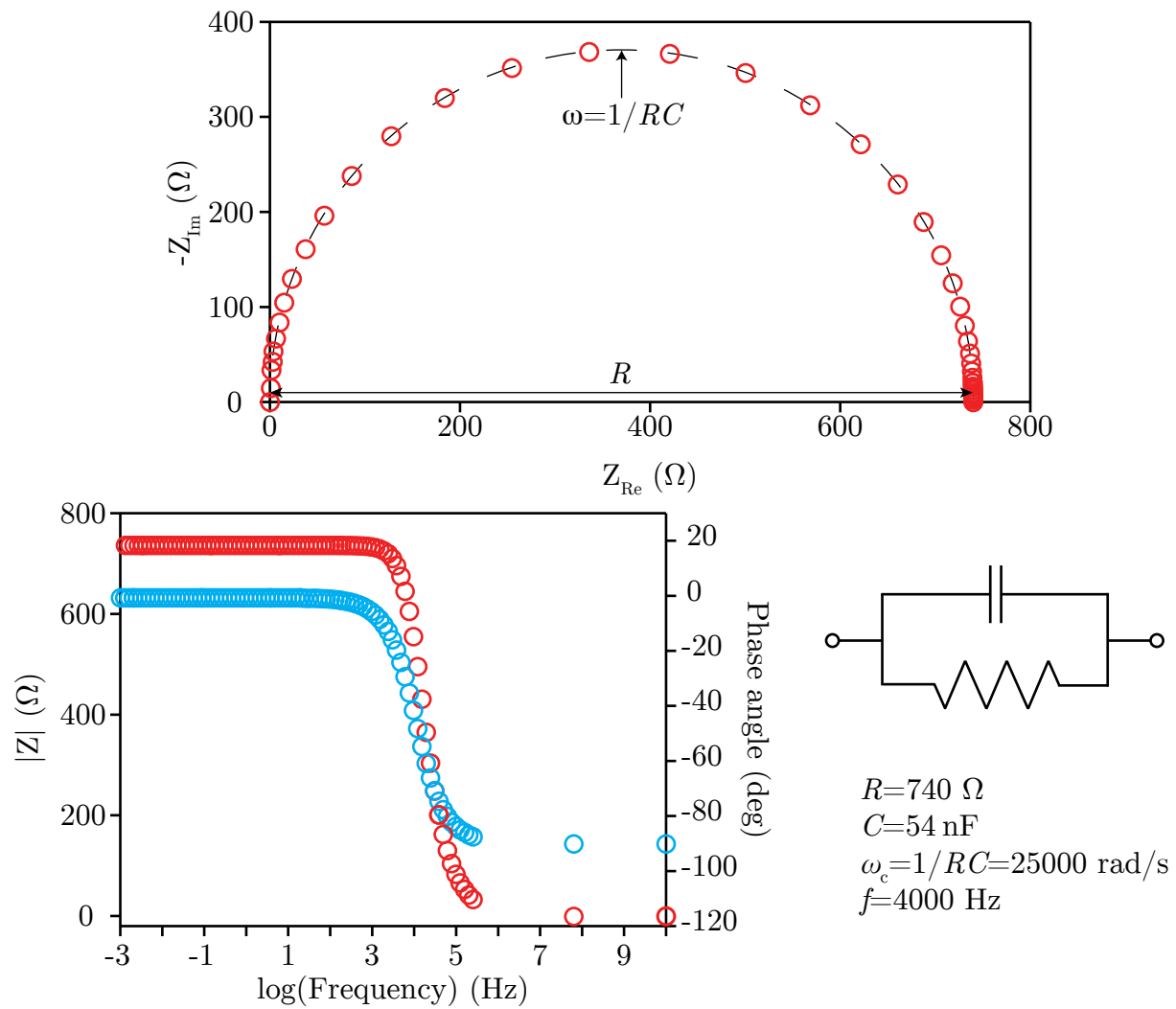


Figure 1.6: Simulated impedance response of an RC circuit. Top: Nyquist plot showing a semicircle. Bottom left: Bode plot. Bottom right: equivalent circuit diagram.

1.3 Selected physical phenomena and theory relevant to metal oxide nanocrystals

1.3.1 Metal oxide binding and electronic structure

As oxygen is a very electronegative element, and most metals are fairly electropositive, metal oxides are generally made of ionic species, and the metal-oxygen bond is an ionic one. Metal oxide crystal lattices provide the lowest-energy periodic arrangement of metal cations and oxygen anions, and the solid is stabilized by a combination of the Madelung potential and electronic polarization of the metal and oxygen ions, such that oxygen atoms in the lattice act as a ligand for metal centers. In general, metal oxide crystal structures are built from discrete MO_4 tetrahedral units or MO_6 octahedral units, though some other coordination geometries are possible.

The properties of metal oxides can be partially understood through the lens of the metal-oxygen bond. The large difference in electronegativity between oxygen and metals leads to a large discrepancy in energies of their respective atomic orbitals that participate in bonding, which leads to considerable energy splitting in the molecular orbital diagrams (Figure 1.7). The resulting properties of the crystalline solid depend strongly on this splitting and the electronegativity difference between the metal and oxygen, which eventually determines if the metal oxide will be an insulator, semiconductor, or metal.

As the crystal is built up from tetrahedral or octahedral building blocks, continued hybridization between molecular orbitals eventually leads to overlapping orbitals and degenerate electronic states, eventually leading to the formation of electronic bands (Figure 1.8). The character of each band can be predicted from the molecular orbital diagrams (Figure 1.7), and in general, the valence band of a metal oxide is primarily of oxygen 2p and 2s character. The conduction band is a mixture of oxygen 2p and 2s orbitals in combination with the orbitals containing the valence electrons of the metal. In indium oxide, for example (Figure 1.8), the conduction band has significant In 5s character. Deeper bands arise from lower energy orbitals, such as metal d electrons.

Bonding and band structure can have a profound influence on the ability of a metal oxide to conduct electricity. The energies of the valence band and the conduction band with respect to vacuum, the band gap energy, and the position of the Fermi level within the band gap will dictate the concentration of free carriers in a metal oxide and the ease with which additional carriers can be generated with doping or increased temperature. The nature of the valence and conduction bands further dictate how easily holes and electrons, respectively, move within the material. The carrier effective mass is proportional to the second derivative of electron energy with respect to the crystal momentum k , so bands with higher curvature support higher carrier mobility. In turn, the curvature of the bands reflects their orbital nature: highly symmetric and larger s orbitals encourage the formation of dispersive, delocalized bands with high curvature, while smaller and more complex-shaped orbitals, like metal d or f orbitals, lead to flat bands with little curvature. This explains why

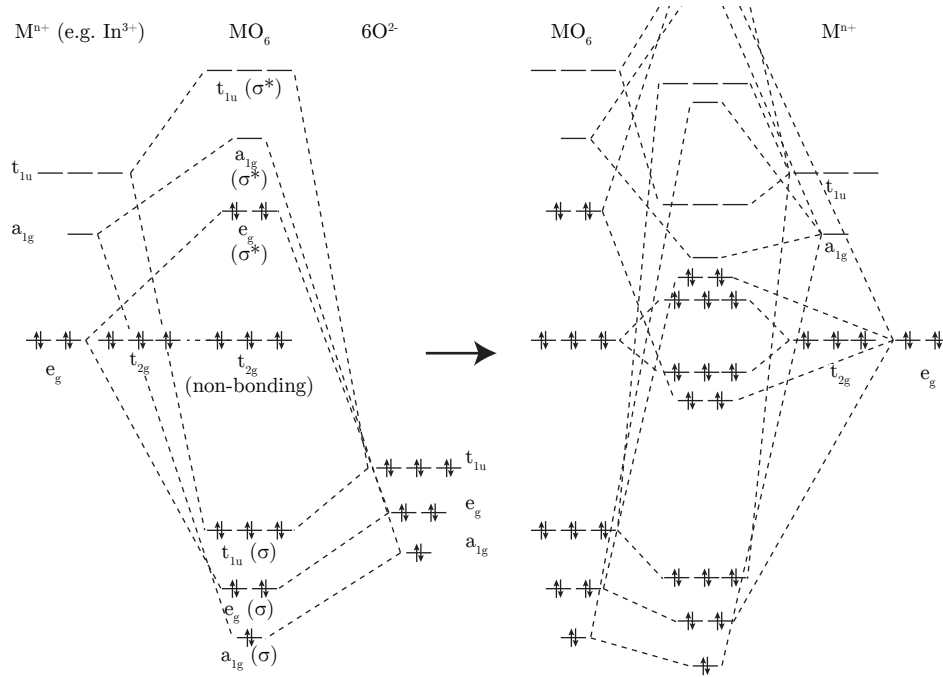


Figure 1.7: Molecular orbital diagrams for metal-oxygen bonds in an octahedral coordination environment.

p-type conductivity is almost never observed in metal oxides, as the valence band is usually flat from its O 2p character, leading to high effective masses for holes. When the conduction band is of significant metal s character, then significant electronic conduction is supported. Indium oxide is an example of a metal oxide that has a band structure appropriate for charge transport, which, combined with its large band gap, make it the prototypical transparent conductive oxide.

1.3.2 Defect chemistry of metal oxides

In any crystalline solid, the equilibrium fraction of point defects can be determined from thermodynamic principles, and is given by the expression

$$X_V^{EQ} = \exp \left[-\frac{\Delta H_v^f}{kT} \right] \exp \left[\frac{\Delta S_v^f}{k} \right] \quad (1.15)$$

where ΔH_v^f is the formation enthalpy of the defect, and ΔS_v^f is the entropy associated with forming a defect. The formation of defects is therefore subject to a balance between the energy input required to make the defect by breaking bonds, etc., and the increase in entropy and possible atomic configurations when a defect is formed. It can be shown with thermodynamic arguments that the Gibbs free energy driving force for defect formation, $d\Delta G/dX_V$, approaches infinity as X_V approaches zero. Thus, it is impossible for any crystalline solid

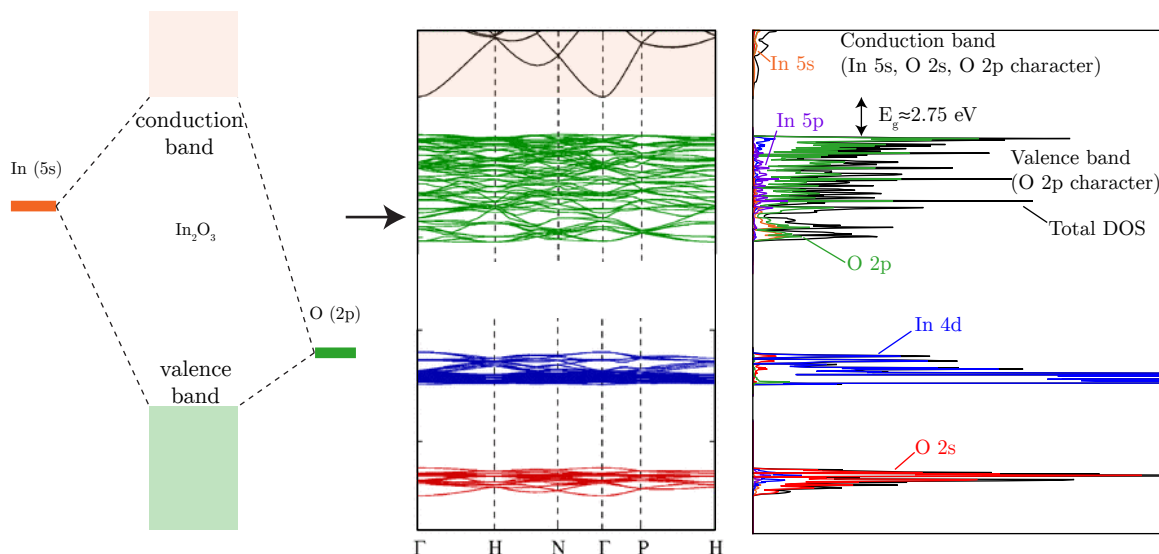


Figure 1.8: Simplified band diagram, simulated band diagram and density of states for indium oxide. Note the predominant O 2p character of the valence band, the In 5s character of the conduction band, and the band gap that makes the material transparent to visible and infrared light. Simulated band diagram reprinted with permission from Reference¹², Copyright 2007 American Physical Society. Density of states diagram adapted with permission from Reference¹³, Copyright 2016 American Chemical Society.

to be truly free of point defects, and most materials have substantial defect concentrations. As point defects can significantly influence material properties, it is imperative to consider their effects.

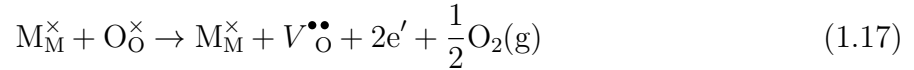
Metal oxides, in particular, have an exceptionally rich defect chemistry because one of their main constituents, oxygen, is present as a gas with considerable activity all over the Earth. Defect equilibria in metal oxides are thus subject to the equilibrium between the metal oxide and surrounding oxygen gas, and the activity of gaseous oxygen (e.g., partial pressure) can strongly change equilibrium defect concentrations. An additional complication is presented by the ionic nature of metal oxides; because the constituents of metal oxides are charged ions, defects in metal oxides are also charged. The impact that *charged* defects in a material have on *charge* transport in metal oxides cannot be overstated. Charged defects mediate and control charge transport to a significant degree and can even be the predominant enabling or disabling factor for conductivity, as they are nearly entirely responsible for the generation or destruction of free charge carriers. Additionally, the presence of charged defects in a crystal strongly impacts charge motion through Coulombic interactions in a process called *ionized impurity scattering*, which is extensively explored in Part II of this dissertation. Finally, charged defects themselves can move, enabling additional modes of charge and mass transport in solids. Solid oxide fuel cells, for example, rely on the diffusion of negatively

charged oxygen ions in a solid ceramic electrolyte, which is only enabled by the presence and counter-diffusion of positively charged oxygen vacancies.

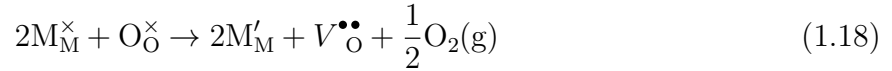
Charged defects and defect chemistry reactions in metal oxides are typically described with Kroger-Vink notation, which is a short-hand method defining the identity, location, and charge of a defect:

$$M_S^C \quad (1.16)$$

where M is the identity of the defect, S is the defect site, and C is the charge of the defect, with neutral charge denoted by x, positive charge denoted by a dot and negative charge by an apostrophe. The most common and important intrinsic defect in metal oxides is the oxygen vacancy ($V_{\text{O}}^{\bullet\bullet}$), which is positively charged. This positive charge must be compensated by negative charge in the system, which come in the form of free electrons (e') by the following defect reaction:



Charge compensation can also come in the form of another defect, such as a reduced metal ion (which often forms a small polaron, where the electrons generated by oxygen vacancy formation partially localize on the metal site):



Other important intrinsic defects include Schottky defects, metal Frenkel defects, oxygen Frenkel defects, and electronic defects, with their respective defect reactions written as:

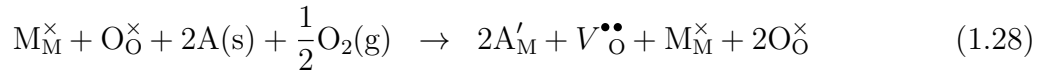
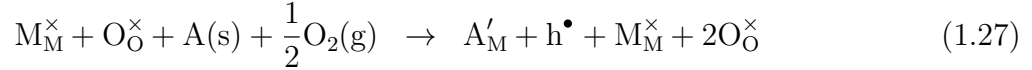
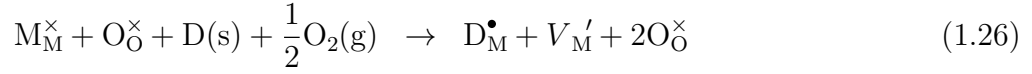
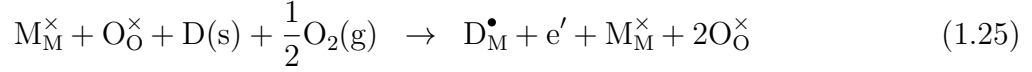


Important extrinsic defects, which are the result of external impurities being added to the material, include oxygen interstitial formation with compensation by holes or by metal oxidation:



Aliovalent substitutional doping (that is, doping with an ion of a different valence) is another source of important extrinsic defects, which can be compensated either electronically or by other defects. Electronic compensation forms the basis for conductive metal oxides like tin-doped indium oxide, while ionic compensation is critical for solid ceramic electrolytes like yttrium-stabilized zirconia. Substitutional aliovalent dopants can either be acceptors or

donors, and following defect reactions describe substitutional donor doping with electronic compensation, donor doping with ionic compensation, acceptor doping with electronic compensation, and acceptor doping with ionic compensation, respectively:



Substitutional donor and acceptor doping on anion sites is also possible (e.g., in fluorine-doped tin oxide), though less common. Of course, more complex defect reactions, compensation mechanisms, and defect clustering reactions are possible. All defect formation in metal oxides influences charge transport through consuming or producing electrons, and through scattering free charge carriers. The influence of oxide defect chemistry on electronic and ionic charge transport is explored extensively in Parts II and III, respectively, of this dissertation.

1.3.3 Localized surface plasmon resonance in nanocrystals

LSPR in metal oxide nanocrystals is discussed extensively throughout this dissertation, but it is briefly introduced here. Plasmons are generally defined as hybrid interactions between an incident light and conduction electrons, which collectively oscillate and can propagate along the surface of a nanostructure or thin film. LSPRs are a specific type of plasmon common in nanocrystals and nanoparticles that satisfy certain requirements for carrier concentration, particle size, and dielectric properties. To support LSPR, a nanocrystal must generally have a high enough concentration of mobile free carriers for metallic transport, and the nanocrystal dielectric function, which describes the polarization of a material in response to electric fields, must also have a negative real part to support metallic optical behavior. In metal oxides, aliovalent donor doping can be used to generate enough free electrons for metallic conduction, and the dielectric functions of certain metal oxides, particular TCOs, is amenable to LSPR.

In addition, the nanocrystal diameter must be around one-fifth or less of the incident light wavelength. In this “quasi-static” limit, all of the free carriers effectively feel the same force from incident light, and all carriers oscillate collectively in response to periodic electromagnetic fields (Figure 1.9). For metal oxide nanocrystals with LSPR in the near infrared, this corresponds to diameters of around 200 nm or less. The oscillation can generally be understood as the displacement of all free carriers by the electric field of incident light, which is approximately constant over the whole nanocrystal volume in the quasi-static limit. The displaced carriers feel a restoring force exerted by the atomic nuclei in the nanocrystal, and plasmon resonance occurs when the incident light frequency is equal to the characteristic

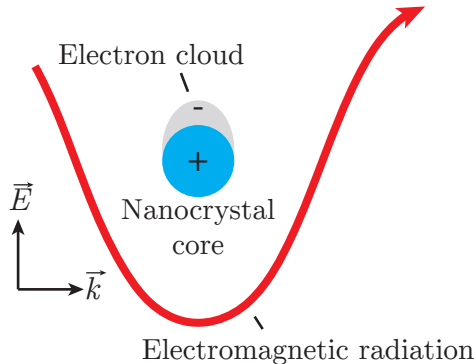


Figure 1.9: Schematic depiction of LSPR and collective oscillation of conduction band electrons in a nanocrystal in response to incident electromagnetic radiation.

restoring frequency of the nanocrystal. This resonance frequency is also influenced by the dielectric environment surrounding the nanocrystal. Nanocrystals with LSPR can absorb and scatter light very strongly at this resonant frequency.

1.4 Overview of dissertation

The rest of this dissertation is divided into three parts as introduced in Section 1.1. Part I examines transport of electronic and ionic charge in electrochromic devices based on colloidal metal oxide nanocrystals. Chapter 2 outlines the emergence of electrochromism in doped metal oxide nanocrystals and the electrochemical charge transport mechanisms that support the electrochromic effect. Chapter 3 introduces nanocomposites of ITO nanocrystals dispersed in a solid polymer electrolyte, poly(ethylene oxide) (PEO). These nanocomposites exhibit mixed conduction of both electrons through the ITO filler phase and lithium ions through the PEO matrix phase, both of which are critical for electrochemical device operation. Through colloidal chemistry and solution processing techniques, the morphology of the composites, and their resulting ionic and electronic charge transport properties, can be tuned. A combination of DC measurement techniques, AC impedance spectroscopy, and morphological characterization is used to establish these connections. Chapter 4 uses the lessons learned in Chapter 3 to develop nanocomposite electrochromic and charge storage electrodes. When the two electrodes are laminated together, they form a free standing solid state electrochromic device in which the connection between electrochemical charge transport and the optical contrast achievable by the device is studied.

Part II of this dissertation turns to the study of electron motion within doped metal oxide nanocrystals that exhibit localized surface plasmon resonance. Doped metal oxide nanocrystals exhibit optoelectronic properties that are not only unique, but that are also tunable. This tunability is a crucial property that enables the current and proposed applications for plasmonic metal oxides; electrochemical tuning of plasmons is the basis for the

plasmonic electrochromism that is examined in Part I of this dissertation. The ability to tune plasmonic metal oxide nanocrystals by changing dopant levels, dopant identities, or size and shape also affords a way to study the interplay between *intra*-particle electron transport, optoelectronic properties, plasmon physics, and materials science. Chapter 5 develops these connections to provide holistic understanding of plasmonic doped metal oxide nanocrystals. Chapter 6 studies the synthesis and properties of ITO nanocrystals, which are a model system to study how aspects like colloidal chemistry, dopant incorporation and location, defect chemistry, and nanocrystal shape impact plasmonic properties. Chapter 7 makes full use of the connections made in Chapters 5 and 6 to develop an entirely new plasmonic nanocrystal material, cerium-doped indium oxide ($\text{Ce:In}_2\text{O}_3$). By considering how defect chemistry impacts electron transport in metal oxides, cerium is chosen as the ideal dopant to reduce electronic scattering and damping in plasmonic indium oxide nanocrystals, and the resulting plasmonic properties of $\text{Ce:In}_2\text{O}_3$ are indicative of exceptionally low electron scattering in this material. The underlying physical reasons for the beneficial effects of cerium dopants in this system are examined further with *ab initio* simulations, and the potential for $\text{Ce:In}_2\text{O}_3$ nanocrystals to be used for near field enhancement or light concentration applications is considered.

Part III of this dissertation combines elements of both Parts I and II before it in the study of proton transport in porous films of ceramic metal oxide nanocrystals. Cerium oxide and titanium oxide nanocrystals can support unusually high proton conductivities, where bulk versions of the same materials cannot, and Chapter 8 examines the mechanisms of proton transport in ceramic nanocrystal films using impedance spectroscopy. Proton conductivity in these materials can be tuned by changing nanocrystal size and by changing the partial pressure of oxygen surrounding the nanocrystals, suggesting a strong connection between the presence of surfaces, the defect chemistry of these materials, and their ability to support proton transport. This connection is examined in depth.

Finally, Chapter 9 summarizes the findings of Parts I-III, and suggests possible future related research directions. These include the study of alternative doped metal oxide nanocrystals for use in mixed conducting electrochromic nanocomposites, utilizing plasmonic nanocrystals for near field enhancement applications in the near- to mid-infrared, and tuning the composition of ceramic nanocrystals for enhanced proton conductivity in fuel cell electrolytes.

Part I

**Electrochromics: ion transport and
inter-nanocrystal electron transport**

Chapter 2

Nanostructured electrochromic smart windows: traditional materials and NIR-selective plasmonic nanocrystals

Reprinted from Reference¹⁴:

Runnerstrom, E. L.; Llordes, A.; Lounis, S. D.; Milliron, D. J. Nanostructured Electrochromic Smart Windows: Traditional Materials and NIR-Selective Plasmonic Nanocrystals. *Chem. Commun.* **2014**, *50*, 10555–10572.

2.1 Introduction

Electrochromism, the phenomenon whereby a material's color, transparency, or other optical property changes in response to electric charge, forms the basis for operation of a number of devices, including displays, adjustable mirrors, and “smart” windows. While reversible color changes in inorganic materials have been studied at least since the discovery of tungsten bronzes in the 19th century,^{15;16} Deb's demonstration of reversible, electrically induced coloration in thin films of transition metal oxides in the late 1960s and 1970s launched significant efforts to study electrochromic materials and devices for applications like displays and mirrors.^{17;18} Motivated by the potential for significant energy savings from reduced cooling and heating loads, the research in this area has shifted towards developing electrochromic windows that dynamically control sunlight entering a building.^{15;16;19–23} This focus on improved energy efficiency and the development of advanced buildings drives the majority of current electrochromic research. An ideal smart window, universally applicable across building types and climate zones, would independently control the transmittance of visible sunlight and solar heat into a building. These two parameters directly affect a building's

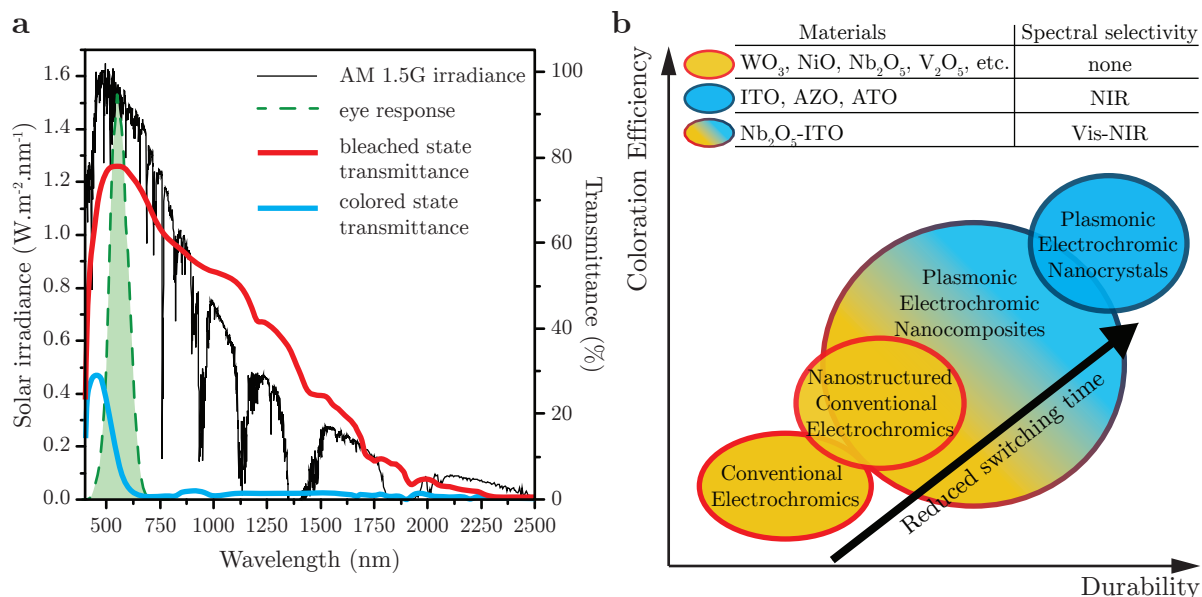


Figure 2.1: a) AM 1.5G solar spectrum (thin black curve) along with the photopic response of the human eye (dashed green curve). Overlaid are the transmittance curves for a commercial electrochromic device (Gesimat) in the bleached (thick red curve) and coloured (thick blue curve) states. Note the significant modulation of both visible and NIR light. b) Scheme illustrating the performance metrics achieved by the different classes of electrochromic materials discussed in this review. Transmittance curves in panel (a) reproduced from ref.²⁴, copyright 2009, with permission from Elsevier.

energy use and influence occupant comfort. For this reason, independent control over the visible and near-infrared (NIR) regions of the solar spectrum is a key target for advanced electrochromic devices, and would contribute to optimum energy efficiency across a building's heating, cooling, and artificial lighting systems. NIR light, in particular, accounts for about half of the solar energy that is incident upon a window (Figure 2.1a), but does not contribute to daylighting within a building. An optimized electrochromic window would thus provide separate, dynamic control over the transmission of visible and NIR solar radiation using materials with high optical contrast, fast switching times, long cycle life, and low manufacturing cost.

Unfortunately, the benefits of electrochromic windows are yet to be realized at scale,²⁰ as conventional materials suffer from significant drawbacks related to cost, durability, and functionality. Existing commercial electrochromic windows most often employ thin films of transition metal oxides as the active material.^{16;23;25} These films are typically grown using costly physical vapour processes such as sputtering or evaporation,^{19–21;23} suffer from material degradation associated with repeated ion intercalation,^{20;21;23;25} and adopt dark, distinct colors in their tinted states^{16;23;26} simultaneously blocking both visible and near-infrared (NIR) light (Figure 2.1a).^{24;27} For these reasons, conventional electrochromics fall short of

the ideal smart window and have struggled to achieve widespread adoption.

In many cases, conventional inorganic electrochromic compounds in nanomaterial form exhibit enhanced properties, such as faster ON/OFF switching times and amenability to potentially low-cost solution processing. However, despite these advantages, nanostructuring does not necessarily confer new functionality. Films made from nanostructured transition metal oxide materials typically display similar optical properties to their bulk counterparts and miss the target of ideal solar control.

Our laboratory is spearheading the development of a new and fundamentally different class of electrochromic devices, leveraging the plasmonic properties of colloidal transparent conducting oxide (TCO) nanocrystals to directly address the aforementioned limitations of conventional materials.^{28–31} These nanocrystals exhibit strong localized surface plasmon resonance (LSPR) absorption in the mid- to near-IR. Electrochemical charging or doping of a nanocrystal film subsequently tunes the LSPR frequency over a wide range of wavelengths. Plasmonic nanocrystal electrochromic devices confer NIR-selective operation, inherently rapid switching, and greatly enhanced durability, and are made using solution processing. This review will cover in detail the scientific history and basis of NIR-selective plasmonic electrochromism and the devices that are enabled by this phenomenon. We will also provide a general overview of electrochromic device operation, briefly discuss conventional electrochromic materials, and consider a few other applications of nanotechnology to conventional electrochromic materials and devices. The relative electrochromic performance achieved by the materials discussed in this review—conventional materials, nanostructured conventional materials, plasmonic electrochromic nanocrystals, and composites of plasmonic nanocrystals in amorphous electrochromic glasses—is summarized schematically in Figure 2.1b.

2.2 Fundamentals of electrochromic device operation

A typical electrochromic window coating, depicted in Figure 2.2, is a multi-layer device consisting of an active electrochromic electrode layer, a counter electrode layer, an electrolyte layer separating the two electrodes, two transparent conducting layers serving as electrical leads, and the supporting substrates. The two electrode layers often consist of transition metal oxides. This device structure is referred to as “battery type” and is the most common geometry for electrochromic devices.^{19;21;23} In the off or bleached state, cations, such as Li^+ or H^+ , reside in the electrolyte and the counter electrode.²¹ When the device is switched on, a voltage applied between the opposing conducting layers drives cations to migrate from the counter electrode, through the electrolyte, and into the electrochromic electrode through a Faradaic process, changing its oxidation state and its optical properties. For a thorough treatment of transition metal oxide electrochromic materials and counter electrodes, the reader is referred to a number of reviews and books.^{15;16;19–23;32–35}

An effective electrochromic device will have fast switching between its “on” and “off” states, good durability characterized by a long cycle life, and a high optical contrast ra-

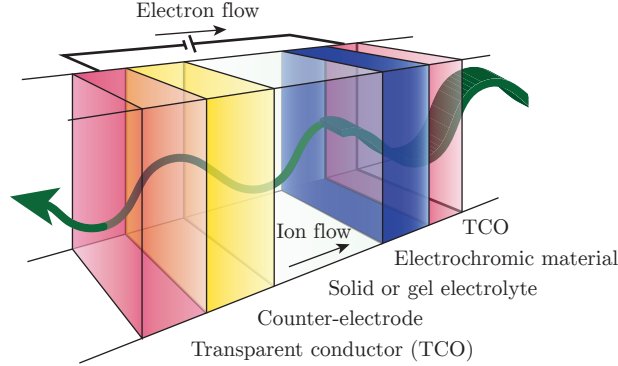


Figure 2.2: Electrochromic device stack schematic, depicted in a darkened state. Electrons flow through an external circuit into the electrochromic material, while ions flow through the electrolyte to compensate the electronic charge.

tio. These characteristics derive, in part, from the properties of the active electrochromic material. Many factors can influence switching speed, including the electronic conductivity of the electrode materials and the underlying conducting layers, the ionic conductivity of the electrolyte, the morphology of the electrochromic layer and the associated changes in ionic diffusion within that morphology, and ion insertion kinetics.²² Durability is typically quantified by measuring the changes in charge capacity or coloration efficiency over many thousands of electrochemical cycles. Assuming that a real-world electrochromic window undergoes one full cycle per day, a 30-year lifetime equates to a cycle life of about 11,000. An emerging industry standard includes testing to at least 50,000 cycles.

To compare performance among different electrochromic materials and devices, researchers use the coloration efficiency as a key figure of merit. coloration efficiency (CE) is given by:^{20;22}

$$CE(\lambda) = \frac{\Delta OD}{Q} = \frac{\ln [T_{\text{bleached}}(\lambda)/T_{\text{colored}}(\lambda)]}{Q} \quad (2.1)$$

where Q is the electronic charge injected into the electrochromic material per unit area, T_{bleached} is the transmittance in the bleached state, and T_{colored} is the transmittance in the colored state. The coloration efficiency therefore gives the change in optical density (or contrast ratio) achieved by the injection of unit charge over unit area, and is typically given in units of cm^2 per Coulomb. In general, materials with higher CEs will have better durability and faster switching times, since less charge is required to produce a given optical response.²⁰

2.3 Overview of current state-of-the-art conventional electrochromic materials

Here we briefly discuss the current state of the art in conventional inorganic electrochromic materials. Electrochromic properties of these materials and the plasmonic metal oxides,

which are discussed later in the article, are summarized in Table 2.1. Tungsten oxide, (WO_3) is the most widely studied electrochromic material. Upon cathodic Faradaic charge injection, WO_3 changes color from a clear, transparent state to a dark blue, translucent state as tungsten ions are reduced. Protons or alkali cations in the electrolyte compensate the injected electrons through insertion into WO_3 octahedral sites, as shown by the following chemical and defect reactions:¹⁶



The physical basis for the coloration is not completely understood,¹⁵ but the prevailing theory is that the injected electrons occupy the previously empty d band, giving rise to new electronic transitions. In crystalline WO_3 , the added electrons occupy delocalized states, while in amorphous WO_3 , they are localized at metal sites, resulting in polaronic absorption that can be described as an electronic charge-transfer transition between adjacent metal sites with different valency.^{15;20;21;23} In general, amorphous WO_3 is considered to have the best overall performance among inorganic electrochromes, due to its high coloration efficiency of over $50 \text{ cm}^2/\text{C}$, fast switching times, and good cycle life.²⁰

The other well-studied transition metal oxides with cathodic coloration are TiO_2 , Nb_2O_5 , MoO_3 , and Ta_2O_5 .^{20;21;23} Like WO_3 , these oxides have edge- and corner-sharing MO_6 octahedra within their crystal structure, which facilitates ion motion through the tunnels or chains of interstitial sites that form in periodic structures of these octahedra.²¹ They also share similar electronic band structures, with intrinsically empty d bands that become populated upon cathodic charge injection, inducing a color change through new intraband transitions.²³ Aside from WO_3 , however, cathodic metal oxides have generally proved disappointing due to factors like poor film durability against electrochemical cycling and low coloration efficiency.

Anodically coloring oxides are usually employed as a counter electrode that colors in a complementary fashion to the primary electrochromic electrode. The most popular of these is NiO , which is transparent in its lithiated or reduced state and gray in its oxidized state. NiO -based thin films have coloration efficiencies ranging from around $30 \text{ cm}^2/\text{C}$ up to $100 \text{ cm}^2/\text{C}$ for Ni-V-oxide films.^{20;21} Other commonly used anodically coloring oxides are IrO_2 and V_2O_5 . If anodic coloration is not needed or desired, then an optically passive, ion-storing oxide layer, such as CeO_2 , CeVO_4 or SnO_2 , may be used as a counter electrode.²⁰

In addition to transition metal oxide-based electrochromic materials, it is worth mentioning electrochromism in molecular materials, such as organic molecules, metal-organic complexes, and polymers. Many molecules, coordination complexes, and polymers are both redox-active and exhibit color changes in different redox states, making them suitable for electrochromic devices. Viologens, which are bipyridine-based salts, display intense coloration upon reduction of the bipyridine dication to a radical cation.¹⁶ Metal-organic coordination complexes with low energy charge transfer or other electronic transitions change color when the metal cation is cycled between oxidation states. One example of such a

complex is ruthenium-2,2'-bipyridine, which is orange in the Ru^{2+} state due to a metal-to-ligand charge transfer band, and transparent in the oxidized, Ru^{3+} state.¹⁶ Finally, conjugated, redox-active polymers are also used in organic electrochromic devices. Poly[3,4-ethylenedioxythiophene] (PEDOT) is a commonly-used electrochromic polymer, which is deep blue in its neutral state and transparent after oxidation.¹⁶ The use of organic molecules in smart windows has met with limited success, as their sensitivity to UV light severely limits their durability and utility. Furthermore, organic electrochromics typically exhibit a “see-saw” effect, coloring in the visible while simultaneously bleaching in the NIR.^{16;20;22} Further discussion of organic electrochromes is outside the scope of this review, but these materials are discussed in numerous other publications.^{16;20;22}

Material/device	Coloration mechanism	Absorption process	Spectral selectivity	Max. CE	Switching speed	Cycle life
Amorphous WO ₃	Ion insertion (cathodic) ²⁰	Polaron absorption, charge transfer ^{15;21}	VIS + NIR (coupled) ²¹	50-80 cm ² /C ^{20;21}	minutes	10,000-100,000 ²⁵
Crystalline WO ₃	Ion intercalation (cathodic) ²¹	Polaron absorption, charge transfer, free carrier absorption ^{15;20;21}	VIS + NIR (coupled)	42 cm ² /C ³⁶	minutes ³⁶	>3,000 ³⁶
NiO	Pseudocapacitive (anodic) ^{20;37}	Polaron absorption, charge transfer ^{19;20}	VIS + NIR (coupled) ¹⁹	30-100 cm ² /C ^{20;21}	53 ms ³⁸	10,000-100,000 ²⁵
ATO nanocrystals ³⁹	Capacitive+insertion (cathodic)	Plasmon/free carrier absorption + charge transfer	Mid-IR, visible (independent)	18 cm ² /C	150 ms	>1,000,000
ITO nanocrystals ^{28;29}	Capacitive (cathodic)	Plasmon absorption	NIR only	375 cm ² /C	50 ms	5,000-20,000
AZO nanocrystals ²⁹	Capacitive (cathodic)	Plasmon absorption	mid-IR, NIR only	400 cm ² /C	60 ms	>20,000
ITO nanocrystals+NbOx glass ³⁰	Capacitive + insertion (cathodic)	Plasmon absorption + polaron absorption	NIR + visible (independent)	30 cm ² /C	10 s of ms (NIR), minutes (VIS)	>2,000
"Ideal" smart window	Capacitive (cathodic + anodic)	Plasmon absorption + polaron/charge transfer	NIR + visible (independent)	∞	seconds	50,000+

Table 2.1: Operation mechanisms and figures of merit for conventional electrochromic materials and new plasmonic colloidal nanocrystal-based electrochromic materials, compared to the desired characteristics of an ideal smart window.

2.4 Nanostructuring approaches for conventional electrochromics

The literature contains numerous examples of electrochromic electrodes made using nanostructures of the materials described in the previous section. For electrochromics, nanotechnology offers the possibilities of improved switching times, higher coloration efficiency, and improved stability against electrochemical cycling. Nanostructuring may also provide economic benefits, as many nanomaterials are compatible with solution processing, which can often be significantly less costly and more energy efficient than processes like sputtering. In this section, we present some interesting advances in nanostructured conventional electrochromic materials. For more detail on these approaches, we refer the reader to other reviews covering this subject in depth.^{16;22;35}

A number of studies on crystalline WO_3 nanoparticles and nanorods (Figure 2.3), synthesized by hot-wire chemical vapor deposition (HWCVD), have been reported.^{15;36;40;41} Nanocrystalline WO_3 is particularly interesting for devices employing protic electrolytes because crystalline WO_3 is stable in acidic conditions where amorphous WO_3 is not.^{15;20;21;23;35} Crystalline WO_3 , however, is not typically used in thin film devices because ionic conduction and switching speeds are quite low in dense films, which lack the disorder and porosity found in amorphous WO_3 . For crystalline nanoparticles and nanorods, the diffusion length for ions is greatly reduced, providing both material stability and faster switching times. Dillon and co-workers found that nanocrystalline WO_3 films not only exhibit coloration efficiencies comparable to the best amorphous thin films, but also have significantly improved durability and fast switching times. Furthermore, the charge capacity, optical contrast, and coloration efficiency were all enhanced as the particle size decreased.^{20;41} The authors saw similar effects for another cathodically coloring material, MoO_x .^{20;21;23;40}

Interesting results have also been reported for nanostructured NiO . In 2005, Deb and coworkers reported pseudocapacitive electrochromism in electrodes of NiO nanoparticles embedded in a Ta_2O_5 proton-conducting matrix (Figure 2.4).^{21;37} By maximizing the surface area of the NiO within the matrix, the authors maximized the specific capacitance of the electrodes and the degree of optical modulation while achieving a coloration efficiency comparable to conventional NiO thin films. This important result demonstrated the feasibility of capacitive electrochromic mechanisms that avoid ion intercalation. Presumably, pseudocapacitive mechanisms in nanoparticle electrochromic electrodes should therefore confer enhanced durability and switching speeds, though the authors did not report these characteristics of their NiO particle films.

In addition to these “bottom up” approaches utilizing nanoparticles, there are also some exciting accounts of using patterning and templating approaches to generate electrochromic nanostructures. In particular, the Steiner group at Cambridge has used block copolymers to template NiO and V_2O_5 into gyrodial and mesoporous three-dimensional networks via electrodeposition.^{23;38;42} These periodic structures exhibit remarkably high surface areas, allowing for exceptional electrochemical and electrochromic performance. The V_2O_5 structure,

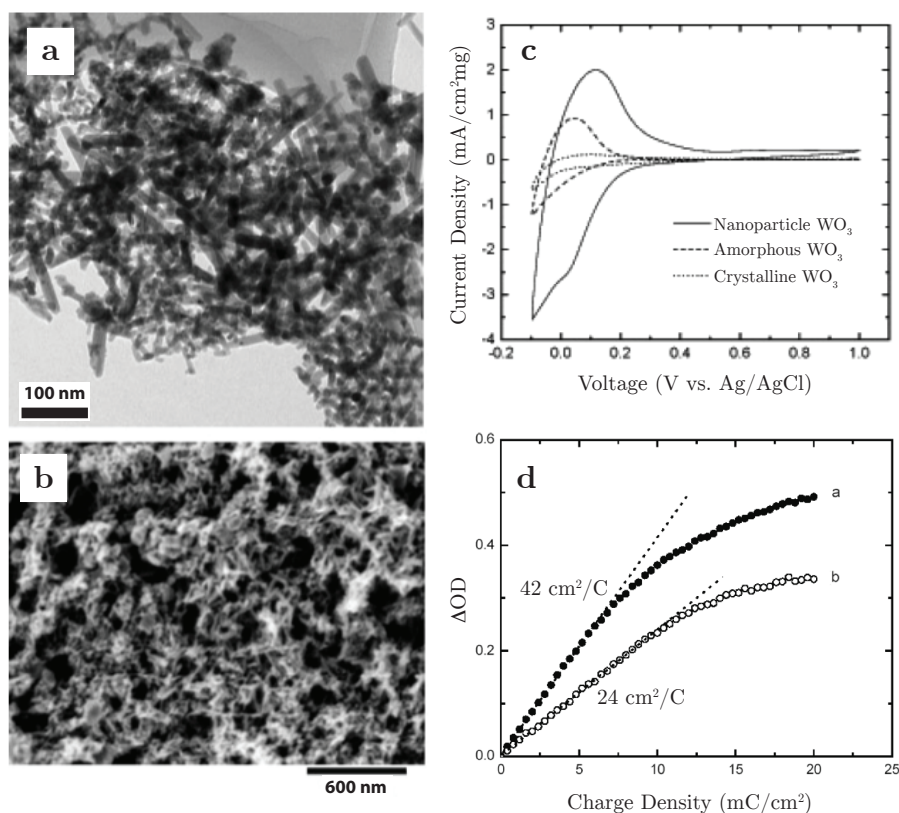


Figure 2.3: WO₃ nanocrystals for electrochromic devices. (a) TEM micrograph of WO₃ nanocrystals synthesized by HWCVD. (b) SEM micrograph of WO₃ nanocrystal electrochromic electrode. (c) Cyclic voltammograms (scan rate: 20 mV/s) displaying the enhanced charge capacity of nanocrystalline WO₃. (d) Change in optical density at 670 nm upon charging a mixture of nanorods and nanospheroids (open circles) and nanospheroids only (closed circles). Reprinted with permission from ref.³⁶. Copyright 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

operated as a pseudocapacitor, obtained a relatively high specific capacitance of 155 F/g along with a fairly strong green-to-yellow color change. Remarkably, the gyrodial NiO structure not only had a switching time nearly two orders of magnitude faster than in thin films, but also displayed significantly higher optical contrast and comparable coloration efficiency (Figure 2.5). Templating approaches are particularly interesting because they can potentially be applied to enhance the performance of many different electrochromic materials, either by reducing ion diffusion lengths within the material or by increasing the electrode-electrolyte interfacial surface area.

The above nanomaterials approaches for electrochromic devices represent promising progress towards creating smart windows that are durable, efficient, and inexpensive. These methods may allow researchers to maximize the performance of devices based on conventional mate-

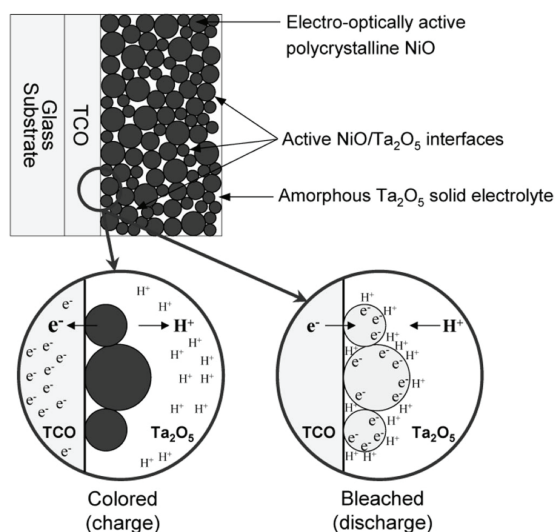


Figure 2.4: Nanostructured NiO electrochromic device. NiO nanoparticles are dispersed in an amorphous Ta_2O_5 matrix, which also acts as an electrolyte for protons. When electrons are injected, protons in the electrolyte adsorb onto the particle surfaces and the nickel ions are reduced at the surface through a pseudocapacitive process. As a result, the electrode bleaches according to the anodic colouration mechanism of NiO. Reprinted with permission from ref.³⁷. Copyright 2005 The Electrochemical Society.

rials; however, it is unclear if truly new functionality can be arrived at by nanostructuring alone. Redox reactions underlying device operation are still frequently accompanied by ion insertion, so durability can remain a challenge even as nanostructuring can moderate the impact of such processes on material degradation. Furthermore, as long as the material compositions are drawn from the traditional selection of transition metal oxides, their optical characteristics remain subject to the limitations introduced in Section 2.1: they do not offer independent control over visible and NIR light, which limits their overall utility.

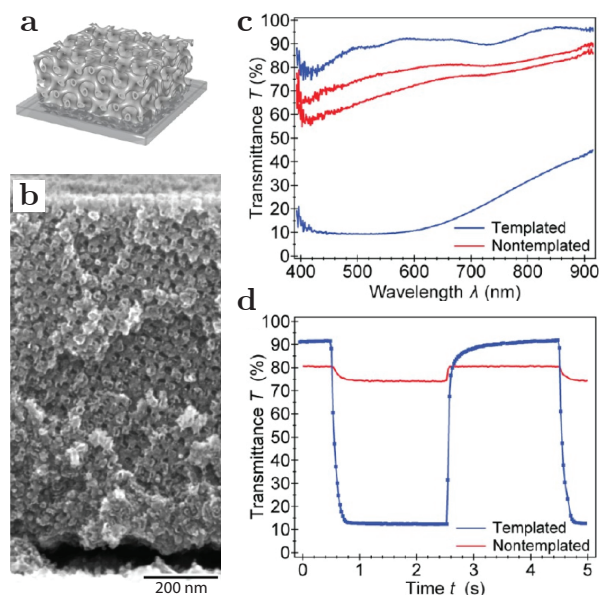


Figure 2.5: Block copolymer-templated gyroidal NiO electrochromic electrodes. (a) Schematic of mesoporous electrode. (b) SEM micrograph of gyroidal NiO. (c) UV-visible spectroscopy shows that templated NiO shows a significantly enhanced electrochromic response compared to non-templated NiO. (d) Time-resolved spectroscopy at 630 nm shows a much faster and deeper response for mesoporous NiO, with colouration and bleaching times of 63 and 53 ms, respectively. Reprinted with permission from ref.³⁸. Copyright 2013 American Chemical Society.

2.5 The emergence of electrochromism in colloidal nanocrystals of non-conventional materials

While nanostructured materials provide some promising improvements in electrochromic performance, nanostructuring alone does not appear to be sufficient to produce an ideal smart window with the characteristics proposed in Table 2.1. Despite their benefits, nanomaterials of conventional electrochromes still fall short of creating new functionality. Nonetheless, one of the most promising characteristics of electrochromic nanomaterials is the exploitation of a new operating mechanism: pseudocapacitance. New, NIR-selective functionality, sought after for an ideal smart window, might therefore be enabled by combining a new operating mechanism that is enabled by using nanomaterials (capacitance) with new materials that exhibit a different type of light absorption process. Such an absorption process would ideally be tunable across the solar spectrum and not broad-band. In the following sections, we will see that colloidal metal and doped metal oxide nanocrystals fit this description. Due to their extremely small size and high surface area, they can easily be electrochemically charged in a capacitive manner. Furthermore, these nanocrystals absorb or reflect light through localized surface plasmon resonance, which is relatively spectrally narrow and can

be tuned across the entire solar spectrum by changing the material or by doping. We will also see that electrochemical injection or extraction of electrons can dynamically change the intensity and spectral position of LSPR absorption. This discovery gives rise to a new type of electrochromic device that has NIR-selectivity and excellent durability, bringing us closer to the ideal smart window. Plasmonic features and tunable absorption in the materials we discuss in the next two sections are specifically enabled by nanostructuring, and our approach has been to employ colloidal nanocrystals to tune size and composition to rapidly advance the development of plasmonic electrochromism.

The field of colloidal nanocrystals and quantum dots is vast, and encompasses nearly all types of inorganic materials. Since the demonstration of quantum confinement in CdS quantum dots by Brus,^{20;21;43} an enormous amount of research has focused on synthesizing colloidal nanocrystals of new materials and observing new nanoscale phenomena. Optical phenomena, in particular, have captured the attention of physicists, chemists, and engineers alike, as nanocrystals tend to exhibit unique absorption, emission, and scattering behavior. In this section, and throughout the rest of this review, we will focus on manipulating light absorption and scattering by free carriers in nanocrystals. Electrochromism results when such manipulation can be carried out electrochemically. We will see that most strategies in this vein rely on the dynamically changing LSPR in nanocrystals.

Localized surface plasmons are collective oscillations of conduction band electrons (or holes in the valence band) in response to incident electromagnetic radiation (Figure 2.6).^{20;44} When the frequency of the radiation is close to the resonance condition of the free carriers, the nanocrystal exhibits significantly enhanced light absorption and scattering. Substantial effort has been expended to understand and control the optical properties of LSPRs in nanocrystals since Faraday's descriptions of gold colloids and Mie's theoretical treatments of their optical spectra.^{16;45} The literature now abounds with examples of manipulating LSPRs in nanostructures, either by synthetic control (changing nanocrystal size or shape,^{16;46} alloying,^{16;47;48} doping^{4;20}) or by post-synthetic treatments (chemical,^{15;21;49;50} photochemical,^{21;51;52} or electrochemical manipulation^{20;21;53–56}). A thorough treatment of these manipulations is far beyond the scope of this review (for discussions on plasmon resonance in nanocrystals and nanostructures, see^{25;44;45;57–66}), but we will introduce the important experiments leading up to the birth of capacitive plasmonic electrochromics.

The relationship between free carrier concentration in a nanocrystal and the LSPR frequency is given by the following expressions:^{21;45;49}

$$\omega_{\text{LSPR}} = \sqrt{\frac{\omega_p^2}{1 + 2\varepsilon_m} - \gamma^2} \quad (2.4)$$

$$\omega_p = \sqrt{\frac{ne^2}{\varepsilon_0 m_e^*}} \quad (2.5)$$

where ω_p is the bulk plasma frequency of free carriers (here, we assume electrons) in the material, n is the carrier density, m_e^* is the electron effective mass, ε_m is the dielectric

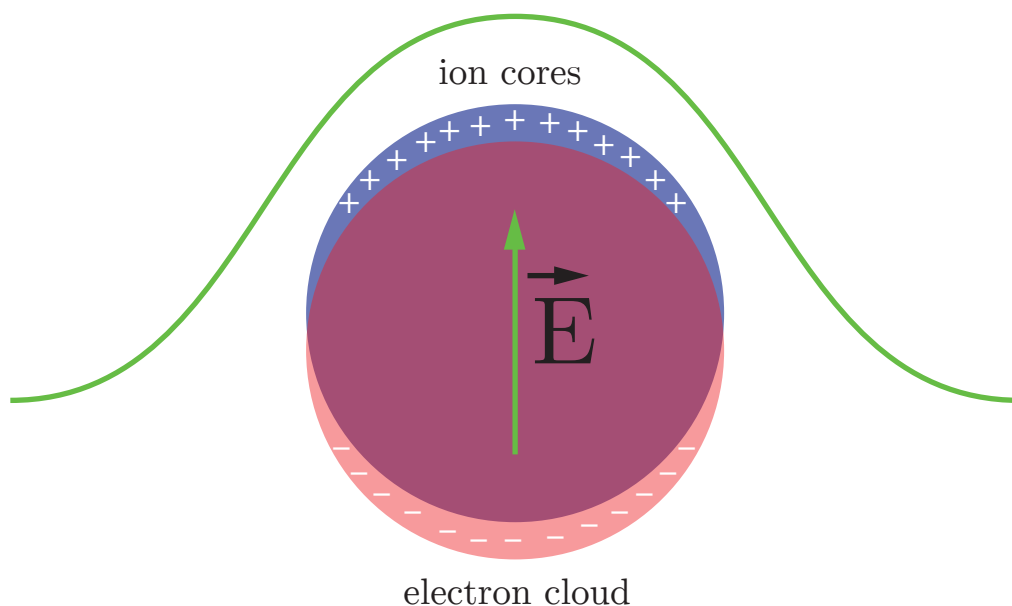


Figure 2.6: Illustration of a localized surface plasmon in a conductive metal or semiconductor nanocrystal. Incident electromagnetic radiation displaces the free electron cloud, which then experiences a restoring force exerted by the positively charged ion cores. At the resonance frequency, scattering and absorption are strongly enhanced.

constant of the surrounding environment, and γ is the bulk collision frequency for free carriers. It is evident that by changing the dielectric environment, or by changing the carrier concentration, one can tune the LSPR frequency. The LSPR frequency and intensity can both be strongly modulated by changing the electron concentration, while dielectric shifts (e.g., those brought about by changing the host medium surrounding a nanocrystal⁶⁷ or by inter-nanocrystal coupling^{28;62}) offer relatively modest LSPR tuning. Furthermore, for the purposes of electrochromism, fast and reversible optical changes are much more easily achieved by changing the electron concentration through chemical or electrochemical doping. We will focus on this approach in the remaining discussion.

Henglein, Mulvaney, and Linnert provided one of the first examples of chemically induced changes to LSPR in colloidal Ag suspensions in 1991.⁶⁸ The authors subjected aqueous suspensions of Ag oligomeric clusters or nanoparticles to ionizing radiation, which generated radicals that would diffuse to particle surfaces and either reduce the Ag colloids by injecting electrons, or extract electrons to oxidize the colloids. Electron injection was confirmed by measuring the associated increase in the DC conductivity of the suspension. Concurrently, the LSPR absorption peak blue shifted, narrowed in width, and grew more intense, confirming the increase in electron concentration in the Ag colloids (Figure 2.7a). Upon oxidation, the decrease in electron concentration caused the LSPR peak to red shift, broaden, and de-

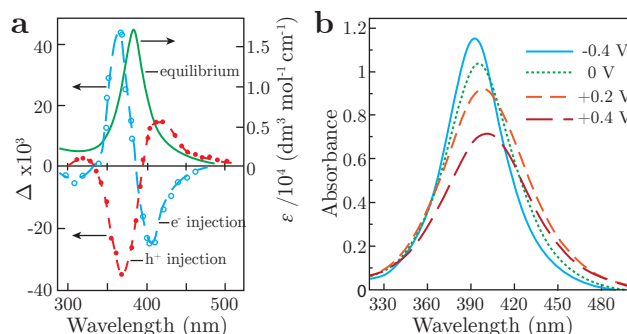


Figure 2.7: Chemical and electrochemical manipulation of LSPR in colloidal Ag nanocrystals. (a) Chemical manipulation of electron concentration using hydroxide radicals. The solid curve is the original plasmon absorbance, while the open circles represent the change in absorbance upon reduction, and the closed circles represent the change in absorbance upon oxidation. Adapted from ref.⁶⁸, copyright 1991, with permission from the Royal Society of Chemistry. (b) Absorbance of Ag nanocrystals at various potentials vs Ag/AgCl. Adapted with permission from ref.⁵⁴. Copyright 1997 American Chemical Society.

crease in intensity. While the optical changes were chemically induced and not electrochromic in nature, this important experiment laid the foundation for plasmonic electrochromism by showing that injection or extraction of electrons in colloidal metal nanoparticles results in a shift in the LSPR wavelength. In doing so, the authors set the stage for the following two decades of research on manipulating LSPR features through chemical, photochemical, and electrochemical doping.

Mulvaney *et al.* built upon this work in 1997 by electrochemically doping colloidal silver.⁵⁴ Using an aqueous electrolyte solution containing polymer-stabilized Ag nanoparticles, the authors employed in situ spectroelectrochemistry to cathodically charge the silver colloids. As individual particles diffused towards the negative working electrode, electrons tunneled into the particles and were compensated by ionic charge in the electrolyte through formation of a double layer. As charging occurred, the plasmon absorption peak simultaneously blue shifted, increased in intensity, and narrowed (Figure 2.7b). It was possible to reverse the process, and even to anodically “bleach” the particles by removing electrons, causing a red shift, broadening, and decreasing intensity of the plasmon absorption peak. Over the entire stable voltage window, 1790 electrons were transferred into or out of each 9.8 nm diameter silver nanoparticle to modulate the plasmon resonance wavelength between 404 nm and 392 nm. While the shift in the absorption peak was small (owing to the high intrinsic carrier density of silver), this experiment demonstrated an entirely new type of electrochromism based on electrochemical manipulation of plasmon absorption in nanoparticles.

Wang, Shim, and Guyot-Sionnest broadened the field into chalcogenide nanocrystals with their demonstration of electrochromism in colloidal dispersions of CdSe quantum dots in 2001.⁶⁹ Fourier transform infrared (FTIR) and UV-visible spectroscopies were used to measure the absorption and photoluminescence (PL) of the charged nanocrystals by moni-

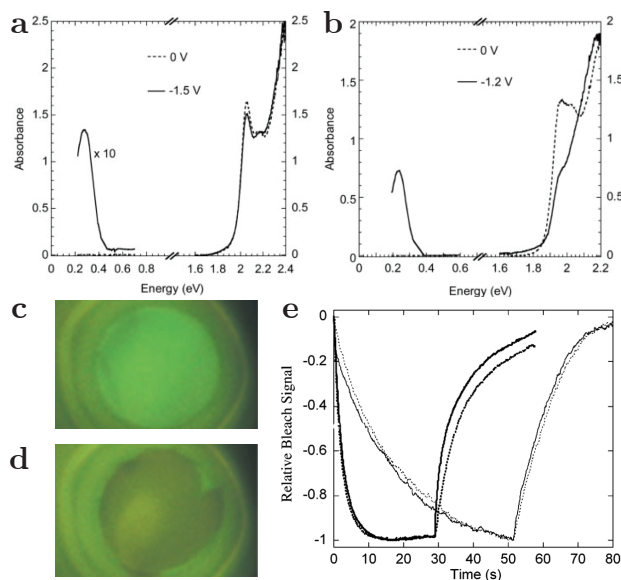


Figure 2.8: Electrochromism of CdSe quantum dots. (a) Optical response of a colloidal dispersion of 5.4 nm CdSe nanocrystals upon applying a negative potential. (b) Electrochromic response of a colloidal suspension 7.0 nm CdSe nanocrystals. (c) Photograph of uncharged CdSe suspension under UV illumination, displaying photoluminescence. (d) The PL is quenched upon charging the CdSe quantum dots. (e) Time response of the bleaching at 1.94 eV for 6.2 nm diameter CdSe nanocrystal films with different surface treatments. The solid lines are the response with voltage set to zero after the negative potential step; the dotted lines are the response of the film disconnected from the potentiostat after the negative potential step. Parts (a) through (d) from ref.⁶⁹. Reprinted with permission from AAAS. Part (e) reprinted with permission from ref.⁷¹. Copyright 2003 American Chemical Society.

toring the reflectivity of the optically polished Pt working electrode. Upon electron transfer into the CdSe, the dispersion exhibited a new mid-IR absorption peak, along with bleaching in the visible and quenching of the PL (Figure 2.8). These optical effects are due to injected electrons occupying the 1s state in the nanocrystals; the new IR absorption is indicative of intraband transitions from 1s to 1p, while the visible bleach is due to filling of the 1s states, which prevents the lowest energy interband transitions as well as PL. Both electron injection and the optical changes were fully reversible, although the authors were not able to inject stable holes or observe any related optical effects. It was also shown that the energy and intensity of these transitions could be manipulated by changing nanocrystal size, owing to the quantum confinement effect in CdSe quantum dots. Guyot-Sionnest *et al.* subsequently built upon these results by processing 4.2-6.8 nm CdSe nanocrystals into thin films.^{70;71} Those films, when properly prepared, exhibited fast, intense electrochromism on a time scale of about 100 ms, and were durable enough to last for over 10,000 cycles.

These types of spectroelectrochemical experiments were extended to highly doped and conductive metal oxide nanocrystals between 1999 and 2002. Boschloo and Fitzmaurice were the first to prepare thin films of nanocrystalline antimony-doped tin dioxide (Sb:SnO₂ or ATO) on conductive substrates and electrochemically charge them to achieve an electrochromic effect.⁷² By performing Mott-Schottky analysis, they measured the pH-dependent flat-band potential of ATO, followed by spectroelectrochemistry. At potentials greater than the flat-band potential, a depletion layer formed within the nanocrystals at the interface with the electrolyte concurrent with an observed decrease in absorption, while at potentials less than the flat-band potential, the absorption increased as electrons were injected into the ATO. The spectral changes were fully reversible, and the charge was injected capacitively, rather than through Faradaic, ion-insertion, or other redox reactions. The authors ascribe the increased absorption at short wavelengths to optical band gap widening through the Burstein-Moss effect, and at longer wavelengths to electron “Drude absorption,” but their spectral results do not extend to sufficiently long wavelengths to observe a shifting NIR absorption peak that would be characteristic of plasmonic electrochromism.

In 2000, recognizing the potential to use capacitive charge injection in nanocrystals for electrochromic devices, zum Felde, Haase, and Weller worked to maximize the electrochromic effect in films of ATO nanocrystals.³⁹ By synthesizing their own nanocrystals to achieve small sizes with controlled Sb content and electrode layer porosity, the authors were able to drastically increase the changes in optical density with voltage, on a time scale of about 150 ms, and with a coloration efficiency of 18 cm²/C (at λ =650 nm). In this case, a NIR absorption peak centered at wavelengths between 2000 nm and 3000 nm was indeed observed in the prepared films, and ascribed to LSPR in part because the peak wavelength depended on the extent of Sb doping. The magnitude of this absorption feature increased as electrons were injected into the nanocrystalline network, yet the frequency of the plasmon peak did not change, suggesting that the concentration of free electrons remained constant (Figure 2.9). To rationalize this observation, the authors proposed that a depletion region exists near the surface of the nanocrystals, arising from factors such as reduction of Sb⁵⁺ to Sb³⁺ at the surfaces and other surface electron trap states. In such a scenario, the depletion layer shrinks as electrons are injected into the nanocrystal, maintaining a constant electron concentration even as the overall population of electrons changes substantially. Strongly negative potentials induced increased absorption in the visible as well as the NIR, which the authors ascribed to electrochemical reduction of Sb⁵⁺ to Sb³⁺ accompanied by cation insertion. Pflughoeft and Weller followed up on this observation in 2002, attributing the visible absorption to Sb³⁺Cl-Sb⁵⁺ and Sb³⁺O₂-Sb⁵⁺ charge-transfer complexes.⁷³

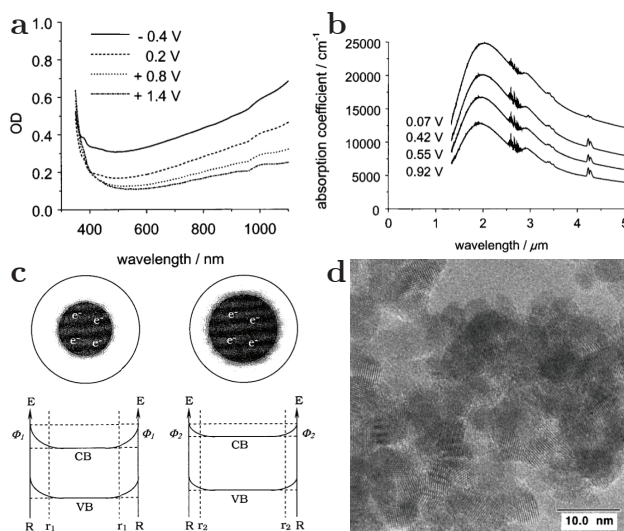


Figure 2.9: Electrochromic response of Sb-doped tin oxide nanocrystal films. (a) Visible absorption at different potentials vs. Ag/AgCl. (b) NIR absorption response at different potentials vs. Ag/AgCl. (c) Illustration of the effects of a depletion layer on the electron concentration. As the potential is decreased (from left to right), electrons are injected, but the width of the depletion region also decreases, resulting in no change in the carrier concentration. (d) TEM micrograph of ATO nanocrystals. Reprinted with permission from ref.³⁹. Copyright 2000 American Chemical Society.

2.6 A new paradigm: NIR-selective dynamic plasmonic electrochromism in doped metal oxide nanocrystals

The experiments described above were foundational in elucidating a new type of electrochromism based on electrochemical injection or extraction of electrons into or out of plasmonic nanocrystals *via* capacitive charging. In such nanocrystals, a change in electron concentration should result in a shift in the LSPR absorption frequency and a change in absorption intensity, giving rise to plasmonic electrochromism. These early experimental results, however, fell short of challenging conventional electrochromics for applications such as smart windows:

- Although metal nanoparticles exhibit very strong LSPR absorption and Ag colloids were the first plasmonic electrochromic system, the high carrier concentration ($\sim 10^{23} \text{ cm}^{-3}$) severely limits the spectral range over which the plasmon resonance can be tuned. In an electrochemical capacitor-like geometry, the maximum number of electrons that can be injected into each nanocrystal is limited by factors such as the voltage stability window of the electrolyte and the electrode, the size/surface area of individual nanocrystals, and the polarizability of the nanocrystals and electrolyte. If the electron concentration

is already quite high, then this maximum number of injected electrons will have a smaller effect on the plasmon absorption. Metals also screen the electric fields from the electrolyte more strongly than other materials, further limiting the extent to which the electron population can be modulated.

- While ATO nanocrystals showed much stronger electrochromism than metal nanocrystals, the majority of the electrochromic effect occurred at longer wavelengths in the NIR and mid-IR where there is not much solar insolation. Whether due to processing methods or inherent material limitations, an electrochemically-induced blue shift in the LSPR frequency to more relevant wavelengths has not been observed for ATO.
- Likewise, the optical changes of electrochromic CdSe are unsuitable for smart windows. Visible contrast is not sufficiently high, and the IR response of CdSe is in the mid-IR, where it is not useful for blocking solar heat gain.

Transparent conducting oxides (TCOs) are a class of material that have the potential to avoid these shortcomings. Bulk ITO and AZO, in particular, have carrier concentrations intermediate between semiconductors and metals ($\sim 10^{21} \text{ cm}^{-3}$), placing their plasma frequencies in the NIR.⁷⁴ Recent work has demonstrated that ITO and AZO can be synthesized as monodisperse and colloidally stable nanocrystals.^{67;75–77} Due to the high conductivity of ITO and AZO, both materials have been shown to support strong LSPRs in the NIR, ranging from wavelengths of about 1600 nm to 4000 nm.^{67;76;77} Thanks to the efforts of many researchers over the past five years, including those in our group, synthetic protocols for ITO and AZO nanocrystals are now robust, allowing for control of nanocrystal sizes, doping levels, and optical properties. As detailed in Section 2.7, the synthetic control achieved over these nanocrystals is a key recent development that has made our work on plasmonic electrochromism possible.

We first reported the exceptional electrochromic properties of ITO nanocrystals in 2011. After synthesizing colloidal ITO nanocrystals of various sizes and doping levels, Garcia *et al* processed them into continuous, electrically connected microporous thin films.²⁸ This was accomplished by spincoating the nanocrystals, with their native organic ligands attached, onto ITO-coated glass substrates. The films were then treated with a formic acid solution to displace the ligands by mass action. Formic acid molecules at the nanocrystal surfaces were easily removed by annealing in an inert atmosphere, providing electrical conductivity throughout the entire film while leaving the micropores between nanocrystals intact, which allowed for electrolyte penetration throughout the film.

Upon immersing the ITO nanocrystal film in a LiClO_4 electrolyte and applying a negative bias in a spectroelectrochemical experiment, a large LSPR blue shift was observed, causing up to unity change in optical density at NIR wavelengths for 150 nm-thick films. Even greater modulation was observed for thicker films. The shift in LSPR absorption frequency indicated that the electron density was indeed changing with electrochemical potential, indicating that the ITO nanocrystals were operating in an electrochemically stable accumulation regime. The large shift also indicated that, unlike ATO nanocrystal films,³⁹ the ITO nanocrystals were relatively free of surface defects and the associated depletion

layer modulation.²⁸ Applying a positive potential easily reversed the optical changes, and the plasmon could even be red shifted from its equilibrium position, causing a bleach in absorption and indicating a transition to a depletion regime. Drude modeling confirmed that the carrier concentration increased over threefold from about $4.5 \times 10^{20} \text{ cm}^{-3}$ at the most positive bias to over $1.4 \times 10^{21} \text{ cm}^{-3}$ at the most negative bias.

Ultimately, smaller, more highly doped nanocrystals gave the strongest modulation of solar transmittance by allowing accumulation and depletion layers to extend farther into their interior volume and increasing the blue shift of the LSPR peak into the range of the NIR with higher insolation. These nanocrystals modulated the integrated NIR solar transmittance by 35% with only a 6% change in integrated visible transmittance. The wavelength-dependent coloration efficiency ranged from $25 \text{ cm}^2/\text{C}$ at 1200 nm to nearly $200 \text{ cm}^2/\text{C}$ at 1700-1800 nm. The electrochromic response was the same in Li^+ -containing electrolytes that support possible insertion reactions as in tetrabutylammonium ion-containing electrolytes where insertion was sterically prohibitive, indicating that capacitive charging is the dominant electrochromic mechanism. This mechanism enabled fast coloration and bleaching processes, and one should expect that capacitive operation should also promote long cycle life. The capacitive nature of the electrochromic effect, and the associated optical changes in the ITO nanocrystals, is depicted in Figure 2.10.

Garcia, *et al* next examined the electrochromism of AZO nanocrystal films and compared them to ITO films,²⁹ utilizing a newly-developed “Meerwein’s salt” ligand stripping procedure to avoid dissolution or etching of the AZO nanocrystals in formic acid.⁷⁸ The NIR modulation of AZO and particularly its durability bettered that of ITO, even though ITO’s coloration efficiency had also been improved since the original report. This was ascribed to the enhanced electrochemical stability of Al^{3+} dopants in AZO relative to Sn^{4+} in ITO, which improved durability and allowed for more negative potentials to be applied to AZO, increasing the number of injected electrons without irreversibly reducing the metal ions. Overall, with changes in optical density of up to 2.5, the best AZO films achieved a 39% modulation in solar NIR transmittance, while the transmittance of visible sunlight changed by only 4%. This corresponded to coloration efficiencies of about $50 \text{ cm}^2/\text{C}$ at 1100 nm and up to over $400 \text{ cm}^2/\text{C}$ at 2000 nm. coloration efficiencies in the ITO films ranged from about $50 \text{ cm}^2/\text{C}$ at 1200 nm to a maximum of about $375 \text{ cm}^2/\text{C}$ at 1700-1800 nm. These values are extremely high compared to conventional transition metal oxide electrochromic materials, which are typically in the range of $20\text{-}100 \text{ cm}^2/\text{C}$.

This study also demonstrated the excellent switching speed and durability of nanocrystal-based electrochromics.²⁹ The switching speeds for AZO were extremely fast, ranging between 0.06 and 0.9 seconds depending on the electrolyte composition, while for ITO the switching speeds were between 0.05 and 3.4 seconds (Figure 2.11). Both ITO and AZO nanocrystal films were subjected to 20,000 electrochemical cycles, and their electrochromic and charge-storage properties were measured both before and after the cycling. The AZO film lost only 11% of its charge capacity with little change in optical performance. On the other hand, the ITO film suffered a 45% reduction in charge capacity. The loss in capacity moderately reduced the optical modulation range of ITO, and was attributed to free carrier loss due to ir-

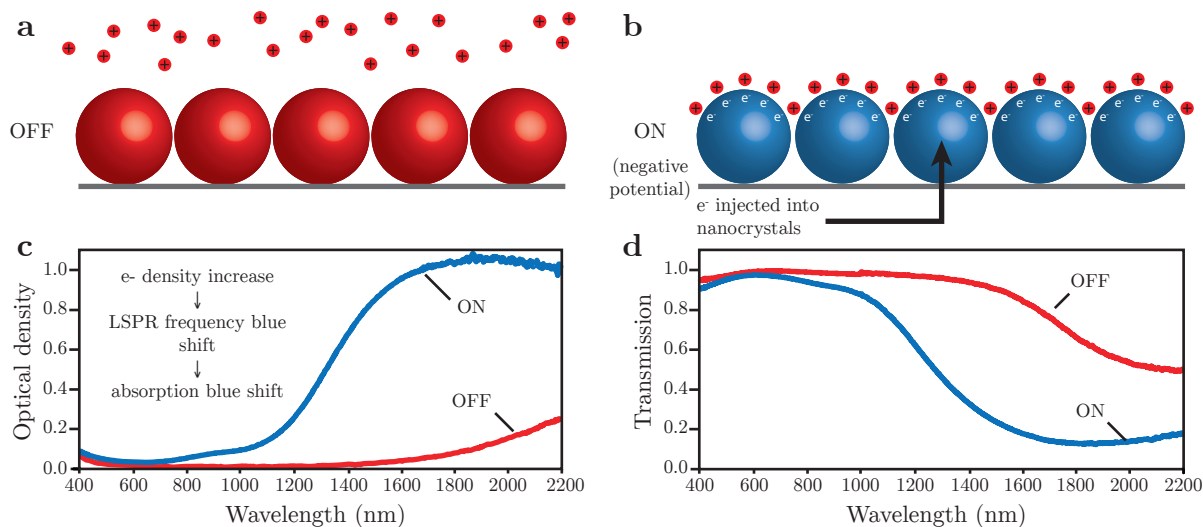


Figure 2.10: Depiction of the microscopic operation of a nanocrystal-based plasmonic electrochromic film, along with the associated optical changes. (a) In the OFF state, positive potential is applied to the nanocrystals, which are depleted of electrons and lithium ions are repelled. (b) In the ON state, a negative potential is applied to the nanocrystals, which injects electrons. Lithium ions are attracted to the nanocrystal surface to compensate the injected charge capacitively. (c) Optical density changes resulting from electron injection. The increase in carrier density causes a blue shift in the LSPR and absorption. (d) Corresponding changes in transmission of the film. Parts (c) and (d) adapted with permission from ref.²⁸. Copyright 2011 American Chemical Society.

reversible reduction of Sn^{4+} to Sn^{2+} . These results demonstrate that TCO nanocrystal-based electrochromics, based on capacitive electrochemical injection and extraction of electrons, have the potential to be effective as NIR-selective smart windows with fast and deep coloration as well as good durability. AZO also has the added benefits of low cost and earth abundance compared to ITO.

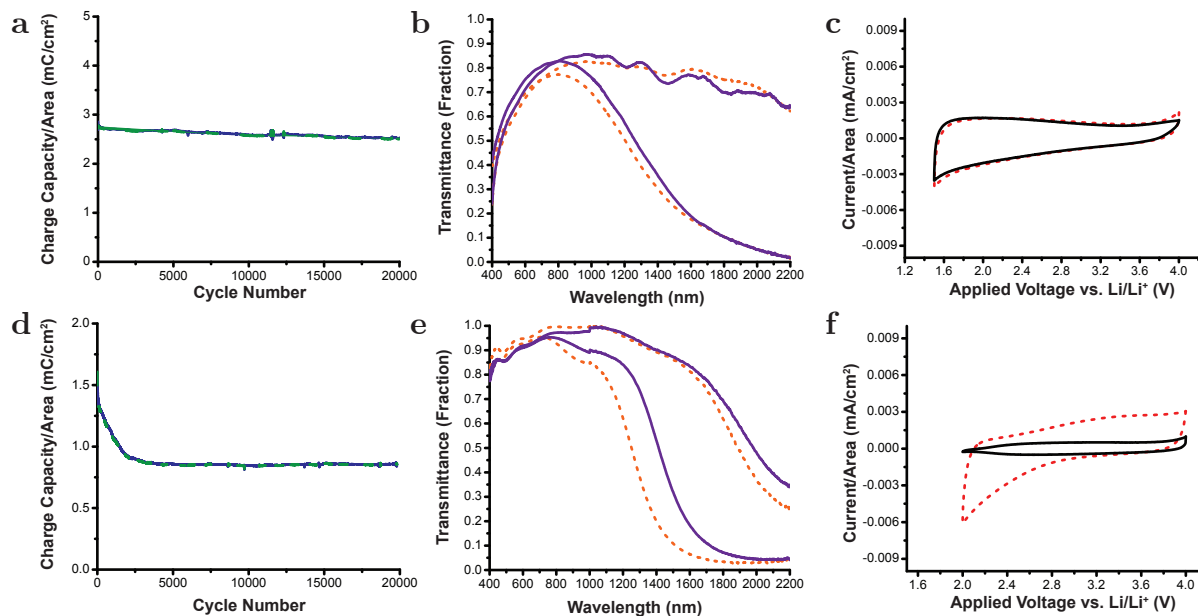


Figure 2.11: Durability testing of AZO and ITO electrochromic nanocrystal films. (a) Charge capacity of AZO films vs. cycle number. (b) Transmittance modulation AZO nanocrystal film before (dashed lines) and after 20,000 cycles (solid lines). (c) Cyclic voltammogram of AZO films before (dashed line) and after (solid line) cycling shows little change in electrochemical properties. (d) Charge capacity of ITO films vs. cycle number. (e) Optical modulation of ITO nanocrystal film before (dashed lines) and after (solid lines) 20,000 cycles. (f) The cyclic voltammogram for ITO shows diminished charge capacity after 20,000 cycles (solid line). Reprinted with permission from ref.²⁹. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.7 Design principles for nanocrystal-based plasmonic electrochromics

The realization of nanocrystal-based plasmonic electrochromics would have not been possible without the recent advancement of methods for synthesizing doped metal oxides and other doped semiconductor nanocrystal colloids. In this section, we present the design principles—doping, size, and material selection—for nanocrystal-based plasmonic electrochromics, and describe how colloidal nanocrystal synthesis can be leveraged to meet these design principles. In particular, we will present doping strategies that enable the generation of free electrons in colloidal metal oxide nanocrystals, and thus, LSPRs in the NIR. We will also address the experimental limitations of aliovalent substitutional doping and highlight the exploration of plasmonic nanocrystal materials beyond TCOs. Finally, we discuss the influence of nanocrystal size and dopant concentration on the LSPR modulation.

Maximizing the shift in plasmon resonance and the associated modulation of NIR radi-

tion is still a key challenge to improving the functionality and the energy saving capabilities of plasmonic smart windows. As observed in ITO and other semiconductor nanocrystals, higher doping shifts the equilibrium position of the LSPR peak to higher frequency, moving it closer to a region of appreciable solar energy. By comparison, the relationship between decreasing nanocrystal size and enhanced optical modulation remains mysterious. At smaller radii, nanocrystals have a larger surface to volume ratio, giving higher capacitance and allowing for more electrons to be injected. Smaller nanocrystals will also have a larger increase in electron concentration within the accumulation region for a given accumulation layer thickness. It is unclear which of these two effects is the limiting mechanism in determining the ultimate free electron concentration achievable by capacitive charging. However, as a general design principle for NIR-selective plasmonic electrochromics, small and highly doped plasmonic metal oxide nanocrystals should be used to maximize optical modulation in the NIR range of the solar spectrum. In addition, materials that weakly screen external electric fields (unlike metals, as discussed at the beginning of Section 2.6) allow the electron accumulation region to extend as far as possible into the nanocrystal core. This allows for the maximum number of electrons to be injected, corresponding to greater changes in the plasmon peak position. These design principles are summarized in Figure 2.12. As this field progresses, we expect that the material that combines small nanocrystal size, high doping level, and low screening of electric fields will provide the best electrochromic performance.

To achieve changes in nanocrystal doping, size, or to utilize new plasmonic materials, our group has turned to organic phase colloidal nanocrystal synthesis. The well-established surfactant-mediated method for colloidal synthesis allows one to grow nanocrystals from molecular precursors in solution phase at moderate temperatures between 150°C and 400°C (Figure 2.13). Surfactant-assisted colloidal synthesis offers excellent control over nanocrystal size and shape, as well as preventing their aggregation and precipitation from solution,^{2;3;79;80} which enables stable colloidal dispersions (Figure 2.13c). Such dispersions can serve as inks for solution deposition of nanocrystal films using potentially low cost and industrially scalable techniques such as spray coating or slot die coating, as well as laboratory-scale techniques like spin coating. More recently, it has become possible to finely control nanocrystal composition, providing enhanced tunability of dopant concentrations and hence LSPR frequency.^{67;77;81} These advances have been critical for the development of LSPR-based nanocrystal electrochromics, and have also contributed momentum to new research on plasmonic optoelectronics.^{82;83}

A critical aspect that was not investigated in the seminal experiments on the electrochromism of ATO nanocrystals was the influence of nanocrystal size.^{39;72;73} Varying nanocrystal size, as was done for colloidal CdSe quantum dots,^{69;70} provides the opportunity to better understand the fundamental mechanisms at work in nanoscale electrochromic materials. In the case of ATO, however, the nanocrystals were synthesized by a coprecipitation method, which limited the opportunity to tune nanocrystal size over a broad range, obtain monodisperse size distributions, and achieve higher degrees of crystallinity. Now that organic phase colloidal methods have advanced for doped oxide nanocrystals, we can access stable colloidal dispersions (Figure 2.13) with monodisperse nanocrystal dimensions that can be

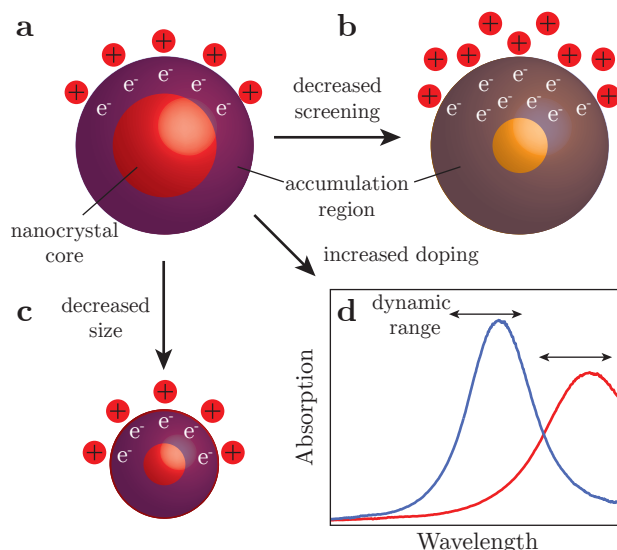


Figure 2.12: Design principles for plasmonic nanocrystal electrochromic materials. (a) Base material with a given doping level, size, and screening level, displaying an electron accumulation region resulting from capacitive charging by cations at the nanocrystal surface. (b) Effect of using a nanocrystal with decreased screening, which allows the accumulation layer to extend further into the nanocrystal core and enhance the change in electron concentration. (c) Effect of decreasing nanocrystal size, allowing the accumulation layer to extend further throughout the nanocrystal volume. (d) Effect of increased doping, which blue shifts the LSPR absorption peak. For a given dynamic range of the plasmon frequency, increased doping allows modulation of NIR transmittance at wavelengths closer to 750-1250 nm.

tuned from 1 nm to 30 nm.

While the field of colloidal synthesis is well developed and small-diameter nanocrystals on the order of 1 nm can be obtained, achieving high doping levels has been more elusive and challenging.^{84–87} The emergence of plasmonic semiconductor nanocrystals has done much to motivate research on doping strategies. Today, chemists have achieved far better control over the incorporation of dopants into colloidal nanocrystals, and can now do so with a high degree of control over the dopant content⁴ (Figure 2.13e).

Growing colloidal nanocrystals from solution phase is a kinetically controlled process; introducing dopants within the lattice (Figure 2.13d) therefore requires a fine balance of the host nanocrystal growth rate and the dopant incorporation rate. A variety of doping strategies have been reported for several nanocrystal compositions, and they have been recently reviewed and discussed in depth.⁴ For the particular case of binary metal oxides, the most popular doping strategy is based on tuning the relative chemical reactivity of the molecular precursors for the host nanocrystal and for the dopant atom. Typical precursors are metal-organic salts comprising the metal of interest and a ligand (e.g., an alkyl carboxylate). By selecting a ligand with the appropriate steric hindrance and negative charge delocalization

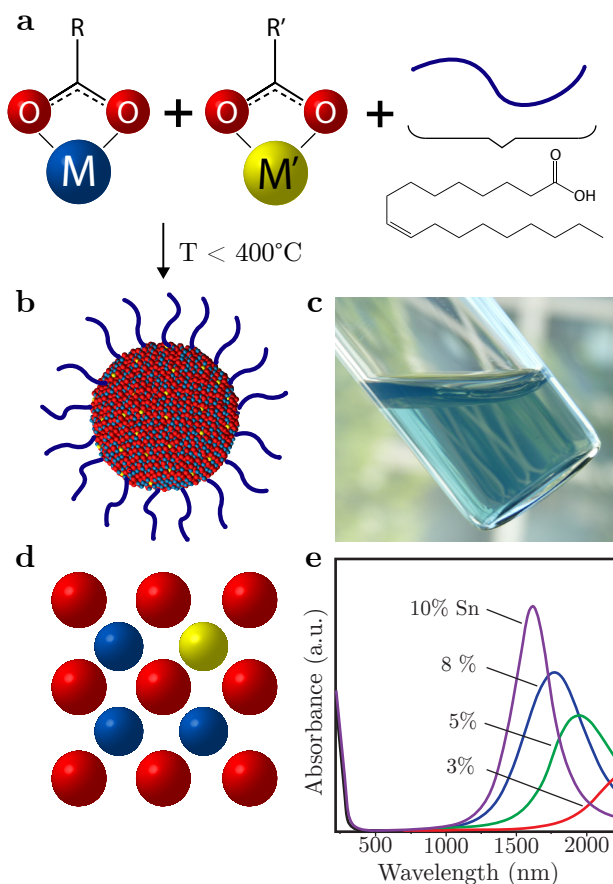


Figure 2.13: Colloidal synthesis of doped metal oxide nanocrystals for electrochromic devices. (a) Molecular precursors (depicted here as metal carboxylates) are combined with ligands (oleic acid depicted) in a non-polar solvent and heated to moderate temperatures. (b) After the precursors decompose and react, inorganic colloidal nanocrystals are formed, which are stabilized in solution by the ligands coordinated to the surface. (c) Optically clear dispersion of colloidal ITO nanocrystals in hexane. (d) Substitutional doping mechanism whereby a donor atom (i.e., Sn) occupies a metal (i.e., In) site in the nanocrystal, thereby introducing electrons into the conduction band. (e) Absorbance spectra of ITO nanocrystals, showing a blueshift, narrowing, and enhanced intensity of the plasmon peak as doping increases. Part (e) adapted with permission from ref.⁶⁷. Copyright 2009 American Chemical Society.

properties, it is possible to tune the ligand-metal bond strength to balance the reactivity of both precursors. By developing this strategy, our group was able to demonstrate the first synthesis of plasmonic, monodisperse Al-doped ZnO nanocrystals of controlled sizes and dopant levels.^{29;77} Substitutional doping strategies have been also proven successful for other TCO nanocrystals, such as Sn-doped In_2O_3 ,^{67;75;81} Nb-doped TiO_2 ,⁸⁸ and In-doped CdO .^{67;75;81}

Understanding the role of size and doping on the electrochromic response of plasmonic nanocrystals is of tremendous importance to generate fundamental knowledge about the mechanism of plasmon modulation as well as generating design rules for these novel materials. The fine control over size and composition offered by colloidal synthesis has enabled our group to pioneer these systematic studies by synthesizing colloidal plasmonic nanocrystals (ITO and AZO) over broad size ranges (4 nm up to 16 nm) (Figure 2.14), with narrow size distributions ($\leq 15\%$ std. deviation in diameter), a high degree of crystallinity, and well-controlled dopant concentrations.^{28;77}

As mentioned earlier, the electrochromic response of our ITO nanocrystal films induced a substantial spectral shift upon charge injection (Figure 2.14g), indicating that the nanocrystals operate in an electrochemically stable accumulation regime. Taking into account the capacitive nature of the electrochemical plasmon modulation, small nanocrystals are expected to show greater optical modulation since the entire volume can lie within the strongly modulated accumulation/depletion region. We confirmed this hypothesis by comparing the optical response of ITO nanocrystals with different sizes and similar doping level. As expected, the change in optical density increases as the average nanocrystal diameter decreases (Figure 2.14h), and films made with the smallest nanocrystals showed the strongest optical modulation. The concentration of free electrons in the as-synthesized nanocrystals, determined by the doping level, also plays a key role because it determines the starting position, width, and intensity of the LSPR absorption peak^{28;67;68;81} (Equations 5-6, Figure 2.13e).

Given that most of the NIR solar energy is located at wavelengths between 750 nm and 1250 nm, it would be optimal to use nanocrystals with LSPRs near that range. Unfortunately, ITO nanocrystals, which so far display the “bluest” plasmons of TCO nanocrystals, have a minimum LSPR wavelength of about 1600-1700 nm.^{28;29;67} This limitation is due to the interplay and competition between doping and defect compensation mechanisms. In metal oxides, aliovalent dopants can be compensated by ionic defects like lattice vacancies and interstitials to maintain charge neutrality. For the particular case of ITO, in which free electrons are introduced by aliovalent substitution of Sn^{4+} for In^{3+} , theoretical and structural studies have verified that neutral $(2\text{Sn}_{\text{In}}^{\bullet}-\text{O}_i'')^{\times}$ defect clusters act as compensating defects.⁸⁹⁻⁹¹ At high doping concentrations, the concentration of these clusters becomes significant, and the defect cluster formation reaction begins to deplete ITO of free electrons. The concentration of free electrons therefore depends on the relative concentration of substitutional tin atoms, $\text{Sn}_{\text{In}}^{\bullet}$, oxygen vacancies, $\text{V}_{\text{O}}^{\bullet\bullet}$, and oxygen interstitial atoms O_i'' . The concentrations of oxygen vacancies and interstitials further depend on the ambient partial pressure or activity of oxygen. This complex relationship has a direct influence in determining the optimum doping level and imposes a maximum carrier concentration that is achievable

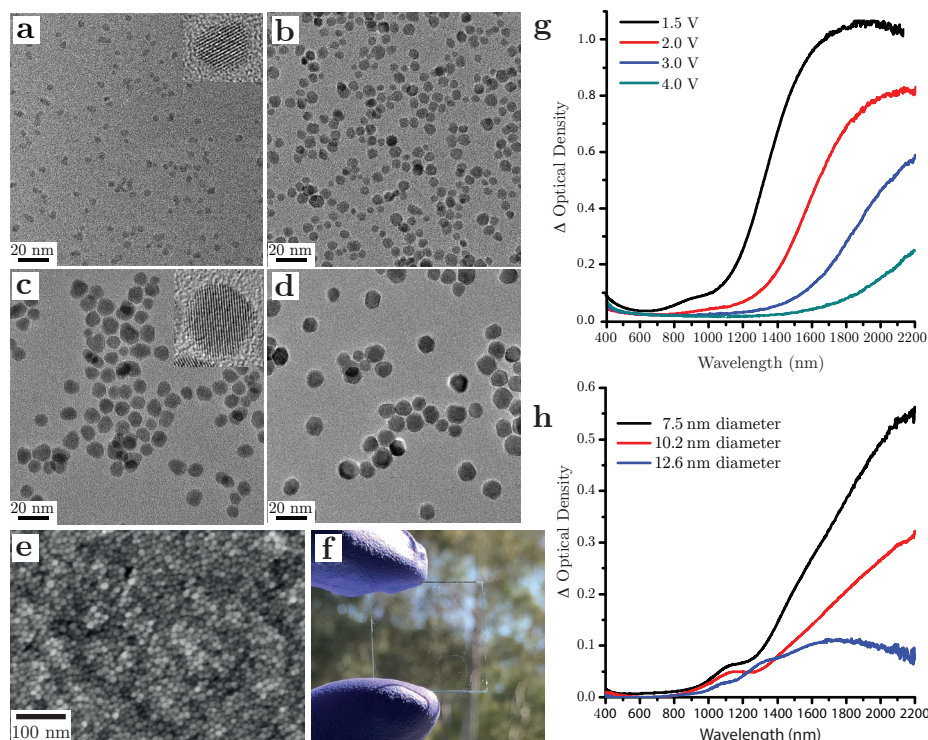


Figure 2.14: Electrochromic ITO nanocrystal-based films. (a)-(d) Transmission electron microscopy images of ITO nanocrystals with sizes (nm): (a) 4.1 ± 0.6 , (b) 7.4 ± 1.4 , (c) 10.2 ± 1.7 , and (d) 12.1 ± 1.5 . (e) Scanning electron image (top view) and (f) photograph of an ITO NC network film on glass substrate. (g) Optical density at different applied voltages of an ITO nanocrystal network film with 4.1 nm diameter, 16.8% Sn nanocrystals. (h) Change in optical density between 1.5V and 4V (vs Li/Li+) for various nanocrystal sizes, each with $4.65 \pm 0.25\%$ Sn. Parts (a)-(d), (g), (h) reprinted with permission from ref. 28. Copyright 2011 American Chemical Society.

by extrinsic doping.⁹² Indeed, as in the bulk, optimum doping levels have been observed for ITO nanocrystals, above which the LSPR peak begins to redshift with increasing doping level.⁶⁷ Development of new plasmonic colloidal metal oxide nanocrystals, with wavelengths closer to the 750 nm to 1250 nm range, will depend on selecting materials that overcome the limitations of defect compensation mechanisms and/or exploit new doping mechanisms, such as interstitial doping.⁶⁶ Vacancy- and cesium-doped tungsten oxide are two examples of recently-developed plasmonic metal oxide nanocrystals with LSPR features within this region of interest.^{93;94}

2.8 Using plasmonic nanocrystals as building blocks for advanced electrochromic devices

Similar to the key contributions of colloidal synthesis in the development of plasmonic electrochromic devices, surface chemistry is being leveraged to integrate plasmonic TCO nanocrystals into mesostructured electrodes with greater functionalities.^{30;31;95} The surfaces of the nanocrystals, when stripped of organic ligands, offer a unique chemical platform to rationally attach other components through interfacial bonding (Figure 2.15a,b,c,f). These components can either add new functionalities to the electrochromic device³⁰ or can be used as architecting agents to form ordered mesoporous nanocrystal assemblies.⁹⁶ For the past 4 years, our group and many other researchers have devoted great scientific effort to exploit and manipulate the surface chemistry of colloidal nanocrystals by employing ligand-exchange or ligand-stripping procedures to expose and/or modify bare nanocrystal surfaces.^{78;97;98} These experimental advancements have led to unprecedented dual-band “nanocrystal-in-glass” composites^{30;99} and mesoporous plasmonic nanocrystal assemblies with ordered, tunable pore sizes and enhanced charge capacity and switching kinetics.³¹ In addition, we recently showed that these electrodes can be successfully integrated into solid-state devices, providing the first demonstration of NIR-selective solid state electrochromic device.³¹ This exciting progress is paving the way for a new generation of advanced electrochromic devices.

As presented in Section 2.6, the simplest nanostructured plasmonic electrochromic electrode is constructed from randomly packed nanocrystals, forming an interconnected open network that yields 34% porosity.^{28;31} Given the capacitive operating mechanism, these electrodes must have high surface areas that are easily accessed by the electrolyte. An ITO nanocrystal electrode with 34% porosity functions well enough in liquid electrolyte to achieve dynamic changes of 40% in NIR transmittance.²⁹ Nevertheless, the accessible surface area of active material is still limited in these films owing to insufficient nanocrystal-electrolyte interfacial contact or interpenetration, inefficient electron conduction within the nanocrystal network, or restricted electrolyte or ion motion within micropores between nanocrystals.^{29;31} All of these effects are detrimental to the dynamic modulation range, coloration efficiency, and switching kinetics of the electrode, and are dependent on the arrangement of ion- and electron-conducting domains in the nanocrystal electrode, the relative length scales of those domains, and the topology of their interfaces. We investigated the influence of pore size by utilizing amphiphilic block copolymer micelles to template ligand-stripped ITO nanocrystals into ordered and conductive mesoporous frameworks. By changing the molecular weights of the hydrophobic or hydrophilic block, the mesoporous architecture was easily controlled, with pores ranging from 29 nm to 37 nm and pore wall thicknesses ranging from 9 nm to 13 nm (Figure 2.15e).³¹ Such exceptional mesoscale control and order was enabled through tailored, strong enthalpic interactions between the hydrophilic block and the ligand-stripped nanocrystal surfaces.⁹⁶ Mesoporous ITO architectures showed comparable optical modulation, higher coloration efficiency, higher charge capacity, and enhanced charging kinetics when compared to randomly packed, microporous nanocrystal networks. The enhancement

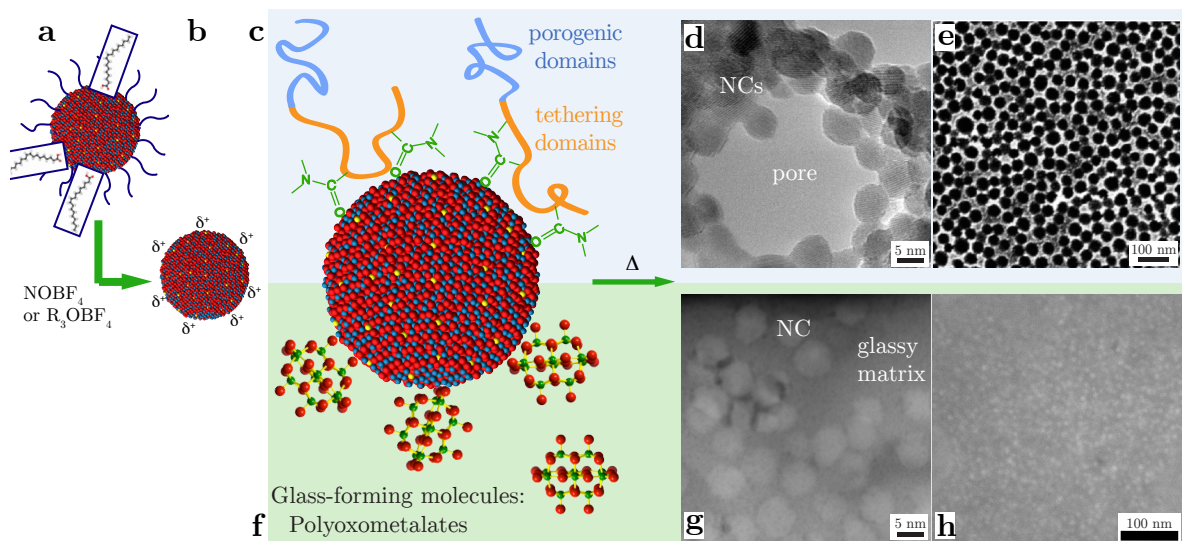


Figure 2.15: Schematic for using colloidal nanocrystals as building blocks for advanced electrochromic materials and devices. (a) Starting with the as-synthesized nanocrystals a ligand-stripping agent is used to produce (b) nanocrystals with bare, positively charged surfaces. (c) The nanocrystal surfaces can be decorated with amphiphilic block copolymers and made to form (d) micelles decorated with nanocrystals (TEM micrograph of a micelle). (e) Upon depositing the micelles and burning off the polymer, a mesoporous structure is obtained (SEM micrograph of film, top view). (f) Nanocrystal surfaces functionalized with POM clusters. Upon deposition and annealing, the POMs decompose to form a glassy matrix surrounding the nanocrystals. (g) TEM cross-section micrograph of a composite film. (h) SEM top-view micrograph of a composite film. Parts (d) and (e) reprinted with permission from ref.⁹⁶. Copyright 2012 American Chemical Society. Parts (g) and (h) reprinted with permission from ref.³⁰. Copyright 2013 Nature Publishing Group.

in switching speed scaled with increasing pore size, indicating that larger pores provided for faster ion transport to the nanocrystal surfaces.³¹

Perhaps even more important than improved coloration efficiency, charge capacity, and switching speed, mesostructured nanocrystal electrodes can be combined with polymer gel electrolytes to fabricate full-cell, solid-state electrochromic devices. We created full-cell devices by using a mesostructured ITO nanocrystal electrochromic electrode, a CeO_2 nanocrystal counter electrode (which was optically passive), and a plasticized, poly(vinyl butyral) (PVB) gel electrolyte containing a lithium salt.³¹ Our PVB electrolyte was easily deposited on each electrode, penetrated into the mesopores of the ITO electrochromic electrode, and allowed the electrodes to be laminated together to produce a robust, solid-state device. The ionic conductivity of the electrolyte was $\sim 10^{-7} \text{ S cm}^{-1}$, which was within acceptable limits for typical electrochromic devices²² and provided good switching speed ($< 10 \text{ s}$) for our devices.

When compared to an unarchitected solid-state device using the same PVB-based elec-

trolyte, mesoporous ITO nanocrystal films displayed greater than two-fold enhancements in optical modulation, coloration efficiency, and charge capacity.³¹ The 60% porosity of the mesoporous film, compared to the 34% porosity in the unarchitected film, provided the solid electrolyte with improved access to and intimate contact with the nanocrystal surfaces. This is a key advance, as the continued development of nanocrystal-based electrochromics will likely depend on the ability to integrate nanocrystals into solid-state devices and manufacturing methods. The capability to produce mesostructured nanocrystal electrodes is therefore incredibly important for the continued development of these devices, as is improved understanding of the interactions between polymer electrolytes, lithium ions within such electrolytes, and nanocrystal surfaces.

Precise control over nanocrystal surface chemistry and assembly also provides an opportunity to combine plasmonic TCO nanocrystals with conventional transition metal oxide electrochromic materials. Such a device could approach the ideal functionality for a smart window, as the nanocrystals and conventional materials could be activated independently to modulate both the visible and NIR regions of the solar spectrum.¹⁰⁰ “Dual-band” functionality would allow the window to operate in either hot or cold climates and respond to changing weather conditions, ultimately pushing past the current performance limits of either conventional or plasmonic nanocrystal electrochromics.¹⁰¹ In 2013, we demonstrated that this scientific challenge could be met by creating a composite material consisting of NIR-selective ITO nanocrystals dispersed in a matrix of a visibly coloring electrochromic material, amorphous niobium oxide (NbO_x).³⁰ To create the composite, anionic niobate polyoxometalate (POM) clusters were chemically linked to the surfaces of ligand-stripped colloidal ITO nanocrystals and thermally condensed, yielding a glassy metal oxide network that is covalently bonded to the nanocrystal surfaces (Figure 2.15). Given that the reduction potential of NbO_x is lower than the potential range for capacitive charging of ITO nanocrystals, the two optical responses can be independently controlled by simply modifying the applied voltage. Thus, for the first time, independent control of NIR and visible light in an electrochromic device has been demonstrated. Interestingly, we also found that structural reconstruction and interfacial doping between the nanocrystals and the glassy matrix strongly affected the optical contrast of the matrix, which was maximized at around 43 vol.% ITO, reaching a value five times greater than that of pure NbO_x when normalized by NbO_x volume fraction (Figure 2.16). Furthermore, the composite electrodes exhibited excellent initial durability, losing only 4% of their charge capacity over 2,000 cycles.³⁰ This, in comparison to the pure NbO_x films (20% capacity loss) and pure ITO nanocrystal films (85% capacity loss) also examined in the study, indicates that the interactions and reconstructions in ITO- NbO_x are key not only to enabling dual-band electrochromic operation, but also enhancing durability, opening the avenue to more robust and more efficient smart windows.

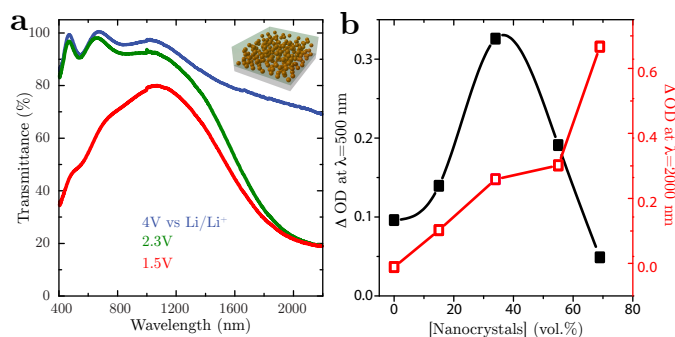


Figure 2.16: Dual-band electrochromic operation of ITO-NbO_x nanocomposites. (a) Changing the applied potential between 4V and 2.3V vs. lithium induces NIR absorption, as electrons are injected into the ITO nanocrystals, changing their LSPR absorption. At potentials below the Li⁺ insertion potential (1.5 V), ions are inserted into and reduce the NbO_x matrix, causing a visible colour change. (b) Optical contrast of the NbO_x matrix (at 500 nm), and ITO nanocrystals (at 2000 nm), vs. ITO volume fraction. Interestingly, the NbO_x contrast is maximized at intermediate nanocrystal concentrations, indicating synergistic interfacial enhancement. Figure adapted with permission from ref.³⁰. Copyright 2013 Nature Publishing Group.

2.9 Conclusion and outlook

Electrochromism has captured the attention of academic and industrial researchers for the past several decades. Unfortunately, sustained and dramatic progress has been elusive, and the promise of electrochromic devices for smart windows, not to mention displays and other applications, has yet to be fully realized. With the advent of nanotechnology, however, it appears electrochromic devices may finally have the impetus needed to live up to their potential. Nanomaterials provide electrochromic devices with enhanced charge capacity, better coloration efficiency, and improved durability, even for conventional electrochromic materials. Furthermore, nanotechnology has provided the field with the discovery of a new class of electrochromism based on plasmonic colloidal nanocrystals, opening the door for new device functionalities, such as NIR selective optical modulation. Significantly, nanomaterials also present an opportunity for industry to move from energy- and cost-intensive vacuum deposition to solution processing methods, potentially drastically reducing the prices of smart windows.

Colloidal TCO nanocrystals, as described in this review, appear to have significant potential to kick-start the progress of smart window technologies. Dynamic plasmonic electrochromism in these materials provides NIR-selective operation with exceptional coloration efficiency, switching time, and durability. Nonetheless, the range of NIR optical modulation in electrochromic TCO nanocrystals is not yet sufficient for smart window applications. Discovery of new TCO nanocrystals, with LSPR absorption peak wavelengths closer to 1250 nm, will be crucial for further development of plasmonic electrochromism. Recent literature

is promising in this regard: newly-synthesized cesium-doped tungsten oxide nanocrystals display LSPR peaks at wavelengths as low as 900 nm,⁹⁴ as do vacancy-doped WO_{2.83} nanorods.⁹³ It remains to be seen if all plasmonic metal oxide nanocrystals are equally amenable to capacitive electrochemical charge injection—if indeed they are, then colloidal Cs_xWO₃ and WO_{3-x} nanocrystals are promising candidates for plasmonic electrochromic devices.

Optimizing and fully understanding dual-band control over visible and NIR light will play a key role in achieving ideal electrochromic device performance and future adoption of smart windows. This will require researchers to explore the feasibility of alternative nanocrystal-in-glass composites, thoroughly characterize the electrochemical cycling durability of these composites, and determine how processing conditions influence durability. There is ample opportunity to explore new material combinations of nanocrystals and POMs; thus far, dual-band functionality has been reported only for ITO-in-NbO_x nanocomposites.³⁰ For optimal performance, new material combinations should be explored, such as those using plasmonic nanocrystals with “bluer” LSPR features and glassy matrices with high coloration efficiencies and better selectivity for visible light. The versatility of the colloidal building block approach enables such exploration as it allows researchers to easily combine new nanocrystal and POM materials as they are being developed.⁹⁹ One outstanding question is whether different nanocrystal-POM combinations will exhibit the same type of interfacial doping or synergy as ITO-in-NbO_x, and whether enhanced electrochromic properties will result. The key for effective dual-band operation will be to discover material combinations for which the electrochemical potentials for capacitive charge injection (changing LSPR frequency) and ion insertion (changing visible absorption via polarons, etc.) are different enough to have three distinct operating regimes (transparent, selectively NIR-blocking, and NIR- and visible-blocking). Our group is currently working to discover new nanocrystal-POM combinations, to examine the bonding synergy between nanocrystals and POMs, and to evaluate electrochromism of new compositions of doped oxides like Cs_xWO₃,⁹⁴ WO_{3-x},⁹³ and Nb-doped TiO₂,⁸⁸ both alone and within nanocrystal-in-glass composites.

As plasmonic electrochromic technology matures, full device integration will become an important gateway to commercialization. One particularly important aspect of device integration is the electrolyte, which, in a commercial device, usually needs to be solid state. We have begun to investigate this aspect, and have demonstrated the feasibility of solid-state nanocrystal electrochromic devices using gelled PVB electrolytes.³¹ This advance was not trivial, as successful device integration required advanced templating methods to generate mesostructured nanocrystal electrodes. It will be necessary to continue developing or modifying solid electrolyte formulations that interface well with nanocrystal electrodes and are amenable to large-scale processing. Solid or gelled polymer electrolytes appear to be promising candidates, and such electrolytes are often utilized in electrochromic devices. This is a significant challenge; polymer electrolytes are often the most closely guarded secrets of commercial smart window manufacturers, and continued research on polymer-nanocrystal interaction and co-processing of polymer electrolytes and plasmonic TCO nanocrystals is needed for this field to advance.

One final challenge that bears mention is the continuing advancement of nanocrystal

synthesis. For one, the advancement of nanocrystal-based electrochromic devices depends on further understanding and manipulation of colloidal chemistry, such that new materials can be synthesized with desired size, shape, and composition. In addition to these laboratory-scale advances, it will also be critical for chemical engineers to understand how to scale nanocrystal synthesis. Current lab-scale synthetic methods typically produce about 1-10 mmol of nanocrystals, which corresponds to 278 mg to 2.78 g of ITO nanocrystals. Industrial-level production of smart windows will eventually require ton-scale nanocrystal production. Scaling nanocrystal synthesis is not trivial, as the increased thermal mass of the colloidal dispersion can dramatically affect nanocrystal growth, and certain synthetic methods, such as precursor injection, are not amenable to large-scale synthesis. Large-scale synthesis has been demonstrated for a few types of nanocrystals, notably iron oxide,¹⁰² but it remains to be seen if the nanocrystals of specific interest for smart windows can be made with sufficient control over size and doping at scale.

As a parting note, we point out that more fundamental research is warranted for this new type of electrochromism. A number of open questions remain regarding understanding the fundamental limits of capacitive charging in TCO nanocrystals. Considering that injected carriers are stabilized by polarization of the surrounding electrolyte, how do the characteristics of the electrolyte contribute to the maximum achievable charging levels? For low potentials and small nanocrystals, it should be possible for the accumulation layer to become as large or larger than the nanocrystal volume. Does this limit the maximum coloration contrast achievable, or will smaller nanocrystals always increase the coloration contrast? We have also seen that polarizable materials, like TCOs, exhibit a broader electrochromic dynamic range than metals. Does this mean that the dielectric constants of the electrolyte and the nanocrystal drastically affect the number of electrons that can be injected? Or is the plasmon shift greater in ITO simply because its starting electron concentration is lower? How important are doping levels and the starting position of the plasmon absorption peak, and will materials like Cs_xWO_3 indeed exhibit greater excursions through the NIR towards the visible? How do electrolyte ions travel within the micropores between nanocrystals, how do they interact with the nanocrystal surface, and how does this change in a solid electrolyte? Careful characterization via techniques such as electrochemical impedance spectroscopy, Mott-Schottky analysis, and quantification of electron injection during spec-troelectrochemistry is needed to further evaluate the performance limits and design rules for plasmonic nanocrystal electrochromic devices. We look forward to the resolution of these mysteries and to inspiring new material design strategies for dynamic windows, displays, and other optical modulation technologies.

Chapter 3

Synthesis, morphology, and mixed charge transport in polymer nanocrystal composites

Adapted from:

Runnerstrom, E. L.; Ong, G.K. Saez, C.; Milliron, D. J. Polymer Electrolyte-nanocrystal Composites with Mixed Ionic Electronic Conduction, in preparation.

3.1 Introduction and motivation

Electrochromic devices, and electrochemical devices in general, are steadily moving towards using nanoscale materials for enhanced electrochemical kinetics and new functionalities. The use of TiO_2 nanocrystals and Si nanowires to give improved rate capability in battery anodes, graphene and metal organic frameworks to give both high capacity and speed to supercapacitors, and nanocrystalline WO_3 to provide better switching speeds and stability in electrochromic devices are but a few examples. Over the past five years, a new type of electrochromic device based on colloidal metal oxide nanocrystals has emerged. Such plasmonic electrochromism has been demonstrated in a number of doped metal oxide nanocrystals, including tin-doped indium oxide (ITO),^{28–30} aluminum-doped zinc oxide (AZO),²⁹ niobium-doped titanium oxide (NTO),¹⁰³ and oxygen vacancy- doped tungsten oxide (WO_{3-x}).¹⁰⁴ Electrochromic devices based on these nanocrystals and their composites have excellent dynamic optical properties, with the ability to independently modulate near infrared (NIR) and visible light. For example, ITO nanocrystal-based devices can block 35% of incoming NIR energy while transmitting 92% of visible light,²⁸ and WO_{3-x} -niobium oxide composites exhibit dual-mode switching and are capable of either blocking 84% of NIR light while transmitting

54% of visible light or blocking 93% and 78% of NIR and visible light, respectively.¹⁰⁴

Each of these nanocrystal-based electrochromic devices, however, has only been demonstrated as a proof-of-concept and commercialization has yet to be demonstrated. They are produced in a small format (about 2x2 cm) by methods that are not industrially scalable (spin casting and ligand stripping for each layer), and generally have only been operated as the working electrode in an electrochemical half cell with a liquid electrolyte. As an exception to this last point, a laminated full device with a gel electrolyte has been demonstrated,³¹ but required nanocrystal templating with a block copolymer, which is rather disadvantageous for industrial production. Importantly, use of a liquid electrolyte is not amenable for use in a industrially-scalable or commercial device. Real-world smart windows require a durable and intimate ionic connection between the electrochromic and counter electrodes to maintain acceptable and reliable performance. Particular requirements for the electrolyte include: an ionic conductivity above 10^{-7} S/cm; electrochemical stability over the operating voltage range of the device; ease of processing; and sufficient mechanical stability and non-volatility to prevent leaking, evaporation, or flammability over the lifetime of the device.²² While liquid-based electrolytes offer high ionic conductivity, they do not satisfy the rest of these requirements, and can even deform or break the glass of a device owing to gravity, especially for large windows. A solid state ionic conductor is a much better candidate for an electrolyte in commercial smart windows. Furthermore, scalable strategies to fabricate full electrochromic devices without the need for extensive and serial layer deposition or ligand exchange are needed.

To this end, this chapter examines a model system, poly(ethylene oxide) (PEO) mixed with lithium bis(trifluoromethylsulfonyl)amide (LiTFSI), as a solid state electrolyte for plasmonic ITO nanocrystal-based electrochromic devices. Specifically, PEO-LiTFSI electrolyte is mixed with ITO nanocrystals to form nanocomposite films that exhibit mixed ionic and electronic conductivity through the PEO and ITO phases, respectively. PEO is a well known lithium ion conductor; the mechanism of conduction is well understood and this system has been studied extensively in the literature for use in battery applications.^{105;106} It has also been studied for use in electrochromic applications, though research in this application space lags behind others. PEO has not, however, been well-studied in mixed-conducting nanocomposite applications such as this one, where both the PEO matrix and the inorganic nanoscale fillers carry charge and play active and crucial roles in device operation. Furthermore, this is among the first studies of solid polymer electrolytes as ion conductors in plasmonic nanocrystal-based electrochromic devices. Likewise, ITO nanocrystals are a very well understood in terms of their plasmonic and electrochromic properties, and their electronic conduction properties are also well studied and understood. These factors provide the opportunity to develop a new materials system without the need for fundamental studies on charge transport in nanocrystals or development of a new solid state electrolyte.

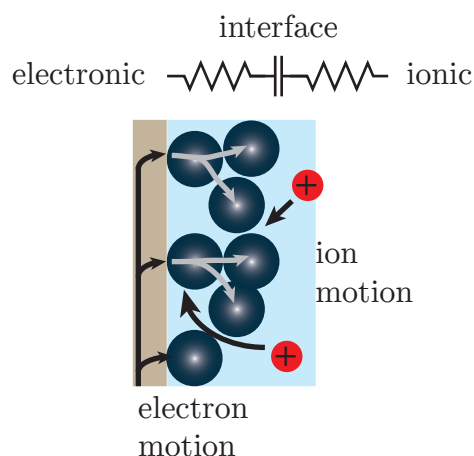


Figure 3.1: Schematic depiction of the importance of good interfaces between a solid electrolyte and nanocrystals (and between adjacent nanocrystals) in a nanocomposite electrochemical device. Well-defined charge transport pathways for both ions and electrons are necessary, as is a strong capacitive interaction at the ITO-PEO interface.

3.2 Synthesis of ITO-PEO nanocomposites and experimental details

A critical requirement of the electrolyte in an electrochemical device, particularly a plasmonic electrochromic device that relies on capacitive interactions across a nanocrystal interface, is that the electrolyte have good binding and wetting characteristics at the surface of the active electrochromic component (Figure 3.1). While this is nearly trivial for liquid based electrolytes, it is not for solid electrolytes. Polymers, in particular, are macromolecules that can adopt random coil configurations that exclude a significant volume. Because of the microporous nature of the nanocrystal thin films that have previously been fabricated, the free space between nanocrystals is on the order of 1 nm or less, smaller than the radius of gyration of PEO molecules.¹⁰⁷ Thus, PEO cannot simply be deposited into the pores between nanocrystals and achieve good ionic contact with all of the ITO nanocrystal surfaces. Such a situation would result in poor device performance and inefficient utilization of active material, as the electrochromic effect depends on capacitive charging at ITO nanocrystal surfaces. A more suitable strategy to fabricate the ITO-PEO nanocomposites is to co-deposit them with solution processing methods. PEO and ITO nanocrystals are both amenable to solution processing, which makes it possible to mix both components in a solution that is cast to yield a nanocomposite film containing ITO nanocrystals well dispersed in, and in intimate contact with, a PEO matrix.

3.2.1 ITO synthesis

The following paragraph is reprinted from Reference¹⁴:

Runnerstrom, E. L.; Llordes, A.; Lounis, S. D.; Milliron, D. J. Nanostructured Electrochromic Smart Windows: Traditional Materials and NIR-Selective Plasmonic Nanocrystals. *Chem. Commun.* **2014**, 50, 10555–10572.

The synthetic basis for this work is our previous work on nanocrystal electrochromics is colloidal synthesis of ITO nanocrystals^{28;67;75;76}. Colloidal synthesis is a powerful technique that allows production of nanoscale crystals with sizes ranging from 1 to 100 nm. Advantages of this technique include good control over the size, shape, and monodispersity of the nanocrystals^{1–3}. The surfactants (also referred to as ligands) that reside on the surfaces of colloidal nanocrystals make them amenable to solution processing and methods for producing complex assemblies³. Recent synthetic developments in nanocrystal synthesis have also increased the versatility of the technique, which can now be used to produce metallic, doped and undoped semiconductor, and doped and undoped metal oxide nanocrystals, among other materials⁴. For electrochromic devices based on ITO nanocrystals, size control and solution processing are key aspects, as a uniform film comprised of nanocrystals of uniform size do not scatter light, which makes the film appear transparent. Size and doping control also strongly affect the electrochromic properties of nanocrystals²⁸.

All chemicals used in ITO nanocrystal synthesis were obtained from Sigma Aldrich (oleylamine obtained from Acros) and used without further purification. Two different synthetic methods have been used to produce ITO nanocrystals for this study. The first is based on literature procedures⁷⁵ and has been employed throughout this dissertation. This method employs indium (III) acetylacetonate ($\text{In}(\text{acac})_3$, 99.99%), tin (IV) acetylacetonate dichloride ($\text{Sn}(\text{acac})_2\text{Cl}_2$, 98%), and oleylamine (OLAM, 90%) as the indium precursor, tin precursor, and surfactant/nucleophile, respectively. In brief, the three starting materials are combined into a 50 mL flask with constant magnetic stirring and an inert atmosphere is maintained by attaching the flask to a Schlenk line. The solution is stirred and heated to 110°C for 10 minutes, then heated to 250°C for two hours to create the nanocrystals. The tin dopant concentration is controlled by the relative amounts of $\text{In}(\text{acac})_3$ and $\text{Sn}(\text{acac})_2\text{Cl}_2$ (i.e., 0.5 mmol indium precursor with 0.027 mmol tin precursor gives nanocrystals with 4.4% tin). The size of the nanocrystals can be controlled by adjusting the metal:OLAM ratio; a 1:12 molar ratio of metal precursor to OLAM leads to nanocrystals about 10 nm in diameter, while a 1:48 ratio gives nanocrystals about 7 nm in diameter. Even smaller nanocrystals about 4 nm in diameter can be synthesized with a 1:192 ratio, but this approach yields too small a number of nanocrystals to be practical.

The other synthetic method is loosely based on a separate literature procedure,⁷⁶ with a number of simplifications and modifications. This method uses indium (III) acetate ($\text{In}(\text{OAc})_3$, 99.99%), tin (II) acetate ($\text{Sn}(\text{OAc})_2$, 99.99%), and oleylamine, omitting the use

of additional solvents, solid carboxylic acids, and solid amines used in Reference⁷⁶. In brief, the precursors are mixed together in a 250 mL flask under inert atmosphere with constant magnetic stirring, with the desired In:Sn ratio and a metal:OLAM ratio of 1:8.33. After degassing under vacuum at 110°C for one hour to remove water, the solution is heated to 230°C for one hour to nucleate and grow ITO nanocrystals about 4.5 nm in diameter. Increasing the reaction temperature to 250°C, 270°C, or 300°C allows synthesis of larger ITO nanocrystals with diameters of 5.3 nm, 6.1 nm, and 6.6 nm respectively. This synthesis is noteworthy because it affords the ability to produce size controlled nanocrystals as small as 4.5 nm in diameter with easily tunable doping. As detailed in the previous Chapter, small nanocrystals result in much better electrochromic performance and higher charge capacity due to their higher surface area-to-volume ratio. Furthermore, this synthesis is easily scaled up and has been successfully used to produce gram-scale batches of ITO nanocrystals (as opposed to the synthesis in the paragraph above, which produces about 200 mg of nanocrystals at a time). The production of small diameter, highly doped ITO nanocrystals at scale has positive implications not only for the study and performance of ITO-PEO nanocomposites, but also for large scale device fabrication and industrialization.

After synthesis, the ITO nanocrystals must be purified to remove excess surfactant and any unreacted precursors or reaction side products. To do so, a miscible non-polar/polar solvent/anti-solvent pair is used, along with centrifugation. The non-polar solvent, *e.g.*, hexane, allows the nanocrystals to be dispersed, and also dissolves excess surfactant. When a polar anti-solvent, *e.g.*, ethanol, is added, the nanocrystals flocculate to minimize the interaction between their surface-bound ligands and the polar environment. If a sufficiently small amount of anti-solvent is added, the nanocrystals will flocculate and can be collected by centrifugation, but the rest of the contaminants will remain dissolved or suspended in the solvent/anti-solvent supernatant, which can be discarded. The process can be repeated for further purification by redispersing the nanocrystals again in a non-polar solvent.

3.2.2 Ligand stripping of ITO

As synthesized, ITO nanocrystals have native ligand or surfactant molecules on their surfaces. This ligand shell, though necessary for the synthesis of monodisperse and colloidally stable nanocrystals, impedes electronic charge transport between nanocrystals, and also prevents electrolyte ions from approaching the nanocrystal surface. To remove the surfactants from the nanocrystal surfaces, a ligand stripping procedure utilizing nitrosonium tetrafluoroborate (NOBF₄) is utilized.⁹⁸ Purified ITO nanocrystals dispersed in hexane are combined with *N,N*-dimethylformamide (DMF) to form a biphasic mixture with the non-polar phase on top. To this mixture, NOBF₄ is added in a 1:2 weight ratio between NOBF₄ and ITO nanocrystals, and the mixture is sonicated for 10 minutes. Based on the deep blue color of ITO dispersions, the stripping reaction was clearly complete with the nanocrystals were transferred to the polar DMF phase. The stripped nanocrystals were then purified *via* centrifugation with DMF and toluene as the solvent/anti-solvent pair. It is important to wash the stripped nanocrystals eight or more times to fully remove both the stripped surfactants

as well as excess BF_4^- . After doing so, the bare ITO nanocrystals are stable in DMF for extended periods of time (years) at high concentrations, as they are stabilized by BF_4^- anions coordinated to the nanocrystal surface and additional dative bonding between DMF molecules and the nanocrystal surface. When ligand-stripped ITO is deposited into a thin film and the solvent is evaporated (in this case, by spin casting from a 1:1 DMF:acetonitrile solvent mixture), a uniform, non-scattering, and conductive nanocrystal film is formed. Note that without sufficient purification, the stripped nanocrystals are prone to gelation and/or aggregation at high concentrations, and ITO-PEO nanocomposites based on unpurified dispersions are prone to phase separation during deposition.

3.2.3 Polymer wrapping of bare ITO nanocrystals

Once the ligands are removed and washed away, the bare ITO nanocrystals can be combined with a polymer that passivates or wraps around the nanocrystal surface. A preliminary investigation in collaboration with I. Pehlivan, S.Y. Li, G.A. Niklasson, and C.G. Granqvist of Uppsala University revealed strategies for successfully mixing small amounts of ITO nanocrystals with poly(ethylene imine) (PEI, 10,000 g/mol), a polymer structurally similar to PEO (with nitrogen atoms in place of ether oxygens) that conducts lithium ions by a similar mechanism.¹⁰⁸ Here, we found that the order of mixing mattered, as adding a methanol solution of LiTFSI to a dispersion of bare ITO nanocrystals in DMF would immediately destabilize the colloid, resulting in a cloudy suspension. Instead, the LiTFSI was premixed with PEI polymer and methanol and stirred to allow the polymer to coordinate with Li^+ ions, and nanocrystals in DMF were subsequently added, resulting in a stable and homogeneous polymer-nanocrystal suspension. The methanol and DMF could subsequently be removed under vacuum to generate a ITO-PEI nanocomposite with appreciable ionic conductivity and tunable NIR absorption by changing the ITO nanocrystal fraction. Note that these procedures were performed inside a glovebox in a water free atmosphere, with anhydrous solvents.

Similarly, the order of mixing has a significant impact on the colloidal stability of ITO nanocrystals when mixed with PEO (20,000 g/mol, Polymer Source). It was possible to create colloidally stable dispersions ranging from 1:16 to 1:4 ITO:PEO by weight by adding ITO dispersed in DMF to a solution of PEO dissolved in DMF at 5% by weight. However, ITO could not be dispersed in solutions of PEO dissolved at 5% by weight in acetonitrile (MeCN) with this approach, which also indicates that even when using DMF as the solvent, the nanocrystals are not wrapped with polymer, but rather stabilized by DMF.

The solution to this problem is to force the PEO to coordinate to the nanocrystal surface by using a solution of PEO in MeCN (5% by weight) as the dispersing solvent for the final washing step of the ligand stripped ITO nanocrystals. Specifically, the nanocrystals are precipitated from DMF with toluene, centrifuged, and the supernatant is discarded. Then, instead of redispersing the nanocrystals in DMF, the pellet is redispersed in the PEO/MeCN solution, forming an optically clear dispersion that is stable for months to years. This is a noteworthy development because dispersions of ligand stripped ITO are

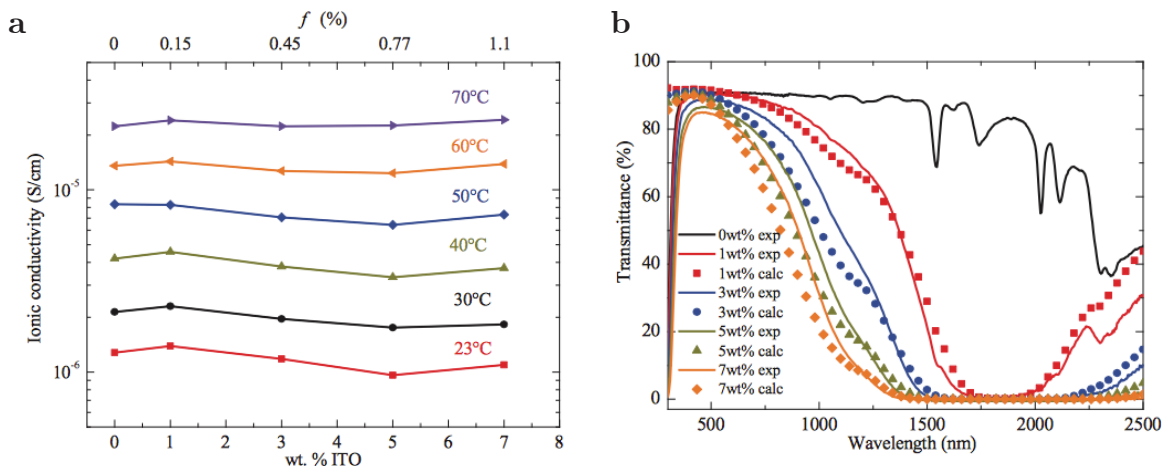


Figure 3.2: Composites of ITO nanocrystals and poly(ethylene imine) used as a polymer electrolyte with NIR blocking properties. a: Temperature-dependent electronic conductivity of PEI electrolytes containing ITO nanocrystals. b: Optical properties of PEI electrolytes containing ITO nanocrystals. Figure reprinted with permission from Reference¹⁰⁸, Copyright 2012 American Institute of Physics.

not particularly stable in MeCN, and because this adjustment to the order of mixing has enabled an ITO/PEO/MeCN dispersion that was not previously accessible by adding an ITO dispersion into a PEO solution. This strategy enables stable dispersions with ITO:PEO weight ratios ranging from 1:20 to as high as 6:1. Furthermore, if the bare nanocrystals are sufficiently cleaned and care is taken to remove excess BF_4^- anions before polymer wrapping, the dispersions can easily be deposited as solid and optically clear ITO-PEO composites by spin casting. Insufficient purification of the ligand stripped nanocrystals generally leads to cloudy films with aggregated nanocrystals.

This technique for synthesizing ITO-PEO nanocomposite films can be generally extended to other systems. Composites of other polymers heavily loaded with ITO are easily made, including poly(methyl methacrylate) (PMMA), poly(ethylene oxide)-poly(*N,N*-dimethylacrylamide) block copolymer (PEO-*b*-PDMA), and cross-linkable poly(ethylene glycol) dimethacrylates (PEGDMA). The methods can also be adapted to other colloidal metal oxide nanocrystals relevant for electrochemical devices, and polymer-nanocrystal composites have been successfully made with cerium oxide, iron oxide, and tungsten oxide nanocrystals.

3.2.4 Addition of lithium salt

LiTFSI dissolved in tetrahydrofuran (THF) at 25% by weight is added to the nanocrystal-polymer dispersions immediately before spincasting. The mass of LiTFSI added is calculated so that the molar ratio of lithium ions to ethylene oxide units on the PEO chains is typically 1:18, which provides appreciably high conductivity to PEO-based solid electrolytes. In

general, the colloidal stability of dispersions containing LiTFSI and the morphology of the resulting composite films were best when water was rigorously excluded from the system. This is done by handling the nanocrystals, polymers, and LiTFSI salt in a water-free glovebox atmosphere. For example, the ligand stripped nanocrystals are washed several times inside of a glovebox with anhydrous solvents before dispersing them in an anhydrous solution of vacuum dried PEO in MeCN, and finally adding vacuum dried LiTFSI dissolved in THF. The resulting solution is stable for several hours to a day.

3.2.5 Film deposition and charge transport measurements

Colloidal dispersions of ITO/PEO/MeCN are stable for a period of weeks to months, allowing for easy film deposition *via* solution processing techniques, such as spin casting or spray coating. When LiTFSI is present, assuming that inert atmosphere is maintained as described above, the stability window of several hours provides ample time for depositing nanocomposite films, which was done using a spin caster inside of a glovebox.

In general, the films were spin casted at 1000 RPM for 60 seconds, followed by a 4000 RPM step for 30 seconds to evaporate any residual solvent, which was especially important if DMF was present in the solution. The films were deposited on either glass or silicon substrates that were cleaned by sonicating for 15 minutes each in Hellmanex solution, acetone, and isopropanol, followed by a 15 minute UV-ozone cleaning step. These cleaning steps are critical, as they render the substrates hydrophilic to ensure good wetting of the nanocomposite solution and adhesion of the film to the substrate. Improperly cleaned substrates resulted in very poor film coverage with a poorly defined and non-uniform thick spot in the center. For AC impedance measurements, electrode stripes (5 nm Cr, 100 nm Au) were deposited by thermal evaporation onto clean glass substrates, and the substrates with electrodes were cleaned again before the composite films were deposited on top.

A 4-point probe Hall effect measurement system was used to measure the percolation threshold of ITO nanocrystals in polymer absent LiTFSI. For all other charge measurements, the colloidal dispersions and the resulting films were handled entirely in a glovebox to maintain a water-free atmosphere, and the subsequent electrical measurements were performed inside of a glovebox to avoid water contamination of the nanocomposite films. This was done using a home-built measurement apparatus with BNC cable feedthroughs, which allowed connections from our AC impedance analyzer (Novocontrol Alpha-AN) and our DC source measurement unit (Kiethley 2604B) to a probe station inside of the glovebox. Coaxial tungsten probes were used to pierce the nanocomposite film to contact the electrodes on the substrate. AC impedance spectroscopy was performed at frequencies from 2 MHz down to 1 Hz or 0.1 Hz, using an AC voltage amplitude of 100 mV. Time-dependent DC resistance measurements were performed by recording the current for a 5s off/5s on/5s off voltage pulse, with voltages ranging from -250 mV to 250 mV. To account for electrode resistance, the transmission line technique was used, where the DC resistance was measured for electrodes of varying spacing. This allowed both 2-point AC and 2-point DC measurements

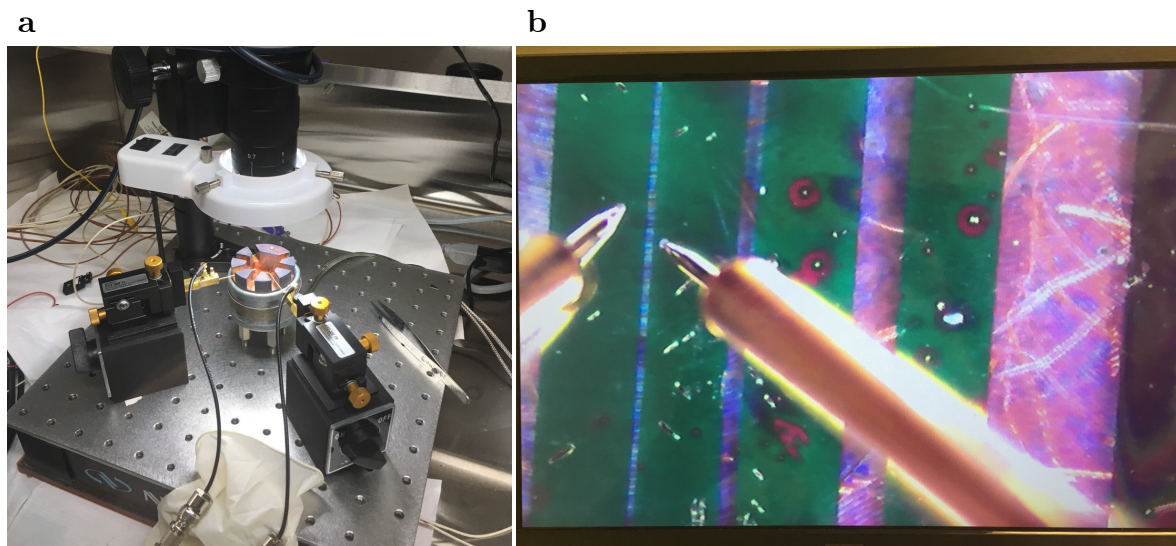


Figure 3.3: a: Inert atmosphere probe station inside glovebox. b: Optical microscope image of coaxial tungsten probes contacting gold electrodes with different spacings (spacing between contacted electrodes is 40 microns).

to be performed on the same sample so that the electrode resistance could be quantified for both measurements.

3.3 Controlling and characterizing morphology and microphase separation in ITO-PEO nanocomposites

To create nanocomposites that are both electronically and ionically conductive, lithium ions must be incorporated into the polymer matrix. In initial experiments done under ambient conditions, adding LiTFSI (dissolved in tetrahydrofuran, or THF) to a ITO/PEO/MeCN dispersion destabilizes the nanocrystals and renders the dispersion cloudy and unsuitable for deposition or device fabrication. Changing the solvent to a 1:1 mixture of MeCN:DMF did allow the dispersion to remain stable upon LiTFSI addition, but the resulting nanocomposite suffered significant and uncontrolled phase separation, with large aggregates of nanocrystals and a non-uniform distribution of nanocrystals throughout the nanocomposite film, which appear hazy and nearly completely opaque. This phase separation and haze are obviously inappropriate for electrochromic windows, which primarily rely on modulating specular transmission and for which aesthetic concerns are paramount. Phase separation is also deleterious from an electrochemical and mixed conduction standpoint, as isolated domains of nanocrystals are likely not electronically connected to the rest of the composite, preventing them

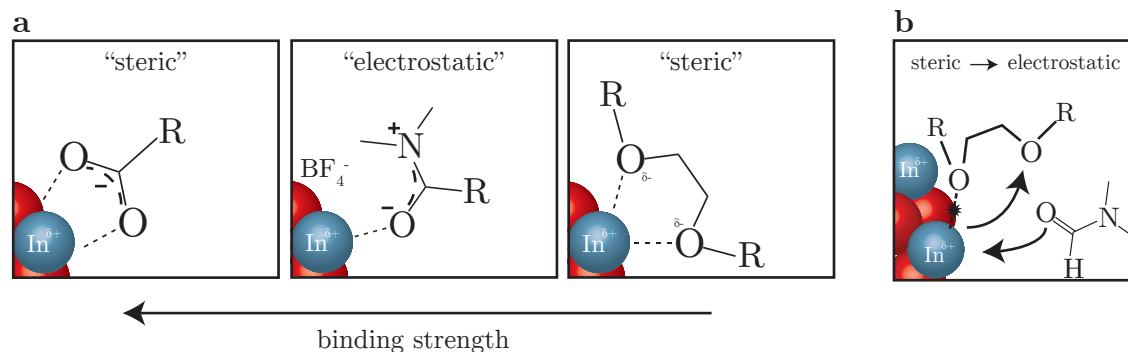


Figure 3.4: Schematic depiction of phase separation in ITO-PEO nanocomposites. a: Schematic of steric/ electrostatic/steric stabilization of ITO colloids by a carboxylate, DMF + BF_4^- , and PEO, respectively, and the relative strength of coordination to the surface. b: Schematic of DMF displacing PEO at the nanocrystal surface, leading to phase separation by changing from steric to electrostatic stabilization.

from contributing to charge transport or the electrochromic effect.

Observing the uncontrolled phase separation of this nanocomposite, nanocrystal aggregation in LiTFSI-free composites prepared with improperly purified ITO nanocrystals, and the destabilization of colloids prepared in ambient conditions upon adding LiTFSI reveals a common thread: ion concentration. This leads to a clear hypothesis: phase separation is due to nanocrystals “salting out” and aggregating during spin casting (Figure 3.4). Bare ITO nanocrystals in DMF are stabilized by an electrostatic double layer at the nanocrystal surface (Figure 3.4a). This double layer is susceptible to compression as the ionic strength of the solution increases, particularly if lithium salt is present, which extrinsically increases ionic strength even before spin casting. Because the solvent rapidly evaporates during spin casting, the ionic strength rapidly increases, compressing the double layer around each nanocrystal. Eventually, the double layer collapses to be so thin that the electrostatic repulsion is overwhelmed by attractive van der Waals forces between nanocrystals, which then aggregate. Normally, a polymer stabilizer or surfactant like PEO would alleviate this problem. The ether oxygens of PEO are capable of coordinating the positively charged nanocrystal surface, which would allow PEO to stabilize ITO colloids by steric effects rather than electrostatic repulsion, and make the nanocrystals less susceptible to phase separation by ionic strength effects. However, DMF present in the solution binds more strongly to the ITO surface than ether oxygens, displacing the PEO from the surface (Figure 3.4b).

3.3.1 Dynamic light scattering

This hypothesis is validated with dynamic light scattering (DLS, Figure 3.5) data, which reveal how the average hydrodynamic diameter in the dispersions changes under different conditions. The bare ITO nanocrystals in DMF have a hydrodynamic diameter of around 4-

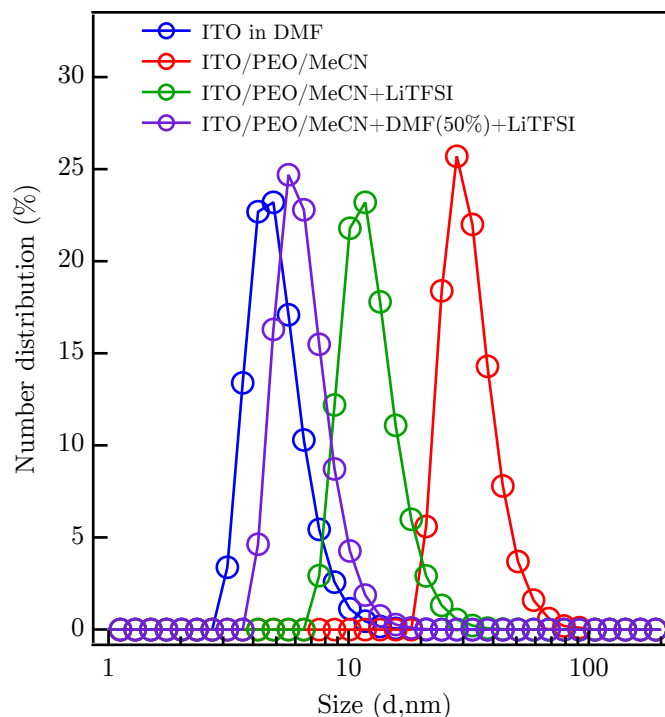


Figure 3.5: DLS of ITO-PEO dispersions, showing the changes in the hydrodynamic diameter of the dispersion with changes in solvent and salt content. Note that using a solvent mixture with 50% DMF in a ITO/PEO/LiTFSI dispersion reduces the hydrodynamic diameter to nearly the same as bare ITO nanocrystals in DMF.

5 nm, which is in good agreement with TEM measurements of their average size. Dispersing the nanocrystals in a PEO/MeCN solution increases the average hydrodynamic diameter in the solution to around 30 nm, indicating that the nanocrystals are being wrapped by PEO, which likely also extends out from the surface in a brush-like configuration. Adding LiTFSI to the dispersion decreases the hydrodynamic diameter to around 10 nm, indicating that the polymer is still on the nanocrystal surface, but that its configuration is likely changed due to lithium coordination. Finally, when DMF is added to the solution, the hydrodynamic diameter returns close to the original hydrodynamic diameter of bare ITO in DMF, indicating that the nanocrystals are no longer sterically stabilized by PEO, but electrostatically stabilized by DMF (and BF_4^-).

3.3.2 Deliberate control of phase separation

Phase separation can be alleviated by excluding DMF from the spin casting solution and by performing the composite preparation in a water-free atmosphere as described above. (The exact role of ambient water is unclear, but it distinctly influences phase separation, which is explored further below.) ITO-PEO-LiTFSI nanocomposites deposited from DMF-free solu-

tions prepared in this way are homogeneous and free of phase separation, further validating the hypothesis. As an additional check, nanocomposite films can be prepared from solutions with systematic variations in DMF content from 0% to 20%. Indeed, the nanocomposite films deposited from solutions containing more DMF exhibit greater phase separation (Figure 3.6), confirming the competition between DMF and PEO at the nanocrystal surface. DMF can thus be used to balance steric vs. electrostatic stabilization of the nanocrystals and provides systematic control over phase separation. This is a useful property of this system, as it may be desirable to induce a small and controlled amount of phase separation in the nanocomposite to affect its conductivity. This idea is explored further in the next section.

3.3.3 Small angle X-ray scattering (SAXS)

Grazing incidence small angle X-ray scattering (GISAXS) is an additional technique that can be used to quantify and understand the phase separation. Because of the small scattering angles, GISAXS is capable of resolving structure on larger length scales than wide angle X-ray scattering or diffraction, so it can be used to evaluate the separation between nanocrystals in the nanocomposite. Figure 3.7a displays the GISAXS scattering patterns, derived from horizontal line scans of the collected 2D scattering intensity map, collected from nanocomposites with varying degrees of phase separation induced by the inclusion of DMF in the casting solvent. The patterns display a well-defined peak at a scattering vector of about $0.1 \text{ \AA}^{-1}$, corresponding to the average center-to-center distance of the nanocrystals. Each scattering intensity profile contains the product of both a structure factor term and a form factor term; the structure factor contains the information about the spatial arrangement of the scattering species in reciprocal space, while the form factor contains information about the size, shape, and electron density distribution of individual scatterers. The form factor can be directly measured by collecting transmission SAXS patterns of ligand stripped ITO nanocrystals dilutely dispersed in DMF. Note that it is not necessary to consider the form factors of PEO and DMF, as they have a dramatically lower electron density than ITO and nearly all scattering is expected to occur from the ITO nanocrystals. The form factor of ITO can then be divided out to reveal the structure factor for each line scan (Figure 3.7a inset). This structure factor contains direct information about the average center-to-center distance of the nanocrystals, given by the peak location. This analysis reveals that adding DMF to the casting solution causes the average separation between adjacent nanocrystals to change slightly, increasing very slightly before dropping by about $2 \text{ \AA}$. This change in nanocrystal spacing may effect the electronic conductivity of the nanocomposite, and is examined further below.

The low- Q region (around $0.01 \text{ \AA}^{-1}$) of the GISAXS patterns contains information about larger, more random aggregate scattering populations, and the shape of this region appears to change slightly with DMF content. It is difficult to interpret this feature accurately from visual examination alone, but modeling this region, with the help of the publicly available NIKA/IRENA Igor Pro macros, makes it possible to estimate the average cluster size in

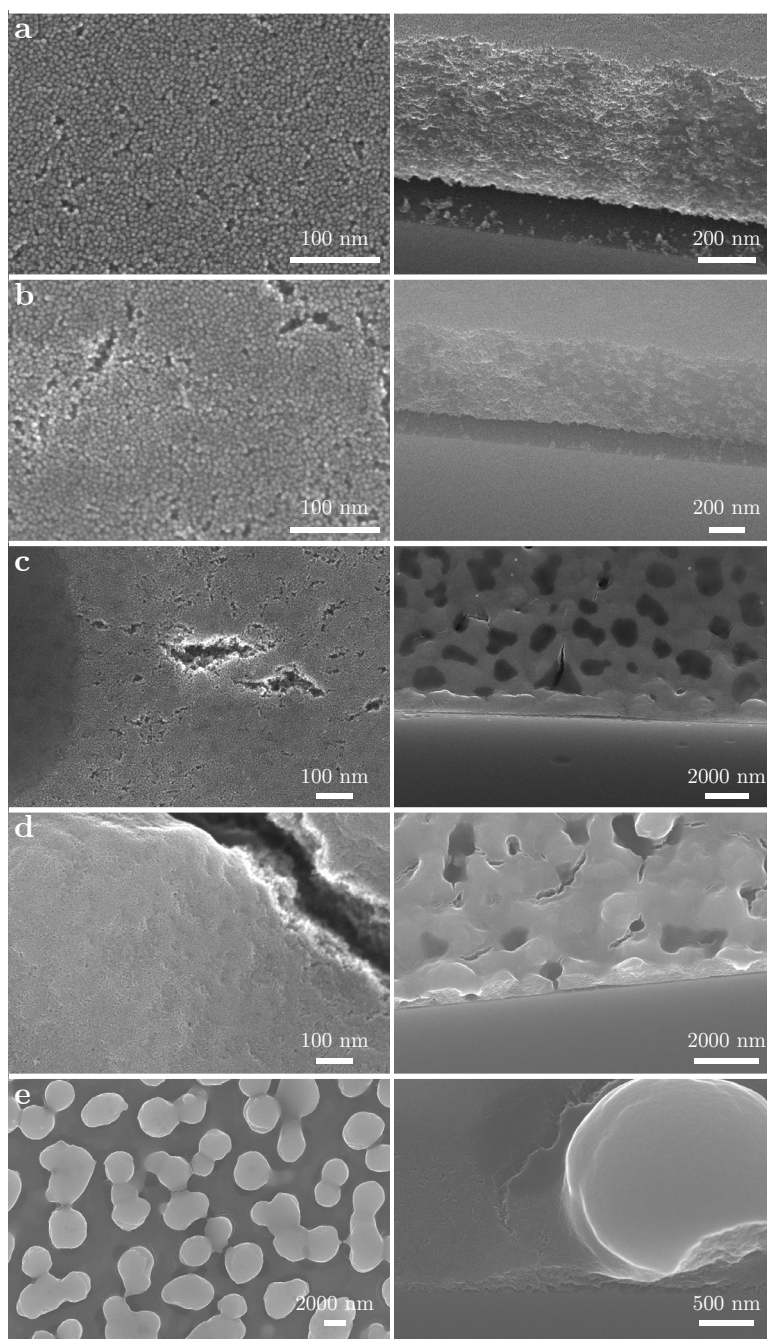


Figure 3.6: Controlled phase separation in ITO-PEO nanocomposites with various amounts of DMF added to the casting solvent. The left column shows top-down SEM micrographs, while the right column shows cross-sectional views. a: 0% DMF. b: 2.5% DMF. c: 5% DMF. d: 10% DMF. e: 20% DMF.

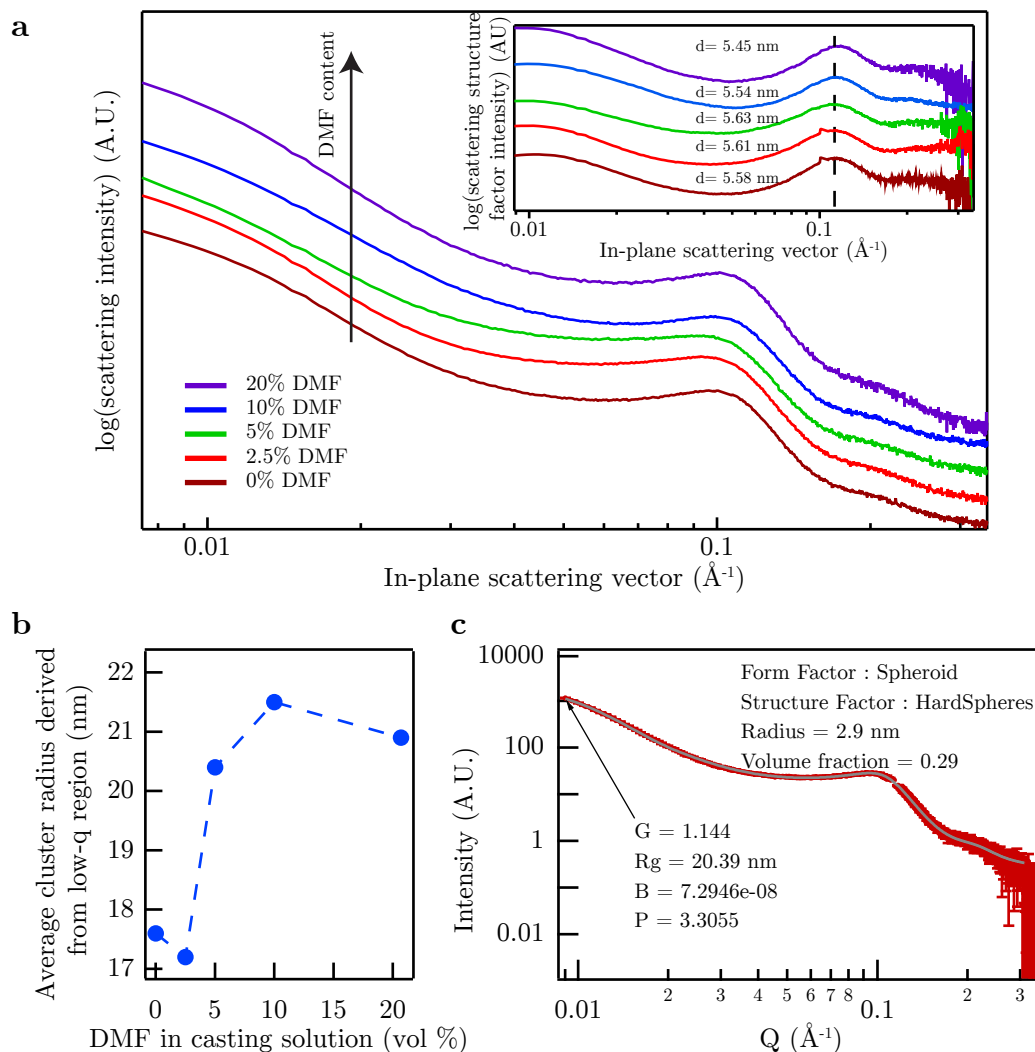


Figure 3.7: GISAXS characterization of ITO-PEO nanocomposites with varying degrees of phase separation. a: Horizontal line scan patterns displaying scattering intensity vs. scattering vector for samples prepared with different amounts of DMF present in the casting solution, each with a well-defined peak corresponding to nanocrystal-nanocrystal scattering, and a broad peak at low Q corresponding to larger clusters of nanocrystals. Inset: Extracted scattering structure factor from each line scan, showing slight changes in the average nanocrystal difference. b: Average cluster radius vs. DMF content as derived from the low- Q region of the line scans. c: Example calculation of cluster size fitting and calculation in the low Q region (Sample with 5% DMF).

each sample. The results of this modeling are shown in Figure 3.7b, with an example fit (5% DMF) shown in Figure 3.7c. It should be noted that these cluster sizes should be considered as estimates, as the low- Q region is not fully-defined and a longer sample-detector distance would be needed to better resolve this area. Regardless, these estimations support earlier observations of phase separation: as the DMF content in the casting solution is increased, the ITO nanocrystals tend to aggregate in larger, distinct clusters, each of which slightly alters the GISAXS scattering profile. This is in good qualitative agreement with the perceived phase separation seen in the SEM micrographs of Figure 3.6.

3.3.4 Effect of ambient water

The presence of ambient water appears to enhance the tendency of the ITO-PEO-LiTFSI system to phase separate. Adding LiTFSI to a ITO/PEO/MeCN dispersion prepared under ambient conditions destabilizes the colloid and causes the nanocrystals to aggregate even before spin casting. Conversely, under water free-conditions, the dispersion remains stable over a period of at least hours after adding LiTFSI. However, it is possible to fabricate nanocomposites under ambient conditions while avoiding phase separation by invoking the results of the ITO-PEI study described above and dissolving the LiTFSI into a polymer before it is exposed to the nanocrystals. This is done by preparing two separate vials of ITO/PEO/MeCN and PEO/LiTFSI/benzene. In the second vial, PEO is dissolved in benzene and the appropriate amount of LiTFSI is added in THF and stirred overnight before the solvent is allowed to evaporate completely, which ensures that the lithium salt is dissolved by PEO. The first ITO/PEO/MeCN dispersion is then mixed with the PEO/LiTFSI mixture immediately before spin casting to minimize interactions between the nanocrystal surfaces and salt ions, resulting in a homogeneous nanocomposite film (Figure 3.8a). When controlled amounts of DMF are added to these dispersions before spin casting, similar trends in phase separation and morphology are observed Figure 3.8), similar to the results shown above.

This technique can also be used under water-free conditions. Interestingly, this leads to a much less dramatic change in morphology when DMF is added (Figure 3.9), which probably results of pre-dissolving or “sequestering” LiTFSI in PEO to minimize its interaction with ITO. Furthermore, this underlines the effect of ambient water, as the nanocomposites prepared this way under ambient conditions clearly exhibit greater phase separation.

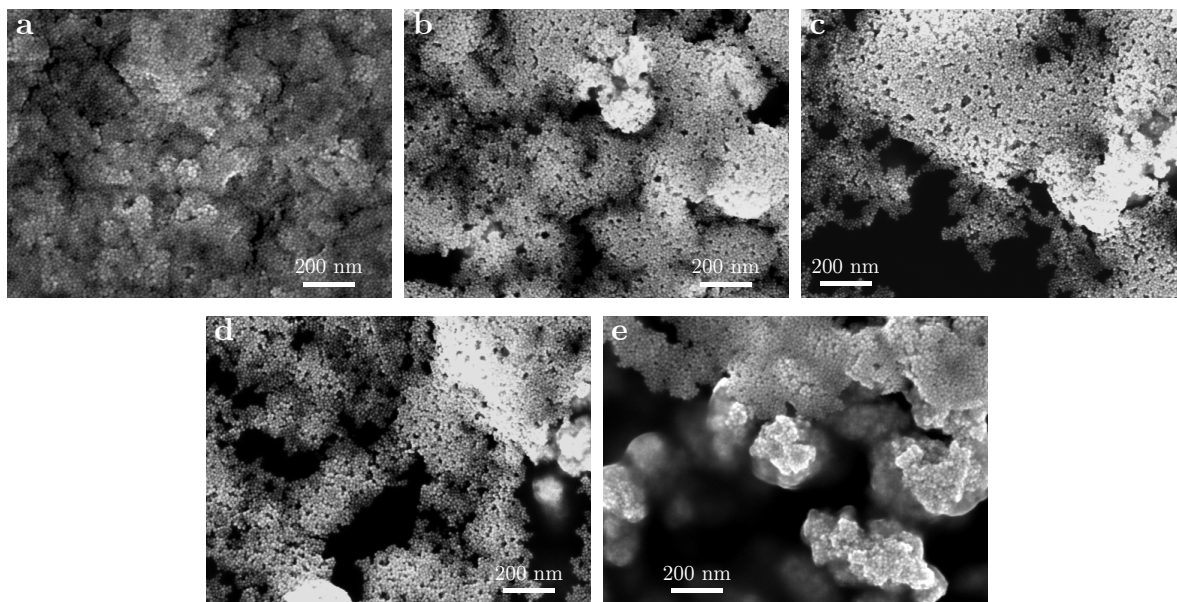


Figure 3.8: SEM micrographs depicting controlled phase separation in ITO-PEO nanocomposites under ambient conditions, with presumed water contamination. a: 0% DMF in casting solvent. b: 2.5% DMF. c: 5% DMF. d: 10% DMF. e: 20% DMF.

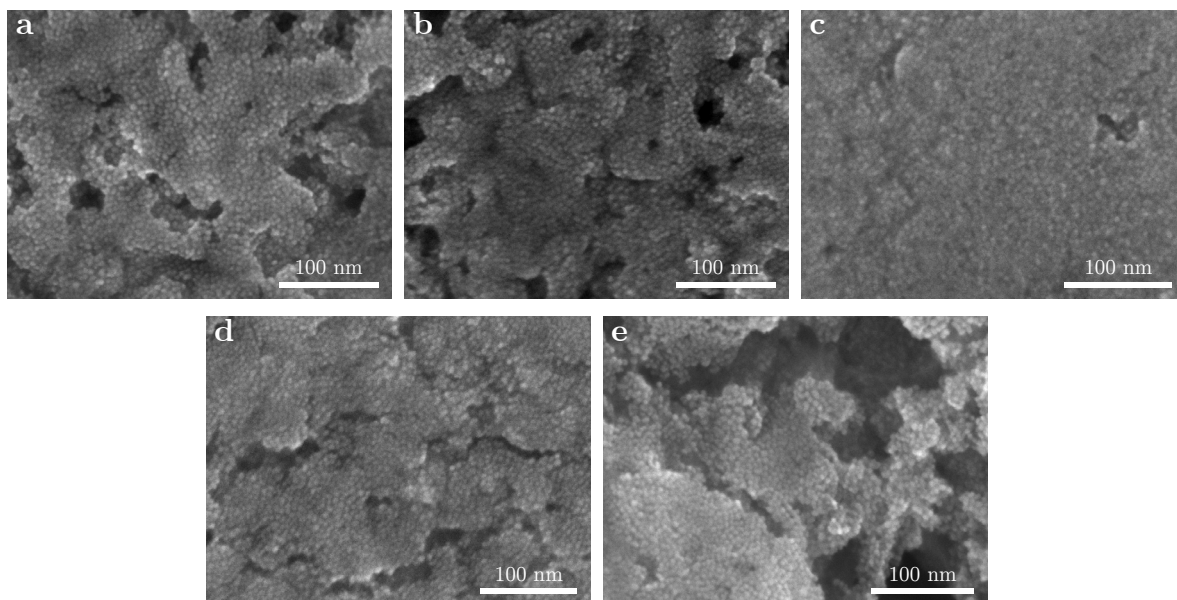


Figure 3.9: Minimizing phase separation in ITO-PEO nanocomposites under inert conditions by pre-dissolving LiTFSI in PEO/benzene in a separate vial before combining with ITO-PEO. a: 0% DMF in casting solvent. b: 2.5% DMF. c: 5% DMF. d: 10% DMF. e: 20% DMF.

3.4 Electrical conductivity and percolation behavior of ITO-PEO nanocomposites

When nanocrystals are dispersed in PEO or PMMA at sufficient volume percentages, long-range conductivity throughout the film can be measured using the 4-point probe technique. Figure 3.10 shows the electronic conductivity of PEO- and PMMA-based nanocomposites containing 4.5 nm ITO nanocrystals at different volume fractions. PEO-based nanocomposites begin to conduct electricity starting at about 6 vol.%, with the conductivity increasing exponentially with volume fraction, particularly after 20 vol% (2:1 ITO:PEO by weight). PMMA displays similar behavior, with conductivity appearing at volume fractions of 0.2 and increasing exponentially. In both cases, the conductivity is about 6-60 times lower than a film of nanocrystals only, which is likely due to the significant volumes of electrically insulating polymer between nanocrystals.

The appearance of long-range conductivity in these nanocomposites and the exponential increase with volume fraction is consistent with percolation behavior. In a system subject to percolation behavior, long-range conductivity will appear at the percolation threshold, or the volume fraction at which the conductive filler is high enough such that there is one or more conductive pathways that traverse the composite. The conductivity of the composite follows the functional form of:

$$\sigma = \sigma_0 (V - V_c)^s \quad (3.1)$$

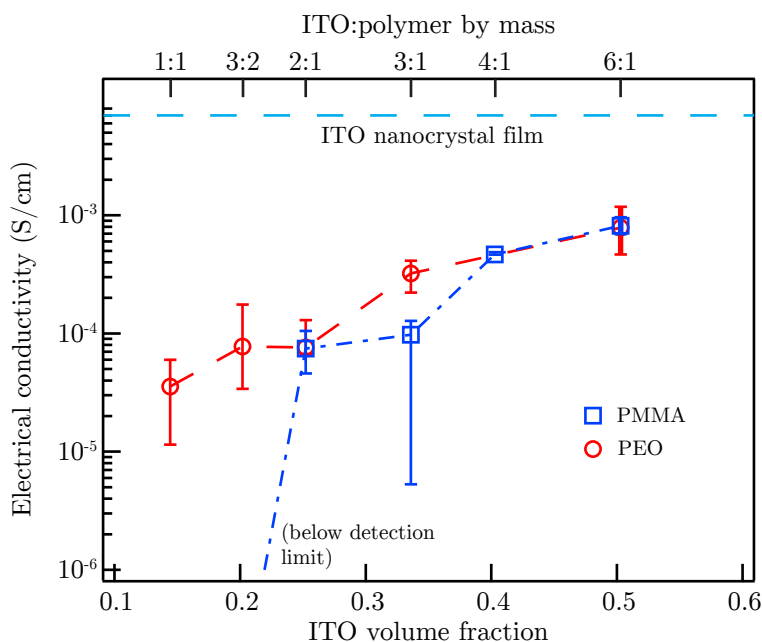


Figure 3.10: Electronic conductivity vs. ITO filling fraction in ITO-PEO and ITO-PMMA nanocomposites, which display percolation behavior.

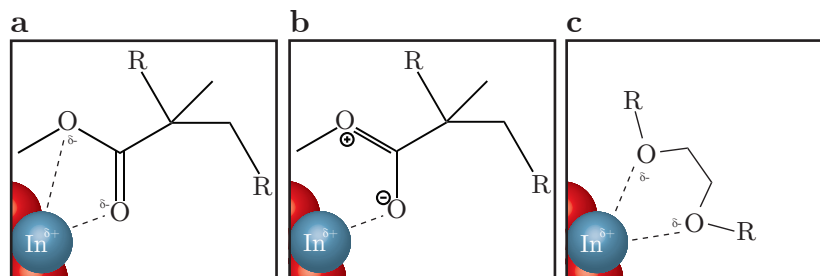


Figure 3.11: Schematic depiction of the differences between PMMA (a,b) and PEO (c) passivation of ITO nanocrystal surfaces. The PMMA has a stronger affinity to the surface due to its resonance structure.

where σ_0 is the conductivity of the nanocrystal filling component, V is the filling volume fraction, V_c is the critical filling volume fraction or percolation threshold, and s is a system-dependent exponent. For monodisperse solid spheres homogeneously dispersed in a three-dimensional matrix, percolation theory predicts a percolation threshold of about 14-16 vol.%, depending on the crystalline packing.¹⁰⁹ For randomly-packed spheres, the threshold is about 16 vol.%. The fact that ITO-PEO composites have a percolation threshold of around 6 vol.% indicates that the nanocrystals are somehow not homogeneously or randomly dispersed, and they are likely attracted to each other to form a percolating network at relatively low volume fractions. Conversely, ITO-PMMA composites display percolation at around 20 vol.%, which is consistent with having randomly-dispersed nanocrystals. The difference between the PEO- and PMMA-based nanocomposites suggests that nanocrystals are better dispersed in PMMA and is consistent with the observed tendency for the PEO-based nanocomposites to phase separate. This is further supported by experiments deliberately adding DMF to ITO/PMMA/LiTFSI/MeCN solutions, in which very little phase separation was observed (see the next chapter). These differences likely stem from the ability of each polymer to coordinate to and passivate the nanocrystal surface: the ester group of PMMA supports a resonance structure, which is expected to bond to the ITO surface much more strongly than the ether oxygens of PEO (Figure 3.11).

3.5 Mixed electronic/ionic charge transport in PEO-ITO nanocomposites

The SEM and GISAXS characterization of ITO/PEO/LiTFSI nanocomposites suggest that the distance between adjacent nanocrystals and the average domain size of clusters of nanocrystals changes as the morphology of the nanocomposite changes with added DMF. Both the electronic conductivity and the ionic conductivity of the nanocomposites are expected to strongly depend on this morphology (Figure 3.12). Electronic transport occurs *via* hopping conduction, which strongly depends on the average distance between nanocrs-

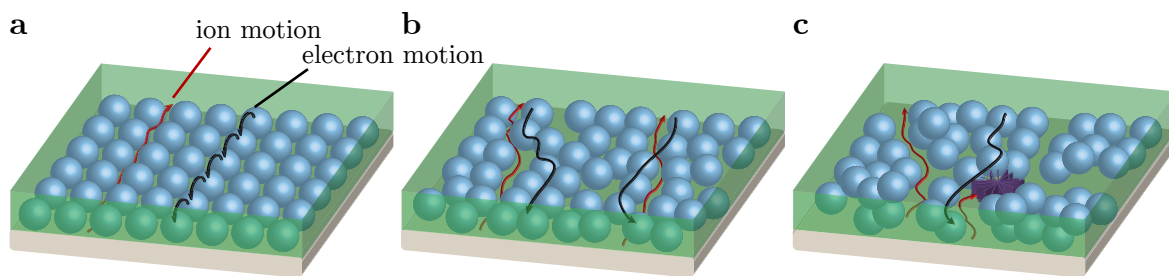


Figure 3.12: Schematic depiction of changes in electronic and ionic conductivity with changing morphology in ITO-PEO nanocomposites. a: With well-dispersed nanocrystals, electrons may have to hop further distances, and ions may have to take tortuous paths for conduction. b: Small amounts of phase separation may open pathways for ion transport and bring nanocrystals closer together for improved electronic transport. c: Excessive phase separation may isolate nanocrystals from each other, hindering electronic transport, and may induce PEO crystallization, which would limit ionic transport.

tals, and excessive phase separation may also electrically isolate clusters of nanocrystals. Likewise, ionic conductivity in PEO depends on segmental chain mobility in the polymer to allow for lithium ions to move between coordination sites, and facile chain motion requires sufficient free volume around the polymer. Thus, some phase separation may be necessary to provide additional free volume to the polymer, and may also open pathways for less-tortuous ion motion between nanocrystals, but excessive phase separation may provide enough free volume for the polymer to crystallize, which would impede ion motion. Below, DC electronic measurements and AC impedance spectroscopy are used in combination to calculate the electronic and ionic conductivities of nanocomposites with varying morphology. Note that the SEM images in Figure 3.6 are representative of the samples discussed below, which were prepared with 0%, 2.5%, 5%, 10%, and 20% DMF (solvent vol.%), and that increasing DMF content in the casting solution corresponds to increasing degrees of phase separation within the nanocomposite.

3.5.1 DC transport measurements: electronic conductivity

The DC electronic conductivity of the nanocomposites was evaluated using the transmission line method, where resistance measurements are performed using electrodes of various spacings. This method is useful because it allows an accurate calculation of electronic conductivity even when the contact resistance is high, which can be common for 2-point measurements. This allows both DC and AC measurements to be performed on the same sample, minimizing the chances for variability or problems with water contamination if the samples are measured with a Hall measurement system (in ambient conditions). Furthermore, an accurate determination of the electronic conductivity and contact resistance enables more accurate interpretation of AC impedance spectroscopy results (see below). Some example

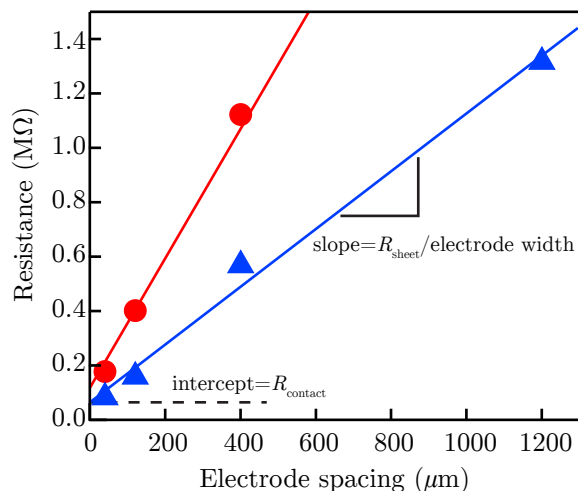


Figure 3.13: DC transmission line measurements of electronic resistance vs. electrode spacing in ITO-PEO nanocomposites. The slope of the fitted line is used to calculate the conductivity, while the ordinate intercept gives the contact resistance.

measurements are shown in Figure 3.13. The slope of the plotted resistances is used to calculate the sheet resistance R_{sheet} and the associated electronic conductivity if the sample thickness is known (determined by profilometry). The ordinate intercept is used to calculate the resistance of the two contacts, R_{contact} . The contact resistance was found to be rather significant, ranging from 12% to 73% of the total resistance, and systematically increased with DMF content/phase separation. This suggests that phase separation has a deleterious effect on the electronic connections between the nanocrystals and the substrate or electrodes, which has implications for electrochemical devices.

3.5.2 AC transport measurements: mixed conductivity

Because it is a frequency-dependent technique, AC impedance spectroscopy is useful for resolving physical conductivity or polarization processes that occur on different time scales. Because of this, it is useful for determining the combined ionic and electronic conductivities of the nanocomposite samples. A representative Nyquist plot for a nanocomposite sample prepared using 10% DMF is shown in Figure 3.14 below. The impedance response is characterized by an asymmetric semicircle with a small tail at low frequencies. This is not the typical impedance response of a mixed conductor, which should show two distinct semicircles corresponding to two time constants. In this case, the significant contact resistance in this case adds an additional time constant to the system, which overwhelms the signal. However, it is still possible to evaluate the ionic resistance from this data, because the contact resistance and electronic resistance of the same sample are known from the DC transmission line measurements. Thus, the impedance response can be modeled by and fit to the equivalent

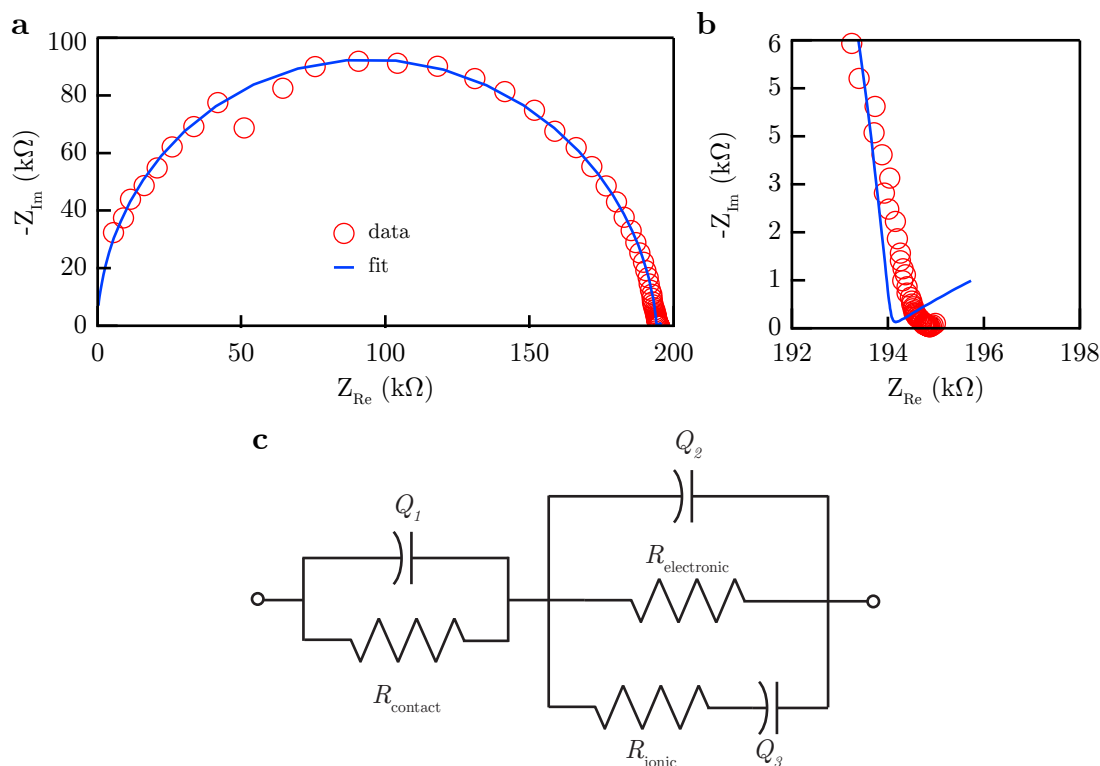


Figure 3.14: AC impedance spectroscopy measurements of mixed conduction in ITO-PEO nanocomposites. a: Representative Nyquist plot of a sample prepared with a 10% DMF solvent and model fit. b: Detail of low-frequency intercept behavior. c: Simplest equivalent circuit of a mixed conductor with contact resistance.

circuit in Figure 3.14c, which is the simplest model for a mixed conductor with additional contact resistance. Since R_{contact} and $R_{\text{electronic}}$ are already known, the unknown R_{ionic} can be determined by the low-frequency intercept at the Z_{Re} axis (Figure 3.14b) according to the relation:

$$R_{\text{intercept}} = \frac{R_{\text{intercept}} (R_{\text{electronic}} + R_{\text{ionic}})}{R_{\text{intercept}} + R_{\text{electronic}} + R_{\text{ionic}}}$$

3.5.3 Mixed ionic/electronic transport changes with morphology

The combined room temperature DC and AC conductivity measurements are displayed in Figure 3.15, showing a clear influence of morphology on the transport characteristics of the nanocomposites. The electronic conductivity generally decreases with DMF content, dropping significantly at 10% and 20% DMF by a factor of about two to ten, respectively. Thus, it seems that driving the nanocrystals closer together with phase separation does not enhance electronic conductivity. Instead, it is likely that the phase separation of nanocrystals into isolated clusters has a negative impact on the electronic percolation throughout the film,

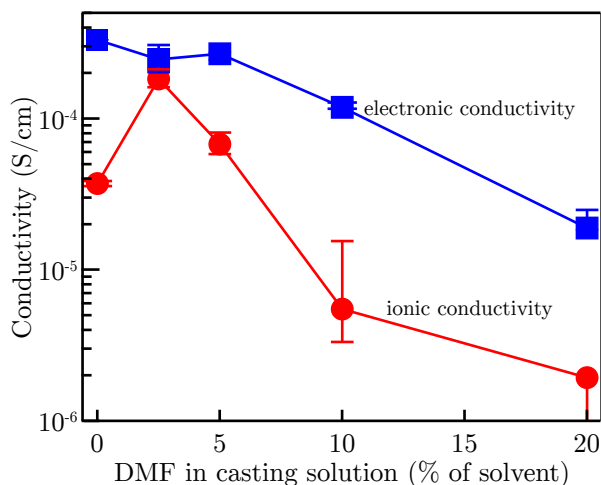


Figure 3.15: Mixed ionic and electronic conductivities of ITO-PEO nanocomposites with systematic variations in phase separation.

as these clusters may be electronically isolated. The fact that the contact resistance systematically increases with phase separation supports this assertion. Although the contact resistance was removed in this analysis to calculate the conductivity of the nanocomposite itself, minimizing contact resistance has important consequences for efficient and fast electrochemical device operation.

Conversely, the ionic conductivity increases by nearly an order of magnitude by adding 2.5% DMF in the casting solution to induce a small amount of phase separation. At higher degrees of phase separation, the ionic conductivity also drops precipitously so far as to become nearly immeasurable, although the uncertainty values increase, which is likely due to the higher contact resistance measured in these samples. In general, the ionic conductivity values are well above the conductivity threshold for electrochromic devices ($\sigma > 10^{-7}$ S/cm at room temperature) and in reasonable agreement with literature values.¹⁰⁵ These changes in mixed conductivity confirm my hypothesis that DMF can be used to tune the morphology and transport characteristics of ITO-PEO nanocomposites. The optimal sample for an electrochromic or electrochemical device is likely the sample prepared with 2.5% DMF, which combines the maximum ionic conductivity with a fairly high, and well-matched, electronic conductivity.

3.6 Conclusions/outlook

Figure 3.16 provides a visual summary of this Chapter. This chapter has demonstrated the synthesis, physical characterization, and mixed ionic/electronic charge transport properties of ITO-PEO nanocrystals. Through the methods developed here, it is now possible to generate these nanocomposites with ionic and electronic conductivities that are sufficiently

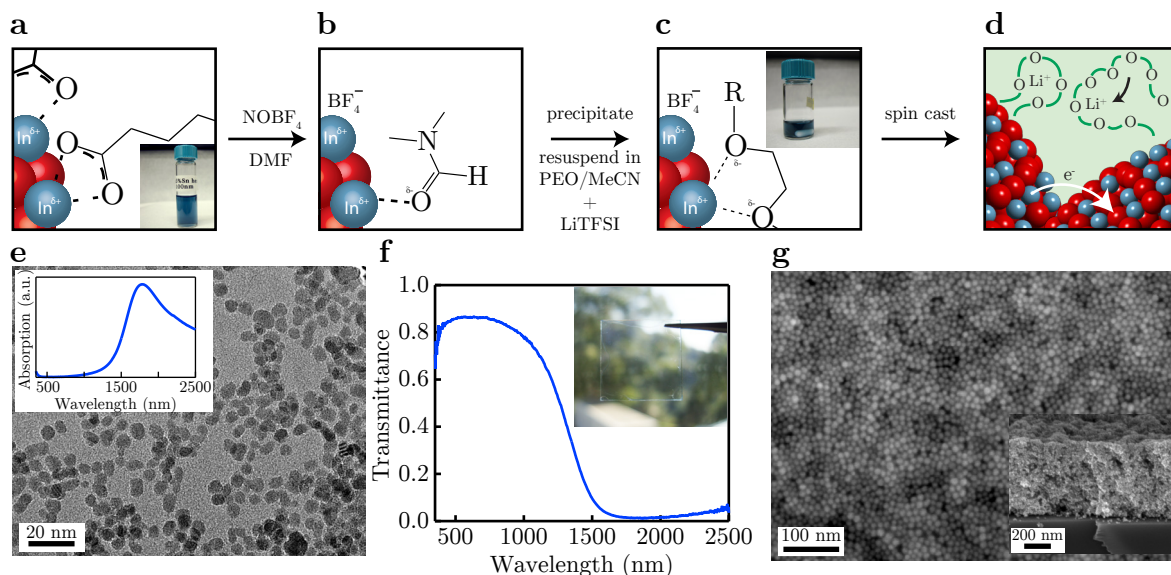


Figure 3.16: Full synthetic process for generating solution-processed ITO-PEO nanocomposite films. a: Colloidal ITO nanocrystals stabilized by their native ligands are synthesized by colloidal chemistry (see Section 3.2.1). Inset: photograph of dispersion of ligand-capped ITO nanocrystals. b: Ligand stripping exposes ITO nanocrystal surfaces (see Section 3.2.2). c: Bare ITO nanocrystals can be wrapped by PEO or other polymers (see Section 3.2.3). Inset: photograph of polymer-wrapped dispersion. d: Deposited ITO-PEO nanocomposites (Section 3.2.5) display mixed ionic/electronic conduction (see Section 3.5). e: Transmission electron micrograph of synthesized ITO nanocrystals with 4.5 nm average diameter. Inset: Optical extinction spectrum showing plasmonic absorption of nanocrystals. f: Transmittance curve and photograph of optically clear ITO-PEO nanocomposite. g: Example SEM micrograph (cross-section in inset) of ITO-PEO nanocomposite with controlled morphology (see Section 3.3).

high for use in electrochromic or other electrochemical devices. Furthermore, by tuning the solvents present in the casting solution, the morphology of the nanocomposites can also be manipulated, which provides the ability to tune their electronic and ionic conductivities. This tunability implies that the performance metrics, such as switching speed, of electrochromic devices and other electrochemical devices that rely on both electronic and ionic transport for efficient operation could be optimized *via* manipulating nanocomposite morphology. This advance comes at a time when interest in nanomaterials and nanocomposites with properties that are tunable by combinations of active and/or inactive materials, and mixed conductors for use in electrochemical devices, is growing considerably. Hopefully, the strategies outlined here will prove useful in the fabrication of future electrochemical devices based on solution-processed colloidal nanocrystals.

A significant added benefit is that the strategies outlined here afford nanocomposites fabricated entirely using solution processing at room temperature. In fact, solution-based

methods potentially use 10 to 100 times less energy than physical methods involving molten or vapor phase materials, such as sputtering or evaporation.¹¹⁰ Solution processing also provides more efficient utilization and reuse of materials, which reduces raw costs and energy use associated with mining, production, and recycling. While spin casting is a very useful technique, it is only suitable for laboratory-scale device fabrication, so future research plans should examine other deposition methods, including spray coating, doctor blading, dip coating, or layer-by-layer deposition.

Chapter 4

Solid state electrochromic devices based on solution processed polymer-nanocrystal composites

4.1 Introduction

The previous Chapter developed methods to make nanocomposites of tin-doped indium oxide (ITO) nanocrystals and a lithium ion conducting polymer, and carefully characterized their morphology and mixed charge transport. The goal of this Chapter is to apply these methods to fabricate solid state electrochromic devices based on plasmonic nanocrystals.

The general architecture for such a device is schematically presented in Figure 4.1. The active material, ITO nanocrystals, is dispersed in a polymer matrix that also contains lithium salt, and deposited onto glass coated with a transparent conductive oxide (TCO) to form the active or working electrode of the device. On another piece of TCO-coated glass, a similar nanocomposite is made, using nanocrystals of cerium oxide (CeO_2), which has been demonstrated as a feasible counter electrode for both tungsten oxide-based and ITO-based electrochromic devices.^{31;111} This nanocomposite forms an optically passive counter electrode or charge storage layer. Finally, the two electrodes are laminated together using a solid or gelled polymer electrolyte, which serves to transport lithium ions between the active and counter electrodes during device operation, and also to separate the two electrodes with an electronically insulating layer. The device can then be operated through an external circuit. Applying a negative voltage to the working electrode relative to the counter electrode will move electrons from the CeO_2 into the ITO nanocrystals through the external circuit, and lithium ions will move inside the electrolyte from the charge transport layer towards the ITO nanocrystal surfaces. This process results in near-infrared (NIR) coloration of the ITO nanocrystals as described in Section 2.6, and the device can be considered in a colored or “on” state. Applying positive voltage to the working electrode reverses the process to bleach the device.

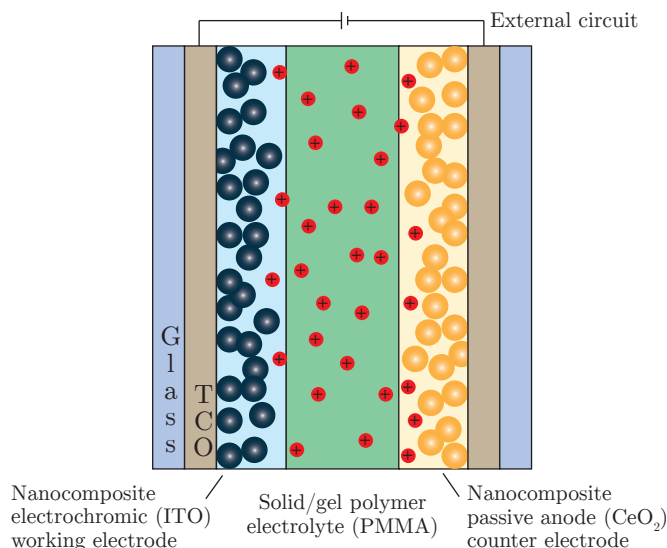


Figure 4.1: Proposed architecture for a nanocrystal-based solid state electrochromic device. The active electrochromic material, ITO nanocrystals, is dispersed in a polymer along with lithium salt and deposited onto a transparent conductive substrate. A similar nanocomposite with an optically passive charge storage material, CeO_2 nanocrystals, is deposited on another transparent conductive substrate. The two electrodes are then laminated together with a solid or gelled polymer electrolyte which also serves as a separator.

Throughout the rest of this Chapter, the methods for fabricating such a device are described in greater detail, and the electrochromic performance of the device is examined. Work evaluating the electrochemical cycling stability of the device is also presented.

4.2 Experimental

4.2.1 Nanocrystal synthesis and ligand stripping

ITO nanocrystals with 10% Sn and an average diameter of 4.5 nm were synthesized as described in Section 3.2.1 using indium (III) acetate ($\text{In}(\text{OAc})_3$), tin (II) acetate ($\text{Sn}(\text{OAc})_2$), and oleylamine.

CeO_2 nanocrystals were synthesized using slight modifications to methods described in the literature.¹¹² In brief, 0.5 mmol of cerium (IV) ammonium nitrate (Sigma Aldrich, 99.99%), 3 mmol oleylamine (Acros, 90%), and 10 mL of 1-octadecene (Sigma Aldrich, 90%) were combined in a 50 mL round bottom flask and attached to a Schlenk line with constant magnetic stirring. The solution was mixed at room temperature under nitrogen for five minutes, then heated to 70°C for 5 minutes until the cerium precursor fully dissolved. The solution was then heated to 180°C for two hours under nitrogen to nucleate and grow

colloidal CeO₂ nanocrystals. After the reaction, the nanocrystals were purified by three rounds of successive flocculation with ethanol, centrifugation, and redispersion in hexanes.

As synthesized, both ITO and CeO₂ nanocrystals contain surfactant or ligand molecules on their surface which must be removed for efficient charge transport in a nanocomposite electrochromic device. Equivalent ligand stripping procedures were performed for both ITO and CeO₂ nanocrystals using nitrosonium tetrafluoroborate (NOBF₄) as described more fully in Section 3.2.2. The NOBF₄:nanocrystal weight ratio was 1:2. After ligand stripping, the nanocrystals were washed six times with centrifugation using *N,N*-dimethyl formamide (DMF) as a dispersing solvent and toluene as a flocculant. The nanocrystals in DMF were then transferred into a glovebox with sub-ppm oxygen and water concentrations and washed three more times with anhydrous DMF and toluene. Note that all subsequent fabrication steps are carried out inside of a water-free glovebox.

4.2.2 Nanocomposite film fabrication

After ligand stripping and extensive nanocrystal washing, the ITO nanocrystals and CeO₂ nanocrystals were precipitated once more with toluene and centrifuged, then redispersed using solutions of poly(methyl methacrylate) (PMMA, 410 kg/mol, Elvacite) at a weight ratio of 4:1 nanocrystals:polymer to form optically clear and homogeneous dispersions. ITO was dispersed using a solution of PMMA dissolved in acetonitrile (MeCN) at 5% by weight, and CeO₂ was dispersed using a solution of PMMA dissolved in DMF at 5% by weight. After dispersing the nanocrystals, the solutions were further diluted with their respective solvents so that the total solids content (ITO+PMMA) was 5% by mass. The solutions were stirred for 12-24 hours before lithium bis(trifluoromethylsulfonyl)amide (LiTFSI), dissolved in tetrahydrofuran (25% by weight), was added to the solutions. The amount of LiTFSI added was such that the ratio of Li⁺:O (oxygen atoms on the PMMA) was 1:10. The dispersion remained stable upon the addition of LiTFSI.

The solutions containing nanocrystals, PMMA, and LiTFSI were spin casted onto glass substrates coated with ITO having a sheet resistance of 200 Ω /square. Prior to deposition, the substrates were cleaned by sonicating for 15 minutes each in Hellmanex cleaning solution, acetone, and isopropanol before being blown dry and subjected to a UV-ozone treatment for 20 minutes. This renders the substrates hydrophilic and is necessary to ensure good wetting of the solutions and good adherence of the polymer nanocomposites. After dropcasting the solutions onto the substrates using a micropipette, the substrates were spun at 1000 rpm for 60 seconds and 4000 rpm for an additional 30 seconds. After spin casting, the nanocomposites fabricated with CeO₂ nanocrystals were dried under vacuum at 80°C for 10 minutes to remove excess DMF.

4.2.3 Device lamination and assembly

After the working and counter electrode nanocomposites are deposited on TCO-coated glass, they are ready for device assembly. Kapton polyimide tape, 50 μ m thick and 0.25 inches

wide, was placed on two edges of the working electrode to define the active device area and also help prevent physical shorting of the device. On top of each Kapton piece was placed five layers of masking tape at a total thickness of about 700 μm . These masking tape layers help to define the geometry of the polymer electrolyte separator.

Separately, a solution of PMMA, LiTFSI, tetraglyme, and THF was prepared with weight ratios of 1:0.67:1.67:5 to serve as the precursor to the gelled electrolyte and separator. This corresponds to a 1:10 ratio of $\text{Li}^+:\text{O}$. This viscous mixture was pipetted into the well defined by the masking tape on the working electrode, and a metal spatula was dragged flat across the masking tape to remove excess and planarize the electrolyte. The working electrode was then placed on a hotplate at 95°C for 15 minutes to evaporate THF, leaving behind a sticky, gelled polymer electrolyte.

After removing the masking tape, the working electrode was then sandwiched together with the counter electrode, taking care to offset the substrates slightly so to allow for electrical contact to the underlying TCO layers. The entire assembly was clamped with two binder clips, and placed in a vacuum oven at 90°C for 10 minutes to laminate the two electrodes together. After the lamination step, care was taken to let the device cool for 15 minutes before removing the binder clips. The resulting laminated solid state device was free standing and mechanically stable, without problems like delamination or movement of the substrates with respect to each other.

4.2.4 Electrochemical characterization

For characterization of the electrochromic and electrochemical properties of the laminated device, a Bio-logic VMP3 potentiostat was used in combination with a ASD/PANalytical UV-vis-NIR spectrophotometer. To make electrical contact between the potentiostat leads and the TCO-coated glass, the exposed nanocomposite on the working and counter electrodes was scraped off.

Before spectroelectrochemical characterization, the device was first subjected to four cycles of cyclic voltammetry (CV) between -4V and 2.5V (voltage of the working electrode with respect to the counter electrode) at a scan rate of 10 mV/s. This was done to irreversibly oxidize the electrolyte to liberate additional free electrons that can be moved between electrodes to assist the electrochromic effect. After this break in step, the electrochromic performance of the device was characterized by measuring the transmittance of the full device at given voltages between 1.8V (bleached) and -4V (colored). Additional CV scans were also performed to evaluate device stability with electrochemical cycling.

4.3 Results and discussion

These experiments were initially attempted using poly(ethylene oxide) (PEO)-based nanocomposites, which were made successfully with both ITO and CeO_2 . Unfortunately, it proved very difficult to laminate the two electrodes together with a PEO-based separator and a num-

ber of problems were encountered. These included mechanical instability, as the 20 kg/mol PEO used was fairly soft, and the PEO-based separator also had a tendency to crystallize, which rendered the device hazy and unable to transport charge effectively. Finally, very little charge was passed during the break in cycle. Ultimately, these problems combined to prevent PEO-based nanocomposite devices from showing electrochromic switching behavior.

Instead, we turned to PMMA-based nanocomposites, as PMMA is also well known polymer electrolyte material in its gelled (i.e., partially swollen with solvent) state, and can have ionic conductivities similar to or greater than PEO-based electrolytes.^{22;105;113;114} Note that the solvent that swells the PMMA is primarily responsible for transporting ions in this system, although the PMMA does partially participate in ion solvation.¹¹³ Such gel polymer electrolytes are useful from an application perspective, as they blend the properties of solid polymers with those of liquid electrolytes to yield an electrolyte and separator that behaves similarly to liquid electrolytes from an electrochemical standpoint, while resisting flow, leaking, or evaporation and having mechanical properties more reminiscent of a solid.²² Indeed, PMMA gel electrolytes have been utilized effectively throughout the literature in electrochromic devices.^{22;115–117} Finally, as noted in Chapter 3, ITO nanocrystals had been successfully dispersed in PMMA and deposited as nanocomposites. It was relatively straightforward to adapt the processing strategies developed for PEO to the PMMA system in order to fabricate homogeneous and optically clear ITO-PMMA-LiTFSI nanocomposites.

4.3.1 Morphology of ITO-PMMA nanocomposites

The PMMA-based dispersions are easier to handle than the PEO-based dispersions in Chapter 3. ITO was readily dispersible in PMMA/MeCN solutions at weight ratios up to 10:1 ITO:PMMA. Furthermore, the dispersions remain stable for long periods after adding LiTFSI, further simplifying processing. A number of ITO-PMMA-LiTFSI dispersions prepared during this experiment were stable for over one year, provided that the ligand stripped ITO nanocrystals were washed appropriately. Upon spin casting, the dispersions yielded films of excellent optical clarity and uniformity (Figure 4.2). This enhanced colloidal stability can be attributed to the stronger interactions between ITO nanocrystal surfaces and the methacrylate groups of PMMA (see Figure 3.11).

Only a few slight modifications from the procedures for PEO-based nanocomposites were necessary. The weight ratio of ITO:polymer was increased to 4:1 here to achieve higher nanocrystal loading for a given film thickness, because a higher density of ITO nanocrystals was necessary to achieve optical densities appropriate for electrochromic device operation. Additionally, because of the high molecular weight of the PMMA used here (410 kg/mol), 4:1 ITO:PMMA dispersions prepared with a 5% PMMA/95% MeCN solution were too viscous to achieve good wetting and film morphology during spin casting. Diluting the solution further to 5% total dispersed solids (ITO+PMMA) in MeCN alleviated this problem. Finally, it was also observed that using pure MeCN as the solvent for nanocomposites with CeO₂ nanocrystals, the films were cloudy and phase separated. Changing the solvent to DMF yielded optically clear and homogeneous CeO₂-based nanocomposites. This was surprising,

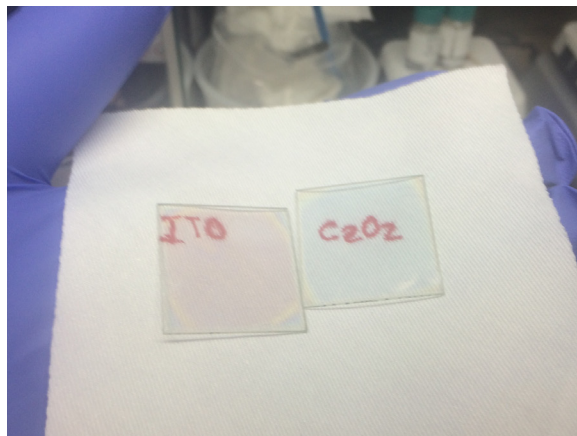


Figure 4.2: Photograph of PMMA-based nanocomposites with ITO and CeO₂ nanocrystals. The substrates measure 2x2 cm.

as DMF was already known to cause severe aggregation and phase separation in ITO-PEO nanocomposites as extensively described in the previous Chapter. Here, it seems that MeCN, rather than DMF, has strong affinity for CeO₂ nanocrystal surfaces and displaces PMMA. This is probably the result of fundamental differences in the surface chemistry of ITO and CeO₂ nanocrystals that have not yet been characterized.

Another surprising result is that the presence of DMF in the casting solution for ITO-PMMA composites has a much less pronounced effect than it does in ITO-PEO composites. Repeating the same study as described in Section 3.3 and shown in Figures 3.6 and 3.7, no significant differences in film morphology or phase separation were observed with increasing DMF content (Figure 4.3), and cloudiness was observed only in films prepared with 50% DMF. In fact, the nanocomposite films appeared to have a qualitatively better and more uniform morphology when about 5-20% DMF was added to the casting solution compared to pure MeCN (Figure 4.3a,b). This could be a result of DMF being a better solvent for PMMA than MeCN, or the addition of a higher boiling point solvent to the dispersion could improve spin casting results. There were also few clear differences in morphology from the GISAXS line scans of these samples. There is a small discernible shift of the nanocrystal-nanocrystal peak towards lower Q , indicating that the nanocrystals are closer together, but additional information about cluster sizes, etc. could not be determined from the low- Q region. One noteworthy observation is that there is a very stark difference in the nanocomposite morphology when LiTFSI is not present in the dispersion or casting solvent—the nanocrystals are quite well dispersed and the GISAXS is fairly featureless with a poorly-defined nanocrystal-nanocrystal peak (Figure 4.3c). By contrast, when salt was added the peak becomes quite intense, indicating some degree of nanocrystal aggregation or ordering induced by LiTFSI, which agrees with the previous chapter. In all, DMF and LiTFSI appear to have similar effects on the morphology of PMMA-based nanocomposites, but these effects seem to be rather muted here as a result of the stronger interactions between

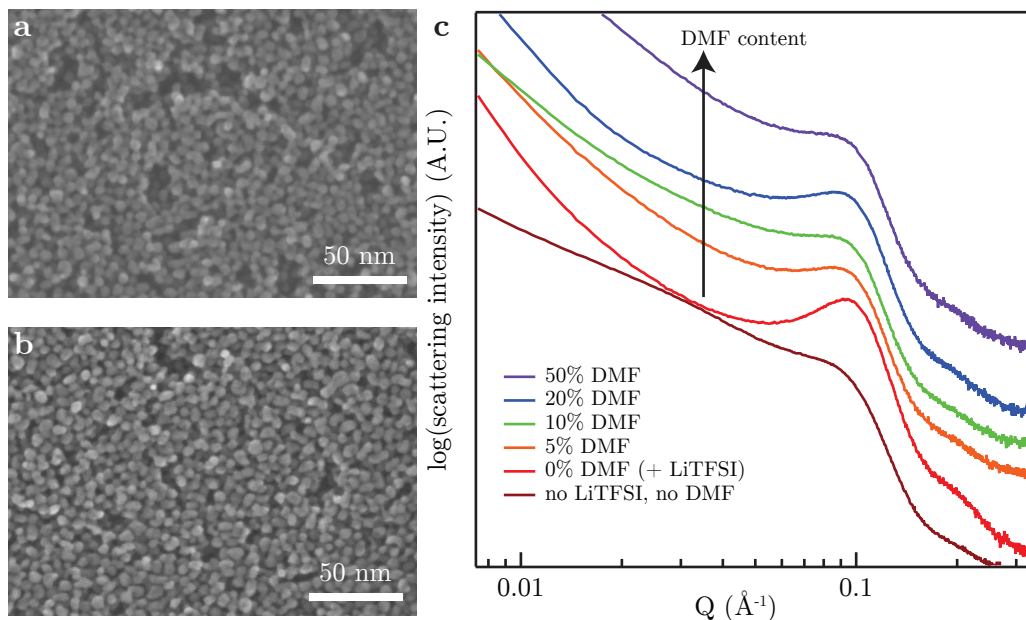


Figure 4.3: Morphology of ITO-PMMA-LiTFSI nanocomposites. a: SEM micrograph of nanocomposite prepared with no added DMF. b: SEM micrograph of nanocomposite prepared with 5% added DMF. c: GISAXS line scans of ITO-PMMA-LiTFSI nanocomposites prepared with different amounts of DMF in the casting solvent.

the PMMA and the ITO nanocrystals.

4.3.2 Electrochromic device performance

The ITO-PMMA and CeO_2 -PMMA nanocomposites can be laminated together using a PMMA gel electrolyte/separator to form a solid state and optically clear electrochromic device (Figure 4.4, inset). Spectroelectrochemical characterization of the device after the electrochemical break in cycle (Figure 4.4) shows that the device works as intended, with a distinct and significant change in NIR transmittance when a negative voltage is applied to the working electrode. This corresponds to injecting electrons into the ITO nanocrystals in the device, which results in a blue shift of their LSPR frequency and NIR absorption (also see Figure 2.10). Applying a positive voltage extracts electrons from the nanocrystals, leading to an LSPR redshift and device bleaching in the NIR. The entire device operates with an applied voltage range of less than 6V.

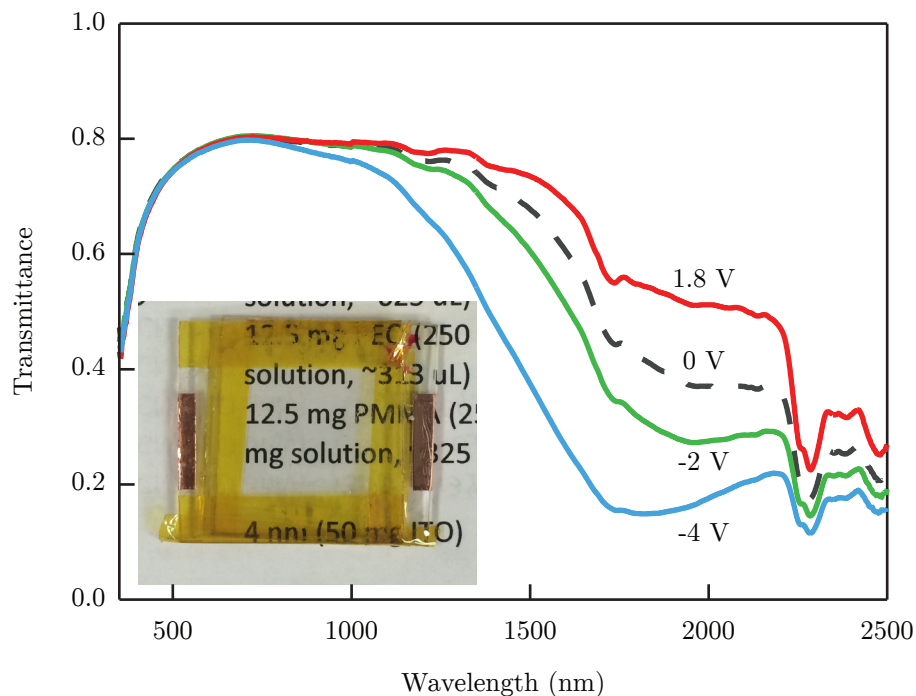


Figure 4.4: Electrochromic performance of an ITO-PMMA nanocomposite-based solid state device. At 1.8 V, electrons are removed from the ITO and stored in the CeO_2 counter electrode, and the device is bleached. Applying increasingly negative voltage injects electrons into the ITO nanocrystals, coloring the device in the NIR. Inset: photograph showing the optical clarity of the assembled device.

4.3.3 Electrochemical behavior of nanocomposite-based devices and electrolytes

4.3.3.1 Electrochemical break in step

Solid state electrochromic devices based on this nanocomposite approach have also been subjected to preliminary electrochemical characterization in order to study charge transport within the device and to begin evaluating electrochemical stability with cycling. We found that it was necessary to perform the CV-based electrochemical break in step described in the experimental methods before appreciable electrochromic performance could be measured. Figure 4.5a shows the CV scans of the device during this break in step, while 4.5b shows the charge passed from the counter electrode to the working electrode of the device during this step. Most of the charge passed is at negative voltages, as the CV curve shows irreversible cathodic current at around -4 V, with what appears to be capacitive current at positive voltages. The active device area is about 4.6 cm^2 , so this break in step corresponds to approximately 5.4 mC/cm^2 of charge passed in the device and stored within the electrodes.

To more carefully study the origin of this charging, an equivalent CV break in cycling

test was performed on the PMMA polymer gel electrolyte/separator formulation simply laminated between two bare pieces of TCO-coated glass without the presence of nanocrystals (Figure 4.5c,d). The CV and charge profiles look very similar in this case, indicating that charge is passed from the electrolyte itself, through the counter electrode and external circuit, into the working electrode. This presumably results from some electrochemical degradation process in the electrolyte. The most likely mechanism is that the tetraglyme additive in the electrolyte is irreversibly oxidized at the counter electrode when cathodic voltages are applied to the working electrode, and the electrons liberated from tetraglyme are then swept through the external circuit and into the working electrode. The electrodes of the device can then reversibly pass and store these additional free electrons to support the electrochromic effect. Note that the charge that can be stored within the electrodes in this polymer-only device, which had a similar active device area, is approximately 2 mC/cm^2 , significantly lower than for devices containing nanocrystals. This suggests that the presence of nanocrystals improves this electrochemical charge generation reaction by providing a large surface area to both the working and counter electrodes, which increases their ability to store charge capacitively and could also enhance the electrochemical reaction kinetics.

4.3.3.2 The role of lithium salt

An additional device was made without adding LiTFSI to either the working electrode nanocomposite or the counter electrode nanocomposite. This was done to determine if it was necessary to include lithium ions and counter ions in the both electrodes, or if the PMMA gel electrolyte/separator could provide the lithium ions necessary for electrochemical charge transport. This device showed nearly no electrochemical or electrochromic activity (Figure 4.6). Very little current flowed during the CV break in cycle, and minimal charge was passed, and even after 20 break in cycles (as opposed to the usual four), the device was capable of storing only about 0.07 mC/cm^2 . Furthermore, the device exhibited no optical switching (Figure 4.6a inset). This result shows that it is crucial to include lithium salt in the nanocomposite working and counter electrodes, and confirms that previous efforts to include lithium in PEO and PMMA nanocomposites are well motivated from a device perspective. Note that this device passed nearly two orders of magnitude less charge than either the properly prepared nanocomposite device or the device with electrolyte only. The lack of lithium salt in the working and counter electrodes likely results in a strong concentration polarization at the electrode electrolyte interface, as the ion concentration abruptly drops to zero across the interface. This causes the electrochemical potential to drop fully across the interface, and appreciable currents cannot flow in the electrolyte without the presence of Li^+ and TFSI^- in each nanocomposite electrode.

4.3.3.3 Electrochemical stability

As a commercial smart window must be able to withstand tens of thousands of electrochemical cycles without performance degradation (see Section 2.2), preliminary durability studies

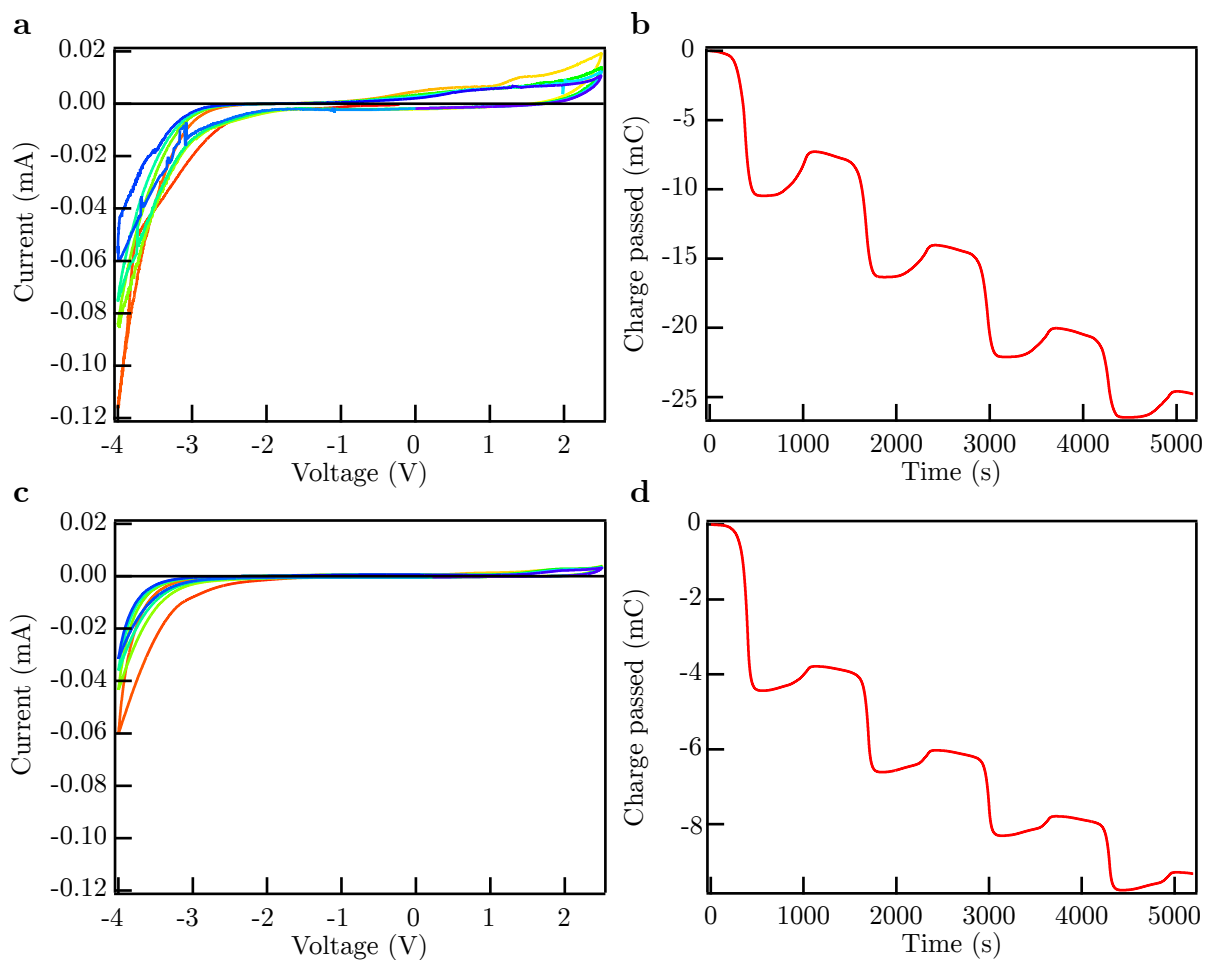


Figure 4.5: Break in cycles of nanocomposite electrochromic devices. a: CV break in (scan rate: 10 mV/s, initially scanning towards negative voltages from the open circuit state) applying between -4 V and 2.5 V across the two electrodes of a laminated electrochromic device for four cycles. Color change from red to purple indicates time elapsed/cycle number. b: Charge passed through the electrochemical circuit vs. time for the CV in panel a. c: CV break in of PMMA gel electrolyte only, laminated between two pieces of conductive glass. d: Charge passed vs. time for CV in panel d.

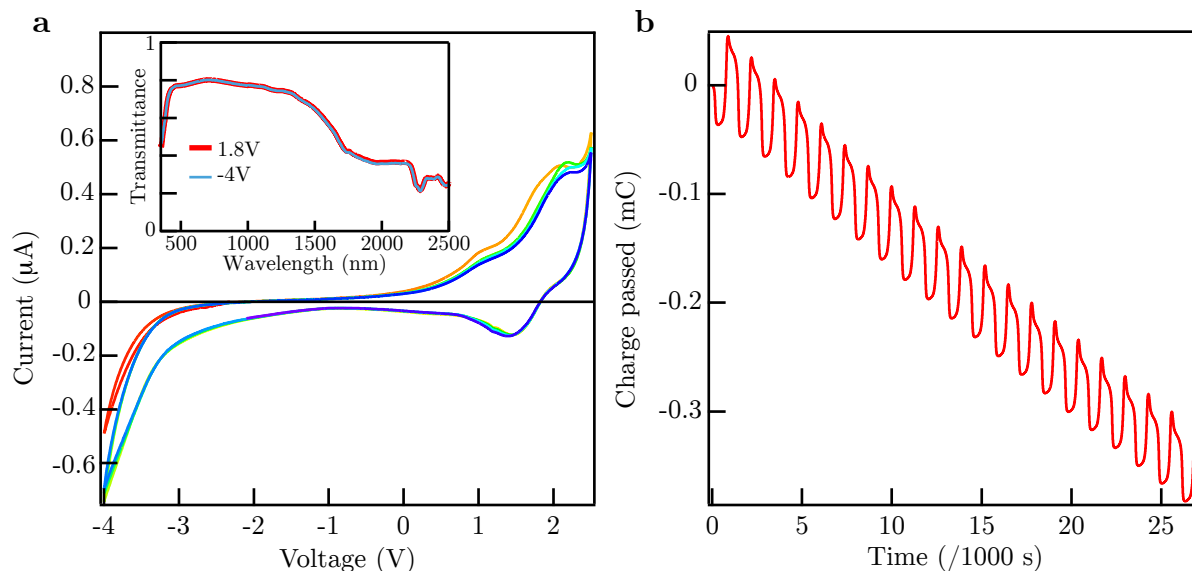


Figure 4.6: Poor electrochemical behavior in an electrochromic device prepared without LiTFSI present in the nanocomposite working and counter electrodes. a: CV scan (10 mV/s, initially scanning towards negative voltages from the open circuit state) showing very low current flow. Inset: transmittance curves of device at different voltages after the CV cycling, showing no electrochromic response. b: Very little charge was passed in this device despite undergoing 20 CV cycles.

on these devices were performed. To begin, the electrochemical stability of the electrolyte itself was evaluated by CV (scan rate: 25 mV/s) between -2V and 2V for 120 cycles (Figure 4.7). The electrolyte appears to be quite stable over this potential range, and the square shape of the CV scan suggests that the minimal current over this potential range is mostly capacitive. While some charge is indeed passed over the 120 cycles (Figure 4.7b), it is a very low value, and if the average linear trend in Figure 4.7b persists, then the electrolyte would be able to sustain over 10,000 cycles before passing the same amount of charge passed in Figure 4.5b. Note that 10,000 cycles corresponds to more than 27 years at one cycle per day in a commercial device.

4.3.3.4 Total charge needed and charge balancing

Although the electrolyte appears to be stable under long term electrochemical cycling between -2V and 2V, the full solid state device undergoes a much deeper modulation when charged to -4V compared to -2V (Figure 4.4). It is unclear why this is, but one possible reason could be an imbalance in charge capacity between the ITO working electrode and the CeO_2 counter electrode which is preventing the ITO nanocrystals from reaching their full charge capacity at -2V. However, when stronger potentials of -4V are applied, the NIR contrast of this device is comparable to the contrast of ITO nanocrystals measured in a

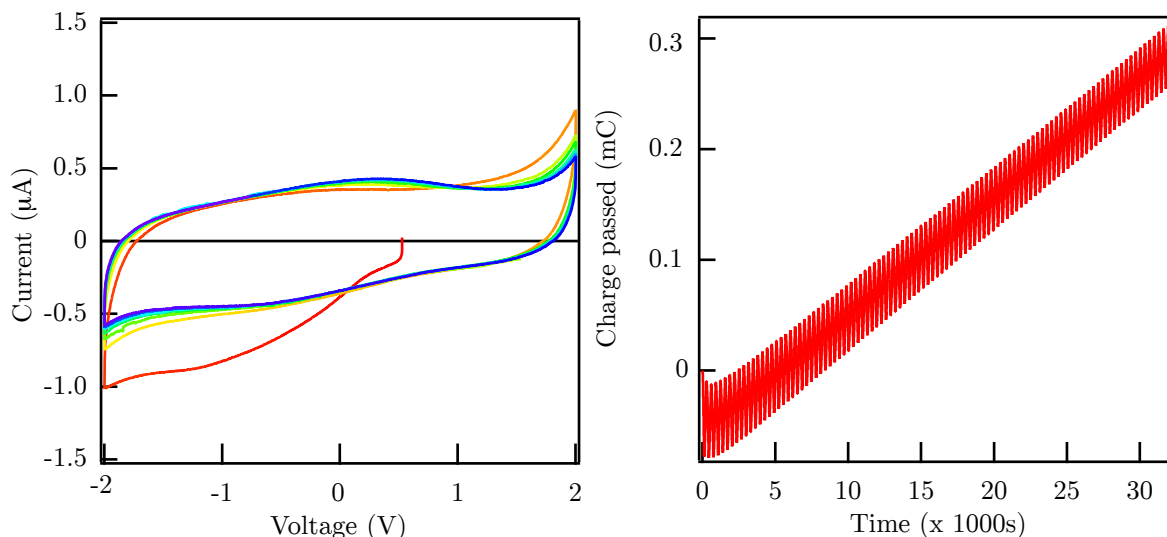


Figure 4.7: Electrochemical stability of PMMA gel electrolyte/separator. a: CV scan (scan rate: 25 mV/s, initially scanning towards negative voltages from the open circuit state) over 120 cycles. b: Charge passed from CV over 120 cycles.

half-cell configuration (Figure 4.8),²⁸ where the charge capacity of the counter electrode is essentially infinite. This makes it likely that the CeO_2 counter electrode cannot store sufficient charge in this device. Additionally, it is possible that the CeO_2 can indeed store enough charge for full modulation, but that additional break in cycles are needed to liberate more free electrons for full electrochromic modulation. Alternatively, the CeO_2 nanocrystals could be partially reduced by chemical means or by electrochemical charging in a half cell before device assembly. This could generate reduced Ce^{3+} ions which could be oxidized in the full device to pass cathodic charge to the ITO working electrode. This may prove challenging, however, as chemical treatments strong enough to reduce CeO_2 may decompose the PMMA matrix, and most organic electrolytes in an electrochemical half cell are capable of dissolving PMMA. In any case, additional study of the charge capacity of both the ITO and CeO_2 nanocomposite electrodes is warranted, and additional effort may be needed to be able to tune the thickness of the CeO_2 counter electrode, and hence its charge capacity.

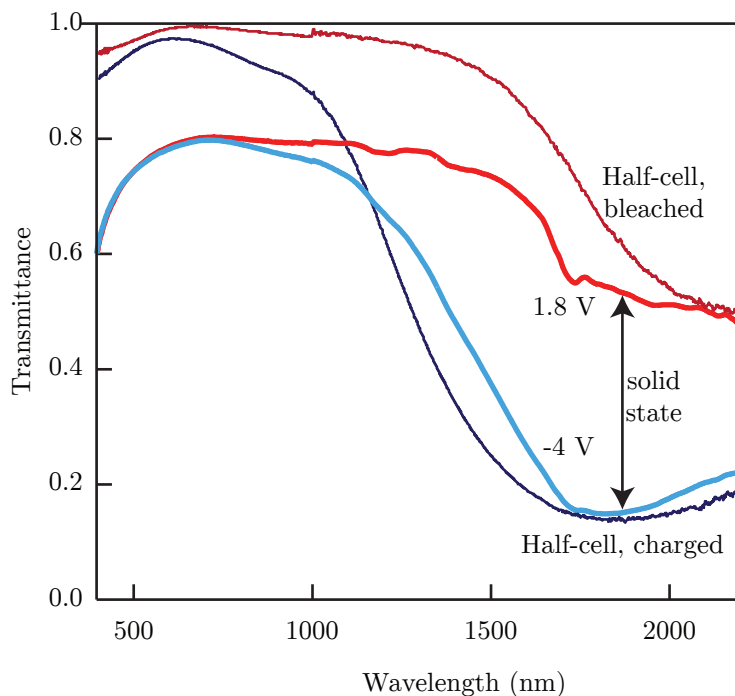


Figure 4.8: Comparison of solid state device electrochromic performance to ITO nanocrystal half-cell measurements. The solid state device shows comparable optical contrast in the NIR when charged to -4V. The transmittance curves for the half cell measurements are reproduced from Reference²⁸.

4.4 Conclusion

This Chapter, and the previous Chapter, have presented a simple, all solution-processed route to solid state electrochromic devices based on plasmonic nanocrystals. The device presented here is the first demonstration of a device achieved without any templating by polymer micelles, or other complicated steps.³¹ Furthermore, good electrochemical performance and stability were achieved, and the devices switch in the NIR with appreciable contrast that is comparable to previous results on ITO nanocrystal films. Additional work to better understand and improve the electrochemical properties of the device is warranted, as are attempts to extend these techniques to other electrochromic nanocrystal materials which may provide better optical contrast, like aluminum doped zinc oxide,²⁹ niobium-doped titanium oxide,¹⁰³ and tungsten oxide.¹⁰⁴ These results are quite promising from an applications perspective, and the fabrication methods are simple and the nanocrystal-PMMA dispersions are stable over a year. Furthermore, the devices made are optically quite clear, which is critical for aesthetic considerations.

Part II

Plasmonics: intra-nanocrystal electron transport

Chapter 5

Doping, electronic charge transport, and defect chemistry in plasmonic metal oxide nanocrystals

Adapted, in part, from Reference⁶⁶:

Lounis, S. D.; Runnerstrom, E. L.; Llordes, A.; Milliron, D. J. Defect Chemistry and Plasmon Physics of Colloidal Metal Oxide Nanocrystals. *J. Phys. Chem. Lett.* **2014**, *5*, 1564–1574.

5.1 Introduction

Colloidal metal oxide nanocrystals are a relatively new and intriguing materials system that can be leveraged for tunable plasmonic applications. Recent advances in colloidal synthesis^{2;4;84;85} have enabled fabrication of highly-doped semiconductor nanocrystals, opening the door to oxide nanomaterials with localized surface plasmon resonance (LSPR). LSPR is more classically studied in metals, where the collective oscillation of free carriers leads to large optical absorption and scattering cross-sections, as well as strong enhancement of electromagnetic fields at the nanocrystal surface. LSPR is further sensitive to particle size, shape, and the surrounding dielectric environment, and in metals, these conditions can be systematically varied to tune the resulting LSPR properties. For example, tracking the change in LSPR with dielectric environment, which changes with binding events, forms the basis for plasmonic bio-sensors.¹¹⁸ In semiconductors, LSPRs are enabled by doping and/or charge injection; this provides an additional degree of tunability *via* doping levels or electrochemical charging. Doped semiconductor nanocrystals now display plasmonic effects spanning the visible, near-infrared (NIR), and mid-infrared (MIR) spectral ranges (Figure 5.1), spurring development of new optoelectronic devices operating at these wavelengths. These tunable

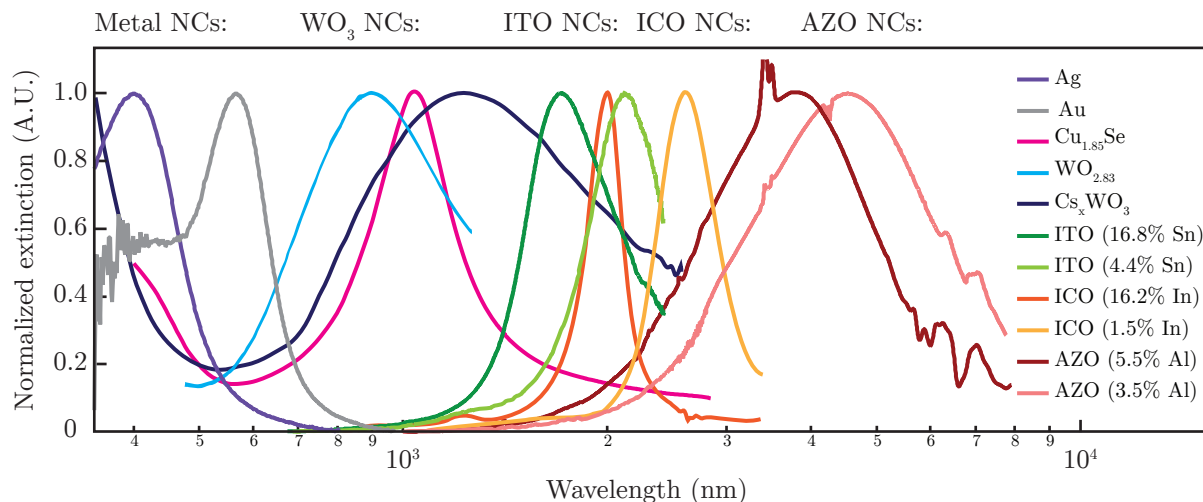


Figure 5.1: Normalized optical extinction from LSPR in metal and doped semiconductor colloidal nanocrystals. Figure adapted with permission from Reference⁶⁶, Copyright 2014 American Chemical Society.

materials have enabled the development of a new class of smart windows, as described in Part I, which are already on the verge of commercialization.^{14;28–30;104;119} Doped semiconductor nanocrystals are also drawing interest for applications including chemical sensing and bio-sensing, telecommunications, and advanced optics and photonics.^{64;120;121} Despite the surge in popularity of plasmonic materials, plasmonic semiconductor nanocrystals in particular are subject to structure-property relationships that have yet to be fully explored. The interactions between structural and electronic properties in semiconductor nanocrystals, especially when dopants are introduced, have revealed a number of fundamental questions on the subjects of charge transport in nanocrystals and plasmon physics that are only beginning to be answered.

This Chapter examines the emergence of LSPR phenomena in metal oxide nanocrystals doped to induce metallic optical behavior, summarizing the structure-property relationships that will be examined throughout the rest of Part II. The defect chemistry underlying doping and compensation is addressed and implications for the plasmon physics of these materials are elaborated. Key fundamental differences that distinguish materials reported in the literature are explained, culminating in an outlook toward emerging research directions as we deepen our understanding of plasmonic phenomena in metal oxide nanocrystals.

5.2 Near field enhancement of infrared light as a model application for metal oxide LSPR

In plasmonic materials, free carriers resonate collectively in response to the oscillatory electromagnetic field of incident light. The high local electric fields that result can effectively concentrate light into nanoscale volumes well below the diffraction limit and can direct the flow of energy through coupled nanostructured and molecular systems and assemblies.^{122–124} LSPR excitations are confined to the physical dimensions of plasmonic nanostructures and, in the limit of small particles (i.e., the quasi-static limit), dipolar polarization modes are dominant. The excitation of these modes by incoming light is strongly allowed and the accompanying *near field enhancement* results in large optical absorption and scattering cross-sections, concentrating light energy into the space immediately surrounding the plasmonic nanostructures. The intense near fields can further interact with nearby molecules or materials to enable strong *coupling* between LSPR modes and other dipolar state transitions, which subsequently enhances the optical cross section of those transitions. In general, the ability of a plasmonic nanocrystal to concentrate light into small volumes scales with its LSPR quality factor, or Q , which is the ratio of the LSPR peak energy to the peak width:

$$Q = \frac{E_{\text{LSPR}}}{\Delta E_{\text{LSPR}}} \quad (5.1)$$

where ΔE_{LSPR} is the peak width. Thus, minimizing peak widths in plasmonic nanocrystals is a strong point of emphasis for near-field enhancement applications.

The field of plasmonics has primarily relied on classical metals like gold and silver, but there has been a recent surge of interest in alternative plasmonic materials whose spectral and dielectric tunability offers new opportunities for manipulating light-matter interactions. Chemical synthesis routes have been developed for doped semiconductor nanocrystals with sufficiently high free carrier concentration to support LSPR and these materials offer chemical and electronic tunability that is not found in classical metals.^{49;50;66;67;75;77;81;83;88;93;94;125–129} Transparent conducting oxides (TCOs) are a particularly interesting class of degenerately doped plasmonic semiconductors whose plasmon resonance frequencies lie far below their band gap transition energies; this energetic separation suppresses plasmonic losses.^{121;130} The properties of TCO nanocrystals complement well-studied LSPR phenomena in classical metal nanoparticles and nanostructures, while also enabling LSPR in materials with earth abundant compositions, such as Al-doped ZnO (AZO).^{66;77}

An important but outstanding research objective is to deliberately synthesize TCO nanocrystals with LSPR properties that are well-suited for near field enhancement applications and for systematic studies of plasmon coupling. Some design principles can be derived by directly applying knowledge from metal nanoparticles, while the materials chemistry of doped metal oxides provides new challenges and opportunities. Near field microscopy and simulations of near-fields,^{131;132} along with direct imaging of metal nanoparticle LSPR modes by electron energy loss spectroscopy^{133;134} has demonstrated that hot spots of exceptionally

high near-field enhancement arise at points of high local curvature at nanocrystal surfaces, as well as between closely spaced metal nanostructures with visible or NIR plasmons.^{135–139} The same principles are expected to apply to metal oxide nanocrystals with NIR/MIR plasmon resonance,¹⁴⁰ which makes the synthesis of highly faceted TCO nanocrystals with sharp edges and corners a worthy goal. To achieve this goal, synthetic parameters, especially precursor and surfactant chemistries, must be tuned to modify the kinetics of monomer formation, crystallization, and dopant incorporation, as well as the relative stability of crystalline facets. However, rational development of plasmonic TCO nanocrystals, in particular, requires going beyond nanocrystal shape control to also consider intrinsic materials properties.

Unlike elemental metals, TCOs are not homogeneous materials: they exhibit electronic properties that are strongly influenced by their stoichiometry, defect chemistry, and crystalline anisotropy. Free electrons in TCOs are compensated by ionized impurities (e.g., Sn^{4+} dopants in tin-doped indium oxide or ITO, and Al^{3+} or Ga^{3+} dopants in zinc oxide). These defects scatter free electrons; such ionized impurity scattering is well-studied in TCO thin films, where it negatively impacts electron mobility.^{74;90;91;141} Defect scattering can also be a dominant factor in the non-radiative damping of LSPR excitations. In general, radiative and non-radiative damping processes reduce the magnitude of the local field enhancement and the resonance lifetime.¹⁴² Therefore, defect chemistry strategies to minimize defect-related LSPR damping are needed, and some progress has been made in this area. For example, when dopants are incorporated near the surface of ITO nanocrystals as opposed to in the nanocrystal cores, damping is reduced (see Chapter 6).¹⁴³ Rational chemical methods for deliberately controlling the distribution of dopants in nanocrystals are still needed (Chapter 6), and these strategies must be simultaneously considered with the chemistry used to control shape. Developing new doping chemistries is another promising strategy. For example, it has been shown that only a fraction of dopants give rise to free electrons (i.e., the activation is well below unity).^{51;77;129;143;144} The dopants that are otherwise compensated can still contribute to damping, however, motivating investigation of the defect chemistry underlying activation. Likewise, dopant-host combinations can be selected to minimize structural and electronic perturbation of the host crystal thereby reducing the cross-section for scattering and the associated contribution to damping (Chapter 7).

Ultimately, developing this understanding and control over materials chemistry is necessary to create TCO nanocrystals that can support intense near-field enhancement of NIR and MIR light. This would enable coupling of infrared excitations to other dipolar transitions, such as molecular vibrations, and further set the state for the development of new chemical sensing platforms and the use of IR light to manipulate chemical and catalytic processes. Metal nanoparticles with visible LSPR have already spurred the development of bio-sensors,^{118;145} enhanced spectroscopies (such as Surface Enhanced Raman Spectroscopy, SERS)^{62;139;146;147} and emerging photocatalytic, photothermal, and photovoltaic energy conversion materials.^{122;124;148–153} If realized in TCO nanocrystals, such coupling could enable these devices to operate in the NIR and MIR as well. Furthermore, such devices could be made dynamic and responsive since semiconductor LSPR energies and intensities can be modulated through electrochemical injection and extraction of free electrons.^{14;28;30;39;72}

5.3 Colloidal synthesis of doped metal oxide nanocrystals

Control over plasmonic properties and coupling necessarily begins with chemical and synthetic control over the nanocrystals themselves. This is particularly true for TCO nanocrystals, which require the incorporation of aliovalent dopants to generate free carriers for LSPR. It is crucial to understand how chemical parameters in nanocrystal synthesis translate to ensemble and single nanocrystal plasmonic properties. More specifically, this requires an appreciation for how precursor chemistry, ligand/surfactant chemistry, and reaction kinetics dictate doping, surface chemistry, and nanocrystal shape and size. This kind of mechanistic understanding has been developed for cadmium and lead chalcogenide quantum dot materials.^{5–7;154–157} Nuclear magnetic resonance spectroscopy (NMR) and Fourier transform infrared spectroscopy (FTIR) have uncovered reaction mechanisms, the kinetics of precursor conversion, and the role of chemical impurities in quantum dot synthesis.^{6;7;155;157–164} NMR has also been used to study how ligands bind to nanocrystal surfaces, including surface stoichiometry,^{11;165;166} the strength and nature of ligand-nanocrystal bonds,^{167–169} how to exchange ligands,¹⁷⁰ and how ligands influence nanocrystal shape during synthesis.^{160;171} This knowledge has, in turn, enabled quantitative and precise chemical control over chalcogenide nanocrystals, which allows for the synthesis of quantum dot ensembles with extremely narrow size distributions,^{154;156} well-defined spherical and anisotropic shapes,^{172;173} and deliberate surface chemistries,¹⁷⁰ ultimately resulting in excellent opto-electronic properties (e.g., spectrally narrow and high-efficiency photoluminescence.)^{154;156} This kind of knowledge is starting to develop for metal oxide nanocrystals, where FTIR has been used in several instances to shed light on the reaction mechanisms and kinetics of metal oxide nanocrystal growth reactions.^{174–176} For example, FTIR has been used to show that nucleophilic substitution mechanisms occur when activating agents, such as amines or alcohols, are present in the reaction mixture during synthesis.^{177–181} By using *ex situ* FTIR, researchers have identified amide or ester reaction byproducts and inferred that activating agents act as nucleophiles in aminolysis or esterification reactions that lead to formation of metal oxides.^{77;177–179;182} Conversely, NMR is just beginning to gain popularity as a method to study the surface chemistry of metal oxide nanocrystals.^{8;183} Overall, understanding of reaction mechanisms and synthetic control over metal oxide nanocrystals is still well behind that of chalcogenides, particularly so for doped metal oxides.

5.3.1 Doping

While the field of nanocrystal synthesis has enjoyed decades of success and development, controlled dopant incorporation has historically been much more challenging.^{4;66;84;85;184} Only recently has it become possible to incorporate dopants into metal oxide nanocrystals in a controlled manner. A number of research groups have been steadily building the knowledge of and ability to control colloidal chemical reactions to achieve effective doping in TCO

nanocrystals with diverse compositions. In these syntheses, dopants are incorporated into nanocrystals during crystal growth, which requires that the reaction rates of the precursors for the host crystal and for the dopant be kinetically balanced.^{4,77} Precursors are typically salts of the metals of interest coordinated by anionic ligands such as alkyl carboxylates, halides, or diketonates. The metal-ligand binding strength, and hence the precursor reactivity, depends on the Lewis acidity of the metal cation and the Lewis basicity of the ligand, in accordance with Pearson's hard-soft Lewis acid-base principle (HSAB).¹⁸⁵ Hence, the binding strength can be tuned by changing the ligand's charge delocalization, by introducing additional complexing agents, or by introducing an activating agent that can directly break the metal-ligand bond through nucleophilic attack. While the associated changes in reactivity have generally not previously been quantified, these qualitative considerations have already been enabling in developing colloidal synthesis methods for doped oxide nanocrystals. For example, Buonsanti et al. showed that tuning precursor reactivity was the key to developing the first successful colloidal synthesis of plasmonic Al:ZnO nanocrystals with controlled sizes and dopant concentrations,⁷⁷ and the same strategy was employed to synthesize well-controlled plasmonic Nb:TiO₂ and Cs_xWO₃ nanocrystals.^{88,94} For both Al:ZnO and Nb:TiO₂, FTIR was used to identify that esterification between the metal precursors' ligands and a long chain alcohol was the likely reaction mechanism. Other researchers have also extended this approach to successfully dope zinc oxide with indium, gallium, and aluminum^{174;186–189} and to dope cadmium oxide with indium, tin, and fluorine,^{81;190–192} greatly diversifying the known compositions of plasmonic TCO nanocrystals.

For the most part, doping of TCO nanocrystals has relied on qualitative considerations of HSAB, rather than qualitative studies of precursor decomposition kinetics. In two notable exceptions, FTIR was used to measure the esterification reaction rates between a long chain alcohol and zinc carboxylate salts, which was compared to and matched with the reaction rate of dopant carboxylate salts to produce high quality In:ZnO and Mg:ZnO nanocrystals.^{175;186} In a few other reports FTIR was used to analyze the reaction mechanisms for synthesis of doped metal oxide nanocrystals, including Al:ZnO, Ga:ZnO, and ITO,^{77;174;176;193} but quantitative measurements are largely lacking. Furthermore, while these studies have helped reveal the basic reaction mechanisms underlying the synthesis of doped metal oxide nanocrystals, the mechanisms underlying dopant-induced shape effects or size/shape control by adjusting surfactant mixtures, and the chemical interplay between dopant incorporation and morphology control are still largely unknown. NMR has been key to unraveling mechanistic details of chalcogenide nanocrystal synthesis and it likely can also be effectively leveraged to elucidate these important nuances that strongly impact synthetic outcomes for TCO nanocrystals.

5.3.2 Shape control

Despite the advances made in doping, synthesis of plasmonic oxide nanocrystals with precisely controlled shapes has been largely elusive. Methods are established for synthetically controlling the shape of metal nanoparticles, semiconductor quantum dots, and some transition metal oxide nanocrystals (cf. gold spheres/polyhedra/plates/discs/rods,^{194–198} TiO₂

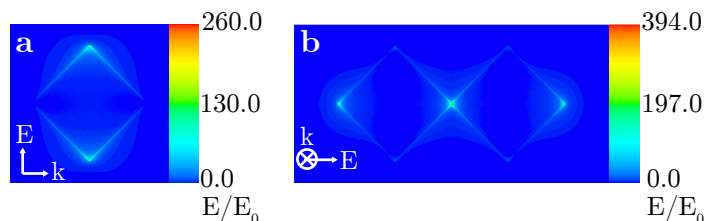


Figure 5.2: Simulated near field enhancement of In:CdO nanocrystals. Near field enhancement/hot spots are observed at: a: The vertices of a single octahedron and b: between vertices of two adjacent octahedra. Figure adapted with permission from Reference¹⁴⁰.

spheres/rhomboids/rods,^{80;177;199–201} and cadmium chalcogenide spheres/rods/tetrapods^{202–204}). Many of the chemical techniques that researchers have relied on to synthesize non-spherical nanocrystals, such as varying temperature, heating rate, or using mixtures of surfactants or other additives for selective growth along given crystallographic directions,^{2;79;160;198;205–212} are either not effective or not sufficiently explored in TCO nanocrystal synthesis; there are no reports, for example, of the colloidal synthesis of ITO nanocrystals (a prototypical TCO nanocrystal material) with well-defined monodisperse shapes other than spheres. And so—despite the promising report of coupling between polymer vibrational transitions and LSPR of nanofabricated ITO rods²¹³—hot spots have not yet been realized around asperities of colloidal ITO nanocrystals. Some progress has been made for TCOs with anisotropic crystal structures: surfactant mixtures were used to synthesize Al:ZnO nanorods with tunable size,¹⁸⁸ but dopant incorporation was minimal and the resulting LSPR was weak. Likewise, the Milliron group has synthesized Cs_xWO_3 nanocrystals of various shapes, such as cubes, spheres, and hexagonal plates,⁹⁴ though more synthetic development is necessary to generate the well-defined and monodisperse shapes necessary for detailed analysis of their LSPR spectra or for coupling studies. One noteworthy accomplishment in this space was made by the Murray group, who synthesized monodisperse In:CdO nanocrystals both as spheres and as octahedra simply by varying the reaction temperature and surfactant concentration.⁸¹ The different shapes gave rise to distinct LSPR spectra and the octahedral nanocrystals, with their more complex shape, displayed multiple peaks in their LSPR spectra, likely arising from different spatial modes. The Milliron group followed up on this report by using extended Drude theory modeling and discrete dipole approximation (DDA) simulations to simulate LSPR in octahedral In:CdO nanocrystals and to predict the achievable electric near field enhancement.¹⁴⁰ In doing so, Agrawal et al. demonstrated that TCO nanocrystals with sharp edges and corners can indeed support strong localization of IR light with near field enhancement factors exceeding 250 (Figure 5.2). Conversely, the near-field enhancement around spherical In:CdO nanocrystals reached only 25, an order of magnitude decrease. These simulations suggest that advancing the synthesis of faceted TCO nanocrystals is a promising strategy for developing nanocrystals capable of strong IR plasmonic coupling.

5.4 Doping mechanisms and defect equilibria in metal oxide nanocrystals

As more and more plasmonic TCO nanocrystals are developed, it is becoming apparent that simply getting dopants into nanocrystals will not be sufficient to generate a mature understanding of LSPR properties, as needed to design materials for efficient near-field coupling. Rather, it is necessary to develop a microscopic understanding of resonating free electrons inside TCO nanocrystals, the mechanisms by which these oscillations are damped, and how to diminish damping by advancing TCO nanocrystal chemistry to tune composition, doping profiles, and nanocrystal morphology.

While doping colloidal semiconductor nanocrystals presents numerous unique synthetic challenges as described above, the defect chemistry of doped metal oxide nanocrystals, at least to a first approximation, mirrors that of the bulk. In metal oxides, the most pertinent defect equilibria are those that change with oxygen activity or partial pressure (pO_2). Most doping and dopant compensation processes rely strongly on pO_2 , and the dominant defect population compensation mechanisms in a doped metal oxide will change with oxygen activity. In metal oxides, free carriers are typically generated by one or more of the following (Figure 5.3):

1. Intrinsic oxygen vacancy doping, which is strongly dependent on pO_2 , particularly at very low oxygen activity.
2. Extrinsic doping by aliovalent dopants, which, in the case of metal oxides, are usually n-type dopants substituted on cation sites. Substitutional doping on oxygen sites is also possible, e.g., in fluorine-doped tin oxide. In principle, p-type acceptor doping on cation sites is possible, though this is rarely achieved in oxides due to the very high effective mass of holes and the tendency for acceptor dopants to be compensated by oxygen vacancies.
3. Extrinsic interstitial doping. This type of doping is possible with crystal structures having large interstitial spaces. The crystal structure of tungsten oxide, for example, contains open tunnels along the c axis surrounded by WO_6 octahedra.^{21;94;214} The channels can accommodate large alkali metal cations to form tungsten bronze with the formula M_xWO_3 , allowing doping up to $x=1$ and strong NIR absorption in both the bulk and nanocrystals.^{94;215}

The ability of these defects to generate free carriers relies on oxygen activity. In the case of n-type doping, aliovalent donor dopants are compensated by free electrons in the conduction band in order to maintain charge neutrality. However, it is also possible for such defects to instead be compensated by oxygen interstitials, and the oxygen activity will dictate the equilibrium between these two compensation mechanisms. In any metal oxide, the population of free electrons, holes, and charged defects will change with pO_2 as the system attempts to reestablish equilibrium and maintain charge neutrality.²¹⁶ These defect equilibria result in a dynamic range of electronic properties of metal oxides, ranging from insulating behavior to

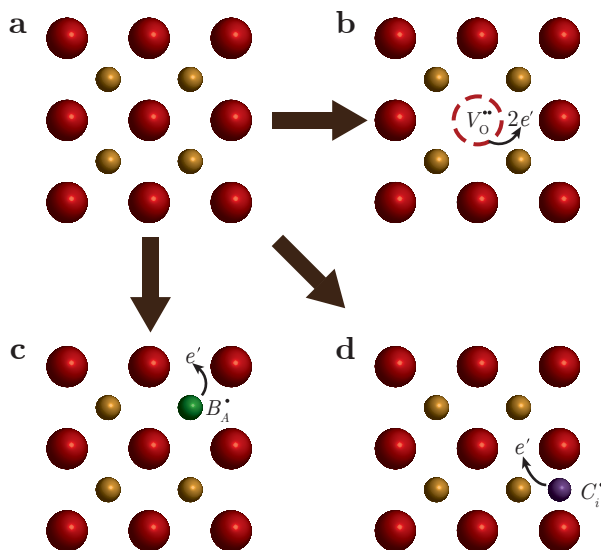


Figure 5.3: The common doping mechanisms in metal oxides illustrated. a: A basic lattice of metal cations (orange spheres) and oxygen anions (red spheres). b: Oxygen vacancies donate two electrons. c: Aliovalent substitutional donor impurities donate one (or more) electron. d: Interstitial impurities may act as donors. For all doping types, electrons can be Coulombically scattered by the charged defects in the lattice. Figure reprinted with permission from Reference⁶⁶, Copyright 2014 American Chemical Society.

metallic conduction for a single material. In addition to changes in free carrier populations, defect populations strongly influence electronic mobility in metal oxides, as defects present distinct scattering cross sections. Thus, defect chemistry in doped metal oxides is a key subject of study when we aim to understand LSPR in doped metal oxide nanocrystals.

Many main group and transition metal oxides support high intrinsic free electron concentrations through significant oxygen vacancy populations. Indium oxide (In_2O_3) and zinc oxide (ZnO) are both capable of oxygen deficiencies of about 1%.^{90;217–219} Likewise, tungsten oxide (WO_3) and molybdenum oxide (MoO_3) can support very high oxygen vacancy populations; nanocrystals of both materials display LSPR in the visible and NIR based solely on this intrinsic doping mechanism.^{83;93;220} In the electronic band structure of a metal oxide, oxygen vacancies generally result in shallow donor levels below the conduction band, which can be thermally ionized to become a charged oxygen vacancy ($V_O^{\bullet\bullet}$), donating two electrons to the conduction band. In the main group oxides, particularly In_2O_3 and ZnO , the ability of oxygen vacancies to bestow n-type conductivity (i.e., the ionization energy) and the exact mechanism by which this occurs, is still under debate.^{219;221}

Aliovalent substitutional doping is the most common and well-understood mechanism for introducing free carriers in semiconductors. In metal oxides, heavy aliovalent doping produces transparent conductors with metallic conductivity, and the most common examples include tin-doped indium oxide (ITO), fluorine-doped tin oxide (FTO), and aluminum-doped

zinc oxide (AZO). In metal oxides, this is done by replacing a host cation with a metal cation of a higher valance. Since the conduction band in metal oxides is largely derived from the valence orbitals of metal cations, substituting a higher oxidation state cation can create a shallow defect level that can be ionized to donate electrons to the conduction band. Electronic compensation of the ionized dopant is not guaranteed, however; aliovalent dopants can instead be compensated by other ionic defects like oxygen interstitials (O''_i), cation vacancies (V_M'), cation interstitials ($M_i^\bullet$), and oxygen vacancies ($V_O^{\bullet\bullet}$). $V_O^{\bullet\bullet}$ is typically the dominant defect in metal oxides for reasonable values of pO_2 , which leads to efficient ionic compensation of acceptor dopants so that p-type conductivity is rarely observed in metal oxides. Interestingly, the bulk equilibrium solubility of substitutional dopants, such as Sn in In_2O_3 , is fairly low (about 6 cation%), though it is higher in thin films,⁹⁰ and remarkably high tin concentrations of 17%-30% have been observed in ITO nanocrystals.^{28;67} In the case of nanocrystals, dopants may be kinetically stabilized, as the nanocrystal is not necessarily in complete thermodynamic equilibrium with its environment.^{84;85} Of course, this also has implications for defect chemistry as applied to nanomaterials.

Of the metal oxides, particularly TCOs, ITO is very well studied in the bulk and presents a model system to study the relationship between electronic properties and defect chemistry. Free electrons are generated by Sn^{4+} substituted on In^{3+} sites ($Sn_{In}^\bullet$), as well as by a small population of oxygen vacancies. Indium oxide crystallizes in the bixbyite structure, which can be thought of as an anion-deficient cubic fluorite structure with 1/4 of the oxygen sites vacant (Figure 5.4). Because of these “structural vacancies”, the bixbyite lattice easily incorporates O''_i , which can ionically compensate $Sn_{In}^\bullet$, and neutral defect clusters of tin and oxygen interstitials significantly impact the electronic behavior and defect chemistry of ITO.^{89;91} The simplest complex, $(2Sn_{In}-O''_i)^\times$, can be reduced at lower oxygen partial pressures to generate free electrons and oxygen gas, but bigger or more complicated defect complexes can be non-reducible, depleting free electrons. The population of these defect complexes depends strongly on pO_2 and dopant concentration, influencing defect equilibria along with the $V_O^{\bullet\bullet}$ population. This ultimately affects the “bottom line” of conductivity in ITO, as changes in defect population will change free carrier concentration as well as the concentration of electronic scattering centers, which impacts mobility. This means that doped metal oxides are generally subject to a tradeoff between free carrier concentration and mobility in order to optimize properties,⁹² and in plasmonic semiconductor nanocrystals, optimal LSPR properties and quality factors are also subject to these concessions, which underlines the importance of understanding bulk metal oxide defect chemistry when studying LSPR fundamentals in metal oxide nanocrystals. Figure 5.5 displays a Brouwer diagram for ITO, illustrating how defect equilibria change with pO_2 and $Sn_{In}^\bullet$ concentration.

Ultimately, bulk defect chemistry likely will not provide a completely adequate description of doped metal oxide nanocrystals. As alluded to above, doped nanocrystals are subject to additional thermodynamic considerations beyond bulk defect chemistry. For example, free carriers in nanocrystals are easily consumed by electrochemical reactions or compensated by local surface charges, and both processes can be particularly easy in small nanocrystals with

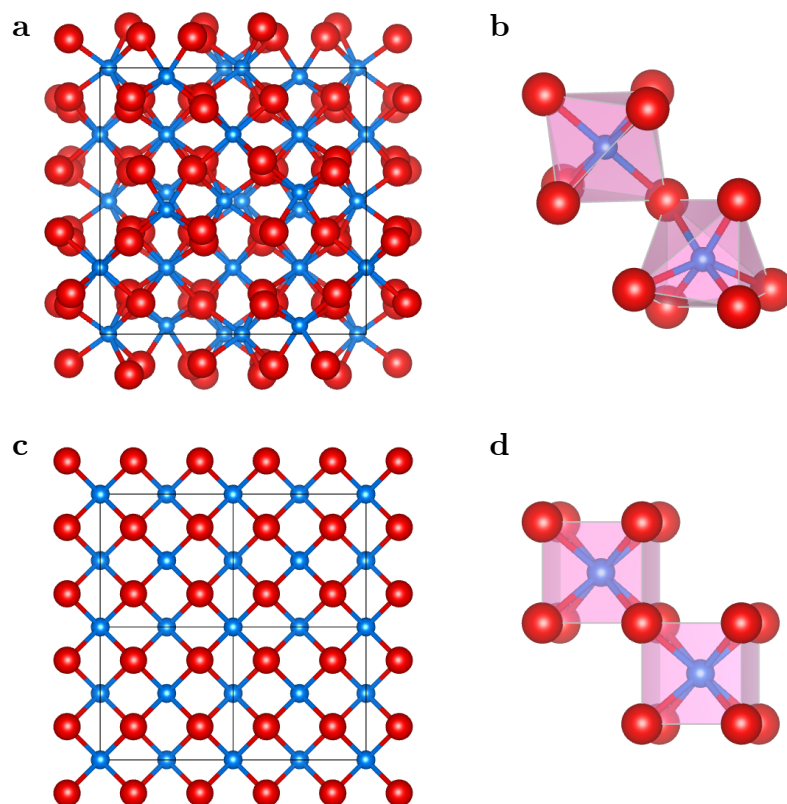


Figure 5.4: a: Crystal structure of bixbyite In_2O_3 . b: Detail of bonding/coordination geometry in bixbyite. c: Fluorite crystal structure (e.g., CaF_2 , CeO_2). d: Detail of bonding/coordination geometry in fluorite.

high specific surface area.^{51;85} Detailed structural studies of dopant incorporation, behavior, and location in colloidal nanocrystals is also lacking, and the formation energy of defects in nanocrystals or at nanocrystal surfaces could be drastically different than in the bulk.^{4;85;222} Defect equilibria may also be fundamentally different in nanomaterials with high surface area to volume ratios; surfaces can generate space charge regions in which the tenets of bulk defect chemistry, such as the electroneutrality condition, break down, and oxygen vacancies have been observed to carry a charge other than $2+$ in nanomaterial systems with significantly altered redox behavior and $p\text{O}_2$ dependence.²²³ Finally, the statistics governing the (stochastic) distribution of dopant density across individual nanocrystals within a nanocrystal ensemble are also highly relevant for study, as they play a role in the inhomogeneous broadening contributions to LSPR line width.^{224;225}

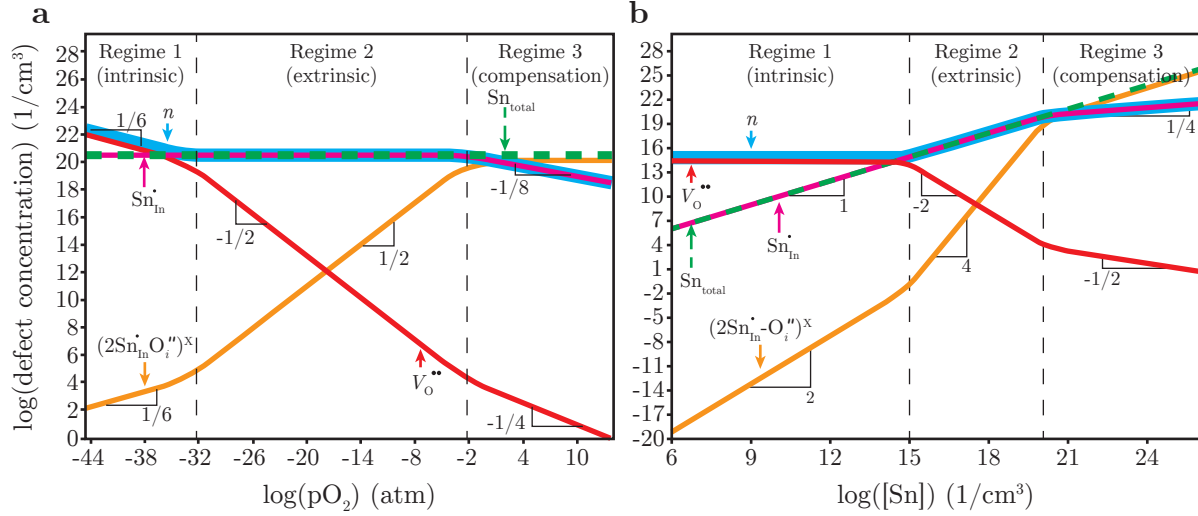


Figure 5.5: Calculated Brouwer diagram for defect equilibria in ITO. a: Defect populations vs. pO_2 at fixed tin concentration [Sn]. b: Defect populations vs. tin doping for fixed pO_2 . Figure reprinted with permission from Reference⁶⁶, Copyright 2014 American Chemical Society.

5.5 LSPR theory and ionized impurity scattering in doped metal oxides

LSPR in nanocrystals with metallic free carrier concentrations is conventionally described by the classical Drude model for a free electron gas. This theory has been effectively applied to understand the plasmonic properties of both metal^{226;227} and semiconductor nanostructures,²²⁸ including metal oxide nanocrystals.^{13;28;120;224;229} The optical properties of a solid are determined by its complex dielectric function, which describes the polarization response of the valence and conduction electrons to an externally applied electromagnetic field. In most cases, LSPR can be adequately described while neglecting polarization from valence electrons and the ion cores. In that case, the frequency-dependent dielectric function, $\varepsilon(\omega)$, reduces to simple Drude-based case:

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \quad (5.2)$$

where the constant ε_{∞} represents the high-frequency background dielectric response of the material (i.e., valence electrons), γ is a damping constant due to electron scattering, with a characteristic scattering time $\tau = 1/\gamma$, and ω_p is the characteristic frequency or plasma frequency of the material, given by:

$$\omega_p^2 = \frac{ne^2}{\varepsilon_0 m^*} \quad (5.3)$$

where n is the free electron concentration, e is the elementary electronic charge, ϵ_0 is the permittivity of free space, and m^* is the effective mass of the electron. The above equation describes a harmonic oscillator (a dynamic negative free electron plasma oscillating with respect to stationary positive ion cores) with a resonant frequency of ω_p and a constant damping frequency given by γ . These equations lead to an LSPR frequency for sufficiently small nanocrystals (surrounded by a medium with dielectric constant ϵ_m) given by:

$$\omega_{LSPR} = \sqrt{\frac{\omega_p^2}{\epsilon_\infty + 2\epsilon_m} - \gamma^2} \quad (5.4)$$

Equation 5.2 dictates the frequency-dependent optical properties of a free electron gas, which depend strongly on electron concentration and the magnitude of damping. From the equations above it is clear that the optical properties of the free electron gas will depend strongly on both the free carrier concentration and the damping of electron motion in this model. This simple model has been used to great effect to describe LSPR in metal nanocrystals, which are generally easy to treat. Metals have a well-defined free electron concentration that is difficult to modify, due to near-perfect screening of external electric fields and the fact that adding or removing free carriers against a high background concentration has little effect on the plasma frequency. Additionally, the main electronic scattering mechanisms in metal nanoparticles are electron-phonon scattering, electron-electron scattering, radiative energy loss, and surface and interface scattering, all of which are frequency-independent. The damping parameter γ , which is directly related to the peak width and shape of LSPR, is thus frequency-independent in metals and can be treated as a constant.

Metal oxides, however, are fundamentally different from metals with regards to electron concentration and damping. In metal oxides, free electron concentration is broadly tunable both by doping and external electric fields, allowing easy tuning of the plasma frequency and LSPR properties. Furthermore, metal oxides are subject to ionized impurity scattering arising from charged defects like dopants and vacancies. This necessitates a modification to the Drude-based dielectric function (Equation 5.2) to include a frequency-dependent damping function $\Gamma(\omega)$ in place of γ :

$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma(\omega)}$$

The electric field emanating from charged defect is itself screened by the free electrons in the material. This necessarily means that ionized impurity scattering processes are frequency-dependent because of the frequency-dependent polarization behavior of the free electrons. Below the plasma frequency, free electrons easily respond to changing/oscillating electric fields. Above the plasma frequency, the electric field oscillates too quickly for free electrons to respond and screen the defect, which in turn scatters electrons much differently. Thus, metal oxides are subject to ionized impurity scattering in addition to the frequency-independent scattering mechanisms listed above, and each of these scattering mechanisms should be considered when studying LSPR in semiconductors.

Ionized impurity scattering is easily understood by considering that metallic conductors can exhibit frequency-dependent, complex dynamical resistivity, with a scattering rate characterized by $\Gamma(\omega)$. The different scattering mechanisms that contribute to this resistivity can be treated additively, thanks to Mathieson's rule:

$$\Gamma(\omega) = \frac{1}{\tau(\omega)} = \frac{1}{\tau_{\text{IIS}}} + \frac{1}{\tau_{\text{e-e}}} + \frac{1}{\tau_{\text{e-phonon}}} + \frac{1}{\tau_{\text{interface}}} \quad (5.5)$$

This relationship between the damping function and scattering time or mobility allows the frequency-dependence of the dynamical resistivity or conductivity to be expressed as:

$$\frac{1}{\rho(\omega)} = \sigma(\omega) = en\mu = \frac{ne^2}{m^*\Gamma(\omega)} \quad (5.6)$$

Ionized impurity scattering thus sets an upper limit on the mobility that is achievable in a semiconductor with a homogenous distribution of charged defects, which is given by:

$$\mu_{\text{IIS}} = \frac{3(\epsilon_r \epsilon_0)^2 h^3 n}{Z^2 m^{*2} e^3 N_i F_{\text{IIS}}^{np}[\xi_d]} \quad (5.7)$$

where ϵ_r is the dielectric constant of the material, n is the electron concentration, Z is the charge of the impurity, N_i is the concentration of impurities, and $F_{\text{IIS}}^{np}[\xi_d]$ is a screening function that depends on the screening parameter $\xi_d \propto \epsilon_r n^{1/3}$.⁷⁴ The mobility of a metal oxide therefore is inversely proportional to the concentration of charged defects, and doubly charged defects, such as oxygen vacancies, scatter four times as strongly as singly ionized impurities.

Hamberg and Granqvist applied the dynamical resistivity framework to ITO, comparing theoretical calculations with experimental measurement of the real and imaginary parts of $\rho(\omega)$ to understand the frequency dependence of ionized impurity scattering in doped metal oxides.^{230;231} (The real part of $\rho(\omega)$ corresponds to free electron scattering.) For frequencies below the plasma frequency, the real part of $\rho(\omega)$ is constant as a result of efficient screening of charged defects by free electrons. Oscillating electrons at these frequencies are thus effectively scattered as if they were drifting under the influence of a DC electric field, which makes the low frequency dynamical resistivity under optical excitation an approximation of the DC electronic resistivity of the material. Conversely, at frequencies above the plasma frequency, free electrons do not respond efficiently to oscillating electric fields, leading to strongly reduced screening of charged defects. Rather, ionized impurities at these frequencies behave more like simple, unscreened Coulombic scattering centers, and the resistivity drops as $\omega^{-3/2}$ (Figure 5.6).²³² Put more simply, as frequency of the oscillating field increases further past ω_p , the scattering cross section of charged impurities decreases, and the interaction probability of defects and electrons decreases as the electrons are displaced over smaller and smaller distances. At frequencies far above the plasma frequency, experiment and theory diverge, as the experimentally measured real part of the dynamical resistivity becomes constant due to residual scattering mechanisms other than ionized impurity scattering.

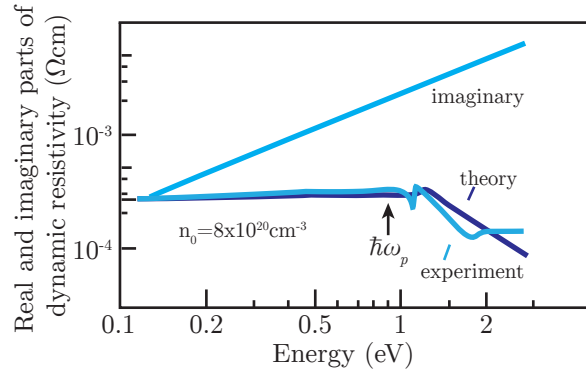


Figure 5.6: Experimentally-measured real and imaginary dynamic resistivity compared to theoretical models. Reprinted with permission from Reference⁶⁶, Copyright 2014 American Chemical Society. Figure originally reprinted from Reference²³¹, Copyright 1986 American Institute of Physics.

Both semi-empirical and empirical theories have been used to generate functional forms for $\Gamma(\omega)$ so that it can be used in a closed form expression of the Drude model.^{231–235} The form of $\Gamma(\omega)$ generally assumes limits of low-frequency and high-frequency damping constants, with a cross-over region joining the high- and low-frequency regimes. The cross-over region follows the $\omega^{-3/2}$ power law dependence described above. Examples of the semi-empirical and empirical models for $\Gamma(\omega)$ are:

$$\Gamma(\omega) = f(\omega)\Gamma_L + (1 - f(\omega))\Gamma_H \left(\frac{\omega}{\Gamma_X} \right)^{-3/2} \quad (\text{semi-empirical}) \quad (5.8)$$

$$f(\omega) = \frac{1}{1 + \exp\left(\frac{\omega - \Gamma_X}{\Gamma_W}\right)} \quad (5.9)$$

$$\Gamma(\omega) = \Gamma_L - \frac{\Gamma_L - \Gamma_H}{\pi} \left[\arctan\left(\frac{\omega - \Gamma_X}{\Gamma_W}\right) + \frac{\pi}{2} \right] \quad (\text{empirical}) \quad (5.10)$$

where Γ_L is the low-frequency damping constant, Γ_H is the high-frequency damping constant, Γ_X is the cross-over frequency, and Γ_W is the width of the cross-over region. The frequency-dependent damping behavior of both of these models is illustrated in Figure 5.7a, showing the clear and smooth transition from the low-frequency damping regime to the high-frequency damping regime, about the cross-over frequency. In general, the greater the difference between Γ_L and Γ_H , the more dominant ionized impurity scattering is. As this difference grows, there is a clear change in LSPR behavior: the peak becomes broader in general with higher scattering, but when ionized impurity scattering grows, the LSPR peak broadens more strongly at lower frequencies, leading to a pronounced anisotropy in line shape (Figure 5.7b).

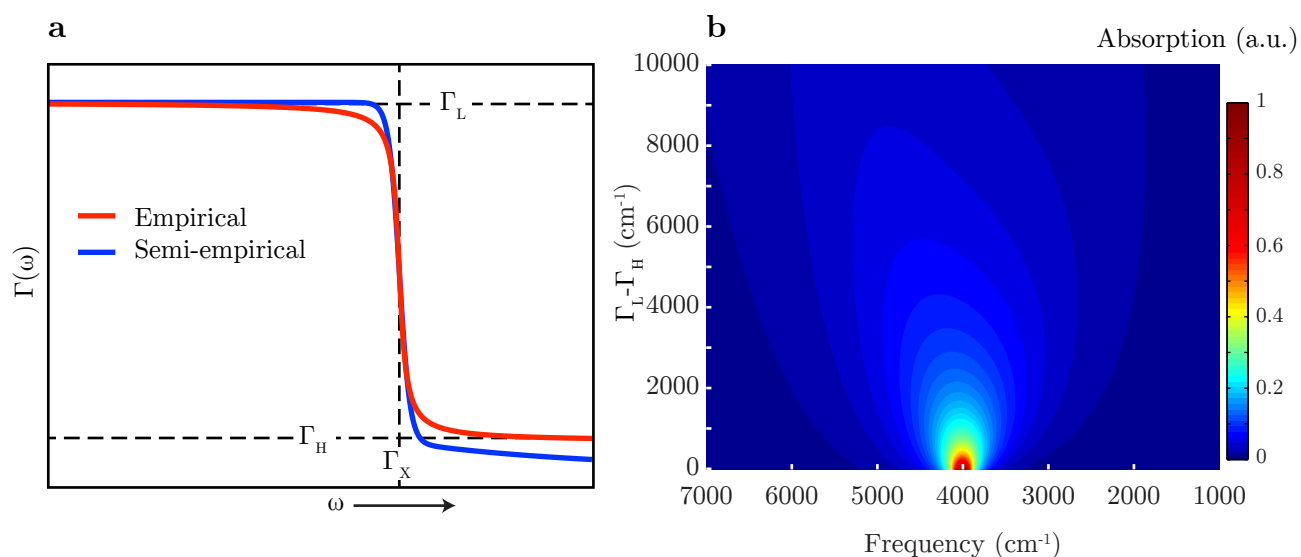


Figure 5.7: frequency-dependent damping effects on LSPR. a: Semi-empirical and empirical forms of the frequency-dependent damping function $\Gamma(\omega)$, showing the high-frequency and low-frequency damping regimes, and the cross-over between the two. b: Simulated effect of increasing Γ_L (i.e., increasing ionized impurity scattering) on LSPR peak shape. Note that the peak blue shifts, weakens in intensity, and significantly broadens asymmetrically towards lower frequencies.

Chapter 6

Synthesis and plasmonic properties of tin-doped indium oxide nanocrystals

6.1 Introduction

As outlined in the previous Chapter, doped metal oxide nanocrystals have featured prominently as materials for highly tunable localized surface plasmon resonance (LSPR) over a wide spectral range spanning the visible/near-infrared (NIR) edge to the mid-infrared (MIR).^{4;28;29;66;77;81;83;88;121;236} This tunability and spectral range makes nanocrystals based on transparent conducting oxide (TCO) materials exciting and highly relevant for a number of applications ranging from smart windows to bio-sensing.^{28;120} However, unlike the properties of plasmonic metal nanoparticles and nanostructures, the relationship between the fundamental materials science that governs TCO behavior and LSPR properties in TCO nanocrystals is not yet fully developed. For example, the chemistry of doping, the behavior and activation of dopants, and the impact of defect chemistry on doped metal oxide nanocrystals are all still emerging areas of study, and the full connection between these topics and LSPR properties is only beginning to be made.^{4;66;84;85;143;144;224;229;237} Case in point: consider the two extinction spectra shown in Figure 6.1. Both of these LSPR peaks come from tin-doped indium oxide (ITO) nanocrystals with very similar size, shape, and doping concentration, synthesized by similar (but not identical) methods. Yet, their spectral signatures are completely different. The simple models for LSPR (Equations 5.2 and 5.4), which have been exceptionally useful for describing plasmonics based on silver nanoparticles and other metal nanostructures, fall short of offering an explanation for the difference in this case. As we will see throughout the rest of this Chapter and the next, however, fundamental materials science concepts, like defect equilibria in metal oxides, can provide the framework needed to fully understand LSPR behavior in TCO nanocrystals.

In addition to developing our fundamental understanding, being able to manipulate or control the peak shape or width of LSPR in TCO nanocrystals is important from an applications perspective. Certain applications may benefit from a more broadband LSPR feature

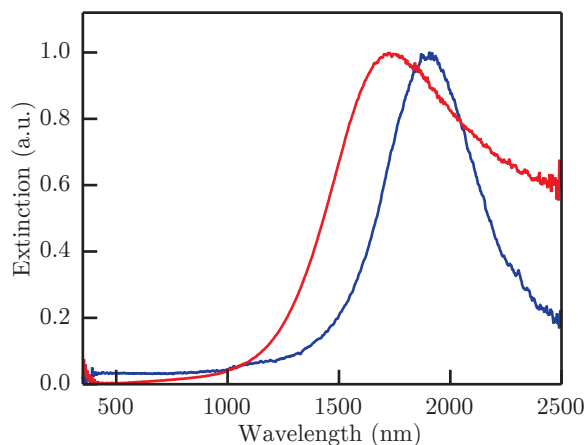


Figure 6.1: Comparison of the LSPR properties of two seemingly similar ITO nanocrystal samples. Note the distinct difference in LSPR peak shape.

in order to absorb or reflect a wider range of IR light; smart windows and radiation shielding come to mind. Conversely, applications like optical notch filters, or those that rely on near field enhancement or subtle shifts in LSPR frequency, like sensing or photothermal therapy, are much better served by LSPR with as narrow a peak and as high a quality factor as possible. Developing the understanding needed to manipulate plasmonic metal oxides in this way will allow TCO nanocrystal materials to achieve maximum effectiveness in multiple applications as seemingly disparate as these.

To successfully manipulate LSPR in TCO nanocrystals, it is necessary to advance the chemical synthesis of these materials so that their properties can be appropriately fine-tuned to support near-field coupling or broadband absorption. For near-field applications, the coupling efficiency between a plasmon in a nanocrystal and another dipolar transition in a nearby molecule or nanocrystal will depend on the size and magnitude of the local near field enhancement. In turn, near field enhancement is proportional to the LSPR quality factor, which further depends on both the electron damping or scattering processes and nanocrystal morphology: minimizing damping will increase the efficiency of hot spot generation by LSPR, and nanocrystals with sharp edges and corners facilitate local electric field concentration. The goals of this Chapter and the next are four-fold: 1) To use colloidal chemistry to manipulate and minimize electronic damping in plasmonic TCO nanocrystals through control over dopant incorporation and distribution, 2) To use colloidal chemistry to tune shape to synthesize TCO nanocrystals with well-defined faceting and asperities, 3) To study new or underused dopants in TCO nanocrystals with an eye towards rational dopant selection to control defect chemistry, minimizing ionized impurity scattering and maximizing activation, and 4) To use optical characterization, modeling, and simulation to understand how synthetic nanocrystal chemistry correlates with LSPR properties and field enhancement, and to guide further synthetic development.

ITO is the most studied TCO material both in thin films and in colloidal nanocrystal

form, where it has demonstrated utility in electrochromic devices, biological redox sensors, and solution processed transparent conductors. Myriad synthetic techniques have been developed for spherical In_2O_3 and ITO nanocrystals with diameters ranging from 3-4 nm to 20 nm or greater,^{28;67;75;76;129;178;190;238–246} with LSPR in the NIR that is tunable with doping,⁶⁷ electrochemistry,²⁸ photochemistry,^{144;184} biochemistry,¹²⁰ and more. ITO is also exceptionally relevant as a commercial material, finding use as a transparent conductor in displays, solar cells, and other devices. This chapter adopts ITO as a TCO nanocrystal material of choice in order to study electron motion within doped metal oxide nanocrystals, and how this charge transport influences LSPR. The fact that the defect equilibria, doping mechanisms, electronic properties, crystal structure, and thermodynamics of ITO are so well understood from both experimental^{89–92;217;247–249} and theoretical^{219;250–254} perspectives makes ITO the ideal model material for such a study. Not only does this provide an opportunity to discover whether the fundamental mechanisms dictating doping, electronic behavior, and defect chemistry of TCO nanocrystals are the same as in the bulk, but it also provides an excellent prototype material with well-known properties that can be leveraged to synthesize plasmonic nanocrystals that are optimized for near-field enhancement applications.

6.2 Colloidal synthesis of ITO nanocrystals

This subject is introduced in Section 3.2.1. To reiterate here, one of the primary methods for synthesizing ITO nanocrystals is based on a literature procedure adapted from Reference⁷⁵. The metal precursors used are indium (III) acetylacetonate ($\text{In}(\text{acac})_3$, 99.99%) and tin (IV) acetylacetonate dichloride ($\text{Sn}(\text{acac})_2\text{Cl}_2$, 98%), both of which were obtained from Sigma Aldrich. Oleylamine (OLAM, 90%, Acros organics) is the third and final constituent of this reaction, and serves as a solvent, surfactant, and nucleophile. To synthesize ITO nanocrystals, the three starting materials are combined in a flask under inert atmosphere and stirred, heated 110°C for 10 minutes, then heated to 250°C for two hours to create the nanocrystals. Tin doping percentage can be controlled by varying the $\text{In}(\text{acac})_3:\text{Sn}(\text{acac})_2\text{Cl}_2$ ratio, and the total metal:OLAM ratio can be decreased to yield smaller nanocrystals (e.g., 1:48 metal:OLAM gives nanocrystals about 7 nm in diameter), or increased to yield larger nanocrystals (e.g., 1:12 metal:OLAM yields nanocrystals about 10 nm in diameter). Throughout the rest of this Chapter, this synthetic method will be sometimes be referred to as the “activation synthesis”.

The Cl^- ligands on the tin precursor present a unique challenge when attempting to synthesize nanocrystals with high tin content. As the tin precursor decomposes, Cl^- is released and is free to become HCl , since water is very likely produced as a side product of the synthesis (see below). The presence of high amounts of HCl in the reaction mixture is expected to dramatically interfere with nanocrystal synthesis, as it could etch the nanocrystals and/or protonate the oleylamine surfactants, since primary amines are fairly strong bases. This would cause the surfactants to leave the surface of the nanocrystals, allowing them to aggregate. Alternatively, free Cl^- ions in the solution can also interact strongly with the

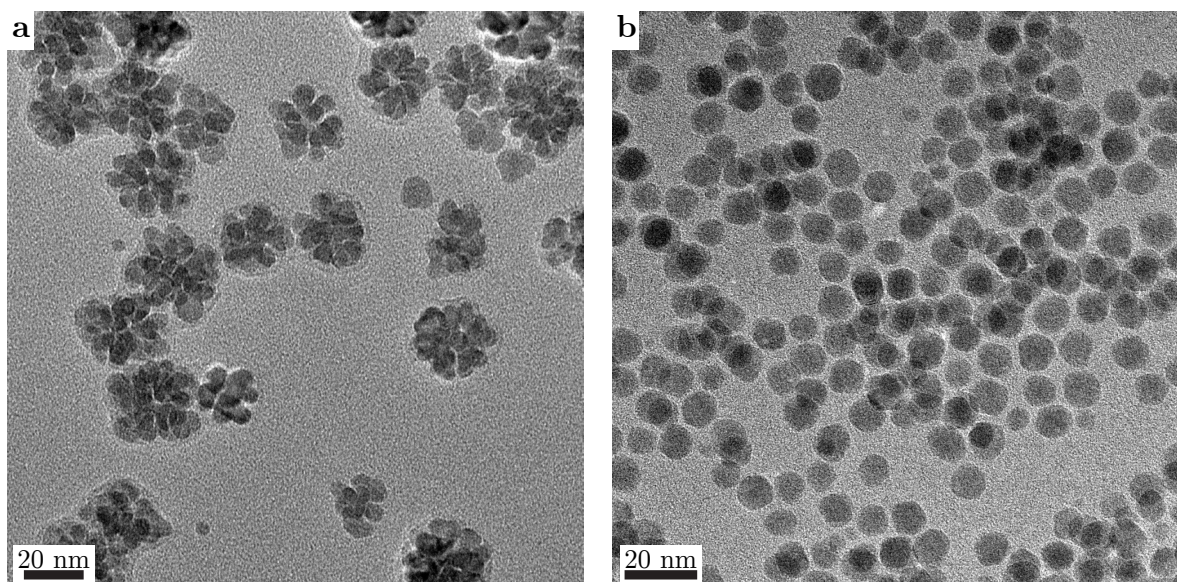


Figure 6.2: Transmission electron microscopy (TEM) micrographs showing the influence of HCl or Cl^- content on ITO nanocrystal synthesis. a: When too much $\text{Sn}(\text{acac})_2\text{Cl}_2$ precursor is present, nanocrystals aggregate *via* oriented attachment to form flower-like supercrystals. b: Flower formation can be alleviated by active venting of the reaction flask, driving HCl out of the system.

nanocrystal surface, displacing oleylamine ligands and/or forming dipole moments that can lead to nanocrystal aggregation by oriented attachment.¹²⁹ When attempting to synthesize nanocrystals with high doping percentages of 8% to 10% tin using this method, ITO “flowers” were obtained instead (Figure 6.2a), with each petal of the flower appearing to be a nanocrystallite attached epitaxially to the other nanocrystals in the flower. The tendency for nanocrystals to aggregate increased with tin content and decreased when the oleylamine content was increased, suggesting that the concentration of HCl or Cl^- is to blame for the aggregation or oriented attachment. Notably, using a larger flask, which provides more head space above the reaction solution, also mitigated phase separation, implicating HCl because of its high volatility. To test this assumption, ITO nanocrystals were again synthesized with 10% Sn content, but with active venting of the flask. This was done by flowing fresh nitrogen in through one of the flask necks using a glass adapter, over the surface of the reaction solution, and out of another neck of the flask. This serves to decrease the activity of gaseous HCl and encourage evaporation from the solution. Indeed, nanocrystals synthesized with this method are very uniform and exhibit no signs of aggregation (Figure 6.2b), suggesting that active removal of HCl from the reaction mixture is necessary to achieve high doping content with good nanocrystal morphology.

The other synthesis used extensively in this chapter, referred to as the “doping synthesis”, is performed using slightly different methods, again based on the literature.⁶⁷ This

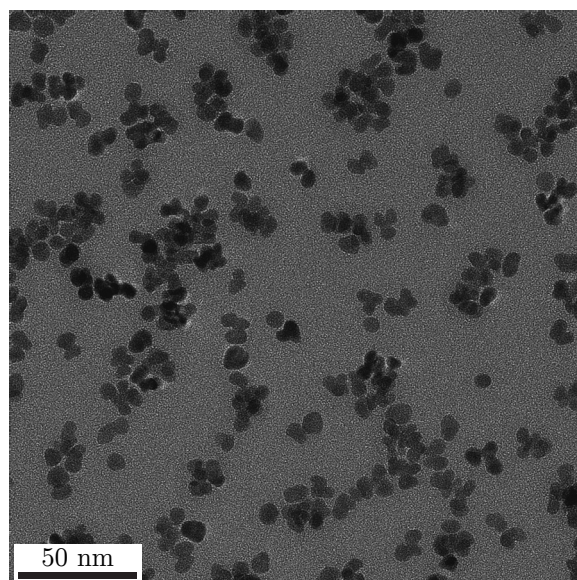


Figure 6.3: TEM micrograph of nanocrystals synthesized by the second synthetic method.

synthesis uses indium (III) acetate ($\text{In}(\text{OAc})_3$, 99.99%, Sigma Aldrich), tin (II) 2-ethyl hexanoate ($\text{Sn}(\text{oct})_2$, 92.5-100%, Sigma Aldrich) as the indium and tin precursors, respectively. Additionally, oleylamine serves as a nucleophile, octanoic acid is a ligand and surfactant, and dioctyl ether is the solvent. In brief, all of the reaction components are mixed together in a flask, degassed under vacuum at 80°C for two hours, heated to 150°C for one hour under nitrogen to allow exchange between acetate ligands and octanoic acid, and then heated to 280°C for 2 hours to nucleate and grow ITO nanocrystals. Thanks to the fact that no halides are present in this reaction, the nanocrystals resist aggregation and remain relatively uniform even at very high tin doping concentrations approaching 15-20%. Some drawbacks to this synthetic method include a general lack of size tunability, as it was not possible to change nanocrystal size by more than about 0.5 nm despite broad changes in growth temperature, metal:octanoic acid ratio, metal:OLAM ratio, and overall concentration. Furthermore, the nanocrystals were generally less uniform in size and shape and less well-dispersed (Figure 6.3) when compared to the other synthetic method. These drawbacks could be related to the octanoic acid surfactant, which has a relatively short alkyl chain and can be a fairly strong acid, both of which could interfere with surface passivation.

As described more fully in Section 3.2.1, a third method to synthesize ITO nanocrystals uses a simple mixture of $\text{In}(\text{OAc})_3$, tin (II) acetate ($\text{Sn}(\text{OAc})_2$, 99.99%, Sigma Aldrich), and OLAM. Again, the absence of halide ligands in this reaction allows for high doping levels and good colloidal stability. Furthermore, as previously described, this reaction can easily be scaled up to produce large amounts of ITO nanocrystals.

The likely reaction pathway for all of these synthetic methods is nucleophilic attack by oleylamine at the carbonyl carbon atom on the indium and tin precursor ligand (Figure 6.4).

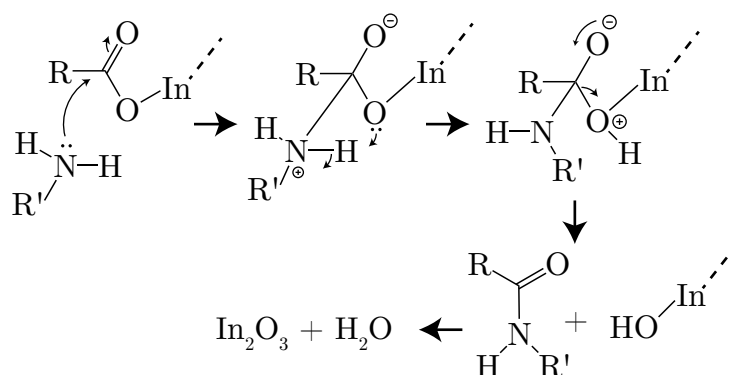


Figure 6.4: Expected reaction mechanism for the formation of ITO nanocrystals by aminolysis. Oleylamine initiates the reaction through nucleophilic attack on the carbonyl center of the ligand, producing reactive hydroxide intermediates that condense into metal oxide nanocrystals.

This aminolysis pathway eventually leads to the formation of indium and tin hydroxides with an amide byproduct. The hydroxides then condense into the ITO nanocrystal with elimination of water as another side product. This and similar reaction pathways has been observed for a number of metal oxide nanocrystal syntheses, including those for indium oxide, zinc oxide, titanium oxide, and vanadium oxide.^{177–179;182;242}

6.3 The impact of radial distribution and activation of tin dopants on the LSPR properties of ITO

Adapted from Reference¹⁴³:

Lounis, S. D.; Runnerstrom, E. L.; Bergerud, A.; Nordlund, D.; Milliron, D. J. Influence of Dopant Distribution on the Plasmonic Properties of Indium Tin Oxide Nanocrystals. *J. Am. Chem. Soc.* **2014**, *136*, 7110–7116.

Herein, we investigate the relationship between the radial distribution of dopants and nanocrystal optoelectronic properties, including plasmon damping and dopant activation, for the two synthetic methods outlined above. Using x-ray photoelectron spectroscopy (XPS) combined with careful characterization of the composition and optical properties of ITO nanocrystals, we demonstrate that nanocrystals with tin-rich surfaces exhibit reduced dopant activation. We suggest that this trend is due to the formation of electronic trap states, including those due to diffusion of compensating oxygen interstitial atoms, which can more readily form neutral complexes with tin that is situated near the nanocrystal surface. Based on fitting of the LSPR using the Drude model we also demonstrate that dopant distribution has an

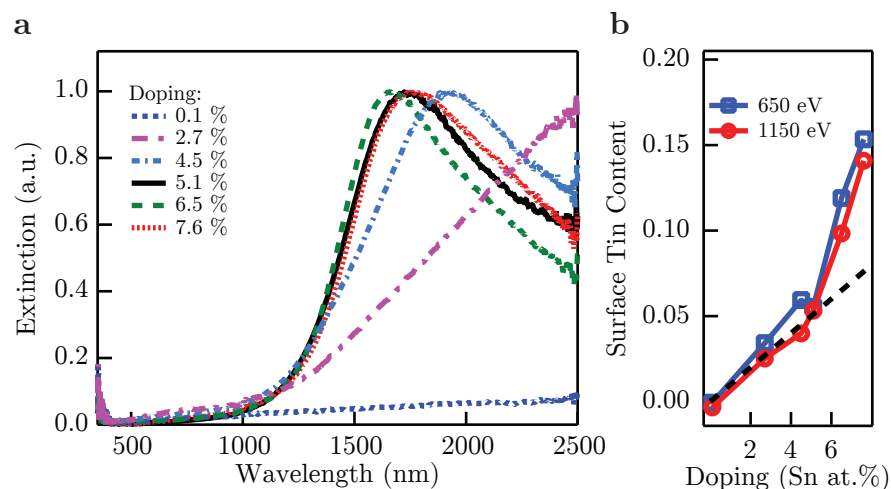


Figure 6.5: a: Optical extinction and b: XPS depth profiling versus doping for the doping series. The dotted black line in panel b shows the expected $\text{Sn}/(\text{In} + \text{Sn})$ ratio for a uniform doping profile. Figure reprinted with permission from Reference¹⁴³, Copyright 2014 American Chemical Society.

important effect on plasmon damping in this system, leading to symmetric, narrowed LSPR line shapes in the case of surface-segregated tin.

Due to the dependence of electron escape depth on the incident photon energy, energy-dependent XPS is an effective tool for probing the depth-dependence of elemental composition near surfaces.²⁵⁵ The spatial distribution of tin was investigated by comparing the integrated area under the background subtracted In and Sn 3d 5/2 XPS peaks at photon energies ranging from 650 to 1150 eV for a number of samples prepared by both the activation and doping syntheses, and compared to the average tin content in the nanocrystals as found by inductively-coupled plasma atomic emission spectroscopy (ICP-AES). Since the 3d 5/2 peaks for both elements are close in binding energy, the error introduced by differences in the escape depth of photo-emitted electrons is negligible.

The electron concentrations and surface composition of the doping series are consistent with the reported doping behavior of thin-film ITO. As doping is increased, a strong extinction feature due to the LSPR grows in intensity, first blue shifting into the NIR and then red shifting above ~ 7 cat. % Sn (Figure 6.5a). The extracted electron concentration for nanocrystals with LSPRs peaking in the range of the spectrometer shows a trend consistent with that observed for bulk and thin-film ITO, with maximum concentration in the range of 5 – 7 cat. % Sn. This trend can be explained by the increasing formation of irreducible Sn complexes with oxygen interstitial atoms at higher Sn concentration.⁸⁹

The doping series shows uniform dopant distribution for low doping levels and surface segregation of tin at higher doping levels (Figure 6.5b). Between 0.1 and 5.1 cat. % Sn there is a linear relationship of doping with the near-surface tin content measured by XPS, with

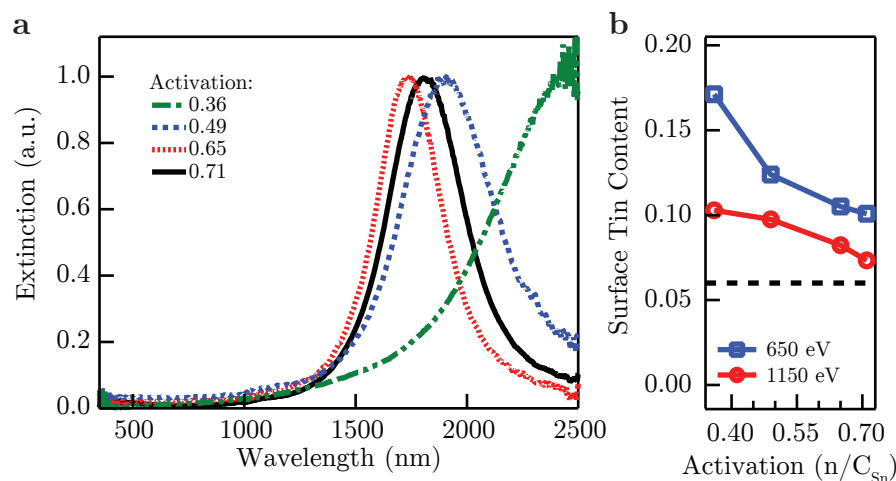


Figure 6.6: a: Optical extinction and b: XPS depth profiling versus doping for the activation series. The dashed black line in panel b corresponds to the average doping level for nanocrystals in this series. Figure reprinted with permission from Reference¹⁴³, Copyright 2014 American Chemical Society.

both photon energies giving approximately the same value. This indicates a uniform dopant profile, with Sn distributed evenly throughout the nanocrystal. By contrast, at 6.5 and 7.6 cat. % Sn, there is a marked increase in surface tin content, with values nearly twice the values measured by ICP-AES. At these doping levels, the measured tin content is also higher for 650 eV photons than for 1150 eV photons. These results indicate surface segregation of tin at higher doping levels, consistent with the formation of Sn-rich surfaces that has been widely documented in bulk and thin-film ITO;^{256–258} similarly, aluminum-rich surfaces have been found in thin films²⁵⁹ and colloiddally prepared nanocrystals of aluminum-doped zinc oxide.⁷⁷

In the activation series, similar doping levels were observed to result in a wide range of free electron concentrations, indicating sample-to-sample differences in dopant activation. This is immediately made apparent by the large spread (more than 700 nm in wavelength) in the LSPR frequencies observed for the activation series (Figure 6.6a), despite approximately equal doping levels of 6.09 ± 0.64 cat. % Sn. Moreover, the observed shifts in the LSPR do not follow the small sample-to-sample variation in doping levels, suggesting the differences in electron concentration arise instead from a compensation mechanism at work in these nanocrystals.

We suspect a combination of defects to determine the dopant activation in these samples. The tendency for ITO to form $(2\text{Sn}_{\text{In}} - \text{O}''_i)^\times$ defect clusters at high oxygen or tin activity makes it likely that tin dopants can be compensated by oxygen interstitials to reduce activation, especially when tin concentration is enhanced at the nanocrystal surface. Drude modeling of optical data on thin nanocrystal films also suggests a large potential barrier to inter-particle electronic conduction,²²⁹ consistent with the existence of an insulating de-

pletion region at the nanocrystal surface due to the formation of surface trap states that consume free electrons. Subsequent studies on ZnO nanocrystal films have shown that these trap states arise from hybridization between the atomic orbitals in the nanocrystal and surface-bound hydroxyl groups, which regenerate free electrons upon removal.²⁶⁰ This action of hydroxyl groups is consistent with the general variability in electron concentration for the activation series, as no special care is taken to remove adventitious water from the reaction mixture during the synthesis. Rather, the reaction mixture is always heated to 110°C for 10 minutes before the nanocrystals are grown, which could lead to random variations in water content during nanocrystal growth. Such water could participate in the reaction *via* hydrolysis mechanisms and could also hydroxylate the nanocrystal surface to form surface traps.

In addition to influencing their electronic properties, the dopant profile in both types of ITO nanocrystal samples also has a strong effect on the optical line shape of the LSPR, which is determined by damping of the plasmon oscillation. The nanocrystals with uniform dopant distribution exhibit an obvious asymmetry around the LSPR peak, broadening more strongly at low frequencies (Figure 6.5a). On the other hand, the nanocrystals with surface-segregated tin have nearly symmetric line shapes (Figure 6.6a).

Asymmetry in the plasmon line shape can therefore be attributed to frequency-dependent damping of the plasmon and can be confirmed by the damping parameters extracted by fitting our experimental spectra with the modified Drude model (see Section 5.5, namely Equations 5.5 and 5.10), shown in Figure 6.7a. The samples with uniform dopant distribution have a crossover frequency near or just to the red of the LSPR and a significantly larger Γ_L than Γ_H , consistent with the expectation for frequency dependent damping by ionized impurities. By contrast, the symmetry of LSPRs of the nanocrystals with surface-segregated tin suggests ionized impurity scattering is suppressed (Figure 6.7b). The fits to these spectra result in crossover frequencies far to the blue of their LSPR peaks and a lower Γ_L than found for the uniformly doped nanocrystals, indicating that the resonance is effectively damped by a frequency-independent constant. To confirm this assertion, the same data can also be effectively fit with a simple Drude model with a constant damping parameter (Equation 5.2), reproducing the line shapes for the surface-segregated samples.

A simple physical model can be used to interpret the differences in line shape observed in the optical spectra based on tin dopant distribution. Nanocrystals with uniformly distributed ionized dopant impurities will experience frequency-dependent damping of the electron cloud similar to what is observed in thin film and bulk samples (See Figure 6.8a). The transition from a low-frequency regime with strong ionized impurity scattering to a high-frequency regime with much weaker damping is expected to occur at energies just below the plasma frequency.²³¹ This transition between two regimes leads to asymmetry about the LSPR peak as observed. For nanocrystals with tin dopants disproportionately concentrated at or near the surface, on the other hand, most of the electron cloud will not interact with ionized impurities as it oscillates at all frequencies (see Figure 6.8b), suppressing ionized impurity scattering and leading to a near-symmetric line shape from frequency-independent damping processes. To validate this interpretation, LSPR spectra for nanocrystals with different doping distribution

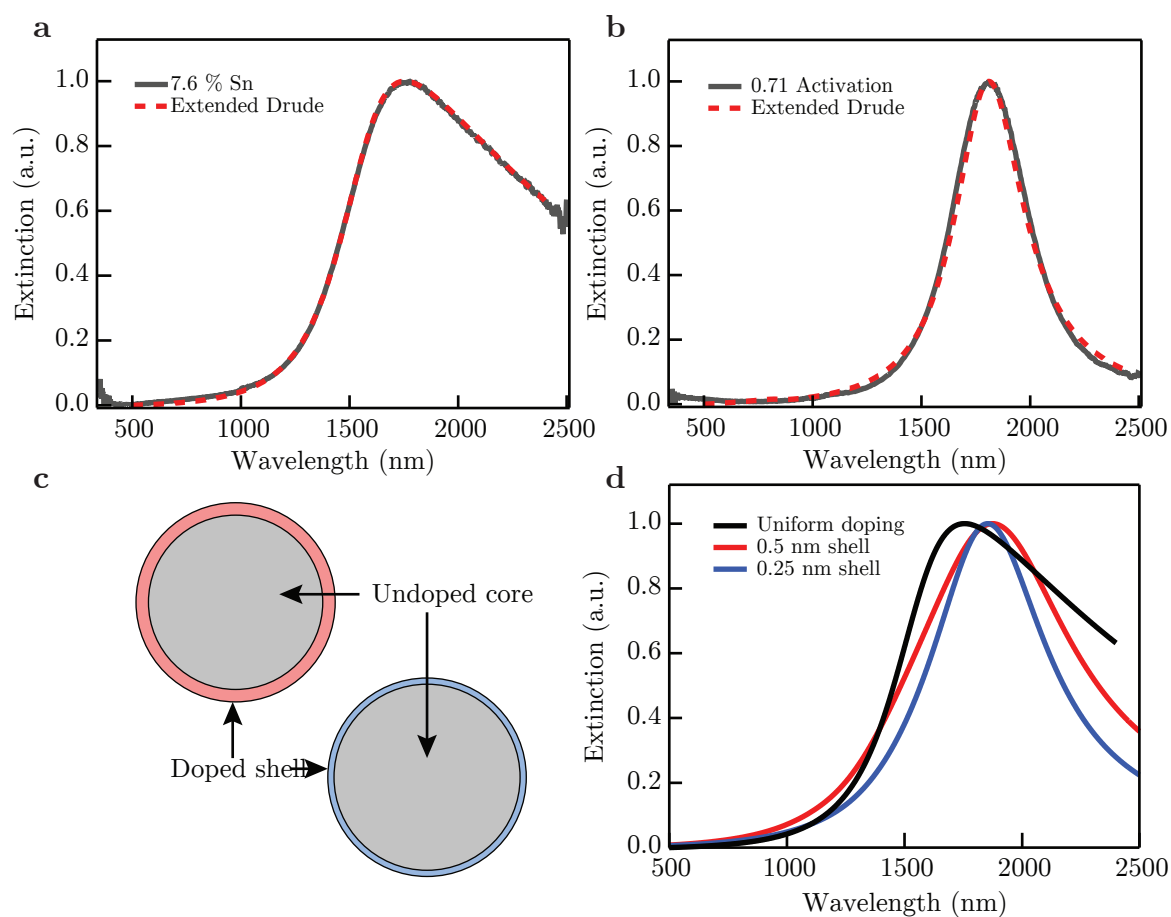


Figure 6.7: Optical extinction and extended Drude fit for a: A doping series sample with 7.6% Sn; and b: An activation series sample with 5.34% Sn and an activation fraction of 0.71. c: A core-shell model with a doped shell and undoped core was employed to simulate the optical extinction of surface-segregated samples. d: Reproduction of the observed peak peak profiles with the core-shell model. Figure reprinted with permission from Reference¹⁴³, Copyright 2014 American Chemical Society.

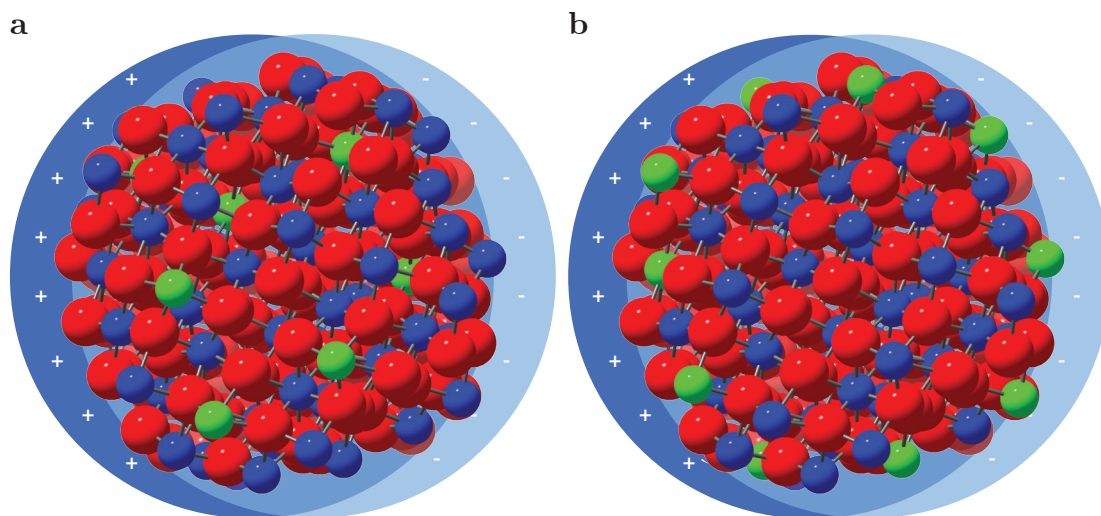


Figure 6.8: Schematic representation of plasmonic nanocrystals with (a) uniform and (b) surface-segregated dopant distributions. When the LSPR is excited, the electron cloud oscillates in response to an external electric field. In panel a, most of the electron cloud is scattered from ionized impurities, pictured in green, whereas in panel b most of the electron cloud is oscillating away from these impurities. Figure reprinted with permission from Reference¹⁴³, Copyright 2014 American Chemical Society.

can be simulated (Figure 6.7c and d), which reproduces the observed experimental trends. A uniform distribution yields the expected asymmetry, while nanocrystals composed of an undoped core with a heavily doped shell have highly symmetric simulated LSPR spectra. The surface-segregated dopants donate electrons to the defect-free core where they experience minimal damping. Furthermore, a thinner shell leads to a narrower line shape, with a close approximation to our data for a 0.25 nm shell. This suggests that tin is primarily segregated within the first few atomic layers of the crystal for these samples.

The difference in the optical properties of nanocrystals with uniformly distributed tin dopants and those with surface-segregated tin, and their relative utility for different applications, such as near-field enhancement, can be quantified in terms of their LSPR quality factor, Q (Equation 5.1). Nanocrystals with surface segregated tin have Q factors more than two times greater than those with uniformly distributed dopants. The Q factors for a number of samples in the activation series are higher than those reported for copper chalcogenide^{49;50} and tungsten oxide⁹³ nanocrystals and similar or slightly smaller in magnitude than those recently reported for indium-doped cadmium oxide nanocrystals.^{81;190} Thus, these ITO nanocrystals with surface-segregated dopants have among the highest Q reported for semiconducting nanocrystals, approaching values found in noble metal nanoparticles and establishing ITO as a promising material for near-field enhancement applications.

6.4 Synthetic control over radial dopant distribution in ITO

The previous section demonstrated the importance of the radial distribution of tin dopants in ITO nanocrystals, the impact that Sn^{4+} has on ionized impurity scattering in ITO nanocrystals, and the significant influence that dopant distribution and ionized impurity scattering have on the LSPR properties of ITO. However, the synthetic methods used to grow the ITO nanocrystals for that study do not offer any precise or systematic control over the location or distribution of tin dopants. Rather, the two disparate syntheses generate ITO with distinctly surface-segregated or homogeneously distributed dopants.

This makes it appealing to develop the means to systematically tune dopant distribution in ITO nanocrystals. While ITO nanocrystals with either surface-segregated tin or homogeneously distributed tin are easily and consistently synthesized using two different literature procedures, the chemical mechanisms that are responsible for different distributions of dopants are so far unclear, which limits the ability to generalize this result to other (e.g., faceted) ITO nanocrystals. Generalizing dopant distribution control to other TCO nanocrystals, like AZO, is even further outside our current understanding of doping chemistry. As the previous section concerned the physical consequences of tin distribution, here, it is important to determine the chemical mechanisms that dictate how efficiently tin is incorporated into the In_2O_3 matrix during synthesis, as well as how that tin is distributed throughout the nanocrystal.

6.4.1 Effect of dopant precursor selection

The first and primary consideration to be made when attempting to control the distribution of tin dopants within colloidal ITO nanocrystals is the reactivity of the nanocrystal precursors, which subsequently implicates Pearson's hard-soft Lewis acid-base (HSAB) theory.^{185;261;262} As Lewis acids, In^{3+} and Sn^{4+} have similar chemical hardness and are considered "hard" acids. When they are bound by the same ligands (Lewis bases), they are expected to have similar reactivities. The magnitude of this reactivity will depend on the chemical hardness of the ligand; when bonded with a hard Lewis base, such as a halogen ion or hydroxyl, an indium or tin complex will be more stable and less reactive. Conversely, when a hard Lewis acid binds to a soft (i.e., polarizable) Lewis base, such as a long-chained alkyl carboxylate or a ligand with delocalized electrons, the ensuing complex is less stable or more reactive. The more similar the relative chemical hardness between a Lewis acid and base pair, the more stable and less reactive the complex or salt.¹⁸⁵

Let us reconsider the two different types of ITO nanocrystals from the previous section, with surface-segregated tin in the activation series and with homogeneously distributed tin in the doping series. In the case of the nanocrystals with homogeneous tin, the indium and tin precursors are coordinated by the same types of carboxylate ligands, namely octanoate, acetate, and ethyl hexanoate ions. These ligands have similar chemical hardness, and so

indium and tin complexes in this reaction should have similar reactivity. This would lead to balanced rates of indium and tin monomer formation and incorporation into growing ITO nanocrystals, explaining the homogeneous distribution of tin. The other, large scale synthesis described above also uses indium and tin acetates in combination with oleylamine. ITO nanocrystals synthesized with these methods have also been observed to display asymmetric LSPR peaks, suggesting that they also have homogeneous tin distributions thanks to the balanced reactivity of indium and tin acetate.

Conversely, the reaction used to generate nanocrystals with surface-segregated tin uses no carboxylic acid ligands or surfactants. The tin precursor, $\text{Sn}(\text{acac})_2\text{Cl}_2$, contains hard Cl^- ligands coordinated to Sn^{4+} , and these ligands are unlikely to be displaced by oleylamine (the activating agent/surfactant in the reaction), as oleylamine is not a charged ligand, and there are no other carboxylates or other anions to displace chlorine. Compared to the indium precursor, $\text{In}(\text{acac})_3$, $\text{Sn}(\text{acac})_2\text{Cl}_2$ likely has a lower reactivity because of these Cl^- ligands binding strongly to Sn^{4+} and stabilizing the complex. This would cause the tin precursor to react at a slower rate and/or at a later time than the indium precursor, explaining the higher concentration of tin at the surface of the ITO nanocrystals synthesized by this method. Considering that nanocrystal doping, especially, depends strongly on precursor reaction rates,^{4;77;186} these described chemical differences in the two synthetic methods appear to be responsible for the different doping profiles.

The obvious hypothesis, then, is that if precursor reactivity is responsible for tin distribution in ITO nanocrystals, then the relative reactivity of the tin and indium precursors can be tuned to systematically control the radial dopant distribution. This hypothesis can be tested by considering the nanocrystal synthesis that gives surface-segregated tin, using oleylamine, $\text{In}(\text{acac})_3$, and $\text{Sn}(\text{acac})_2\text{Cl}_2$, which affords easy manipulation by changing the tin precursor (Figure 6.9). For example, the Cl^- ligands can be exchanged for Br^- ligands to form $\text{Sn}(\text{acac})_2\text{Br}_2$, which may increase the reactivity of the precursor, as bromide is slightly softer than chloride. Likewise, the halide ligands can be eliminated completely to form the $\text{Sn}(\text{acac})_2$ precursor, which should be even more reactive. Indeed, $\text{Sn}(\text{acac})_2$ was witnessed to be highly reactive towards air or moisture, whereas $\text{Sn}(\text{acac})_2\text{Cl}_2$ and $\text{Sn}(\text{acac})_2\text{Br}_2$ were air stable. To further test this hypothesis, the tin precursor can also be changed to be less reactive than $\text{Sn}(\text{acac})_2\text{Cl}_2$, such as tin (II) ethyl hexanoate (abbreviated as $\text{Sn}(\text{Oct})_2$). These carboxylate ligands are harder Lewis bases than acetylacetonate (due to greater charge delocalization and resonance in acetylacetonate ligands⁴), which decreases the tin precursor reactivity. The ethyl hexanoate ligand also reduces reactivity through steric hinderance of nucleophilic attack by oleylamine (see Figure 6.4).

ITO nanocrystals synthesized with equivalent tin concentrations (about 7% Sn) using these different tin precursors display significant changes in their LSPR spectra that are consistent with changes in precursor reactivity (Figure 6.9b). Using the $\text{Sn}(\text{acac})_2\text{Cl}_2$ precursor reproduces the familiar symmetric LSPR peak shape centered at around 1800 nm. Using a less-reactive tin precursor, $\text{Sn}(\text{Oct})_2$, results in a weak, broad, and strongly red-shifted plasmon. This is likely because reducing the precursor reactivity below that of $\text{Sn}(\text{acac})_2\text{Cl}_2$ leads to a more dramatic imbalance in the indium and tin precursor reaction rates, resulting in

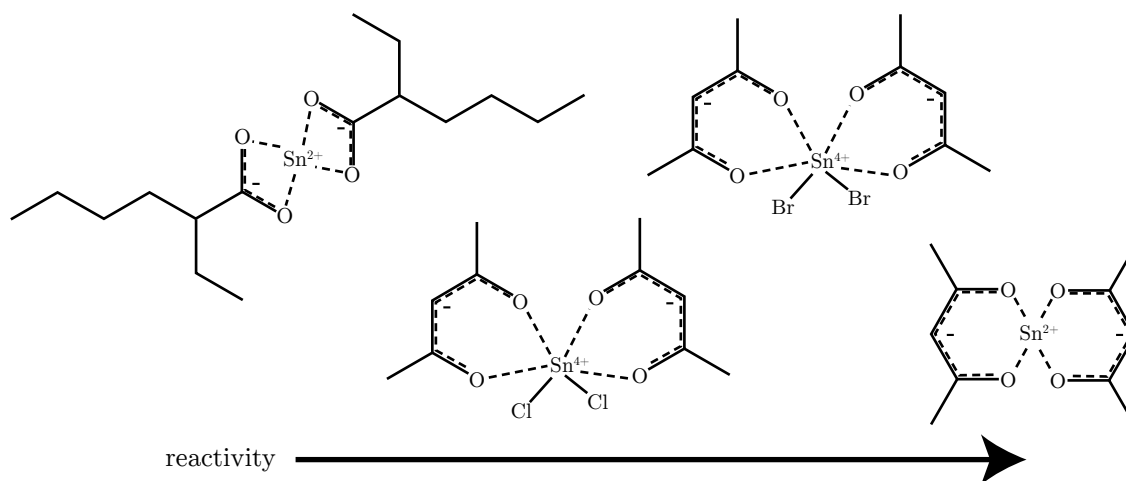


Figure 6.9: Chemical structures of tin precursors used in ITO nanocrystal synthesis, arranged in order of increasing reactivity. From left to right: $\text{Sn}(\text{Oct})_2$, $\text{Sn}(\text{acac})_2\text{Cl}_2$, $\text{Sn}(\text{acac})_2\text{Br}_2$, $\text{Sn}(\text{acac})_2$.

low and/or uneven tin incorporation as evidenced by the LSPR peak of this sample. Using $\text{Sn}(\text{acac})_2\text{Br}_2$ as the tin precursor results in a nearly identical LSPR peak; apparently the Br^- ligands are not soft enough compared to Cl^- to increase the reaction rate. Using $\text{Sn}(\text{acac})_2$ and eliminating the halide moieties, however, results in LSPR that is appreciably broadened towards lower frequencies, reminiscent of the LSPR behavior of ITO with homogeneously distributed tin. This supports the proposed hypothesis that the relative reactivity between the indium and tin precursors is responsible for the distribution of tin dopants within ITO nanocrystals. Furthermore, this provides a way to deliberately tune LSPR peak shape and peak width in ITO nanocrystals, extending the utility of this particular reaction and the utility of ITO nanocrystals for multiple opto-electronic applications.

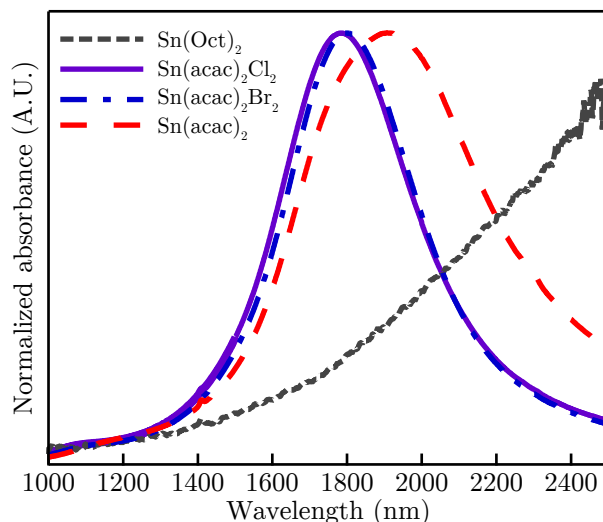


Figure 6.10: Effect of tin precursor reactivity on LSPR in ITO nanocrystals. The LSPR spectra of ITO nanocrystals synthesized with four tin precursors of varying reactivity are displayed.

6.5 Shape control of ITO nanocrystals

As previously detailed, being able to synthesize metal oxide nanocrystals in faceted shapes with well-defined edges and corners is advantageous for near-field enhancement applications, but progress in this area is still lacking. Despite ITO being very well established as a plasmonic oxide, there have been no reports to date of the controlled colloidal synthesis of ITO nanocrystals with well-defined faceted shapes. Shape control is most advanced for metal chalcogenide nanocrystals, where anisotropic crystal structures and the higher surface energies of certain crystal facets have traditionally been used to direct growth. Natural tendencies toward anisotropic growth can be enhanced by tuning parameters like the growth or nucleation temperature, heating rate, and reaction time, or by using mixtures of surfactants that bind preferentially to different crystal facets.

There is no literature evidence that tuning temperature or heating rate will produce ITO with shapes other than spheres, likely due to its relatively isotropic cubic bixbyite crystal structure, where low-index facets do not vary considerably in energy. Indeed, I have failed to synthesize non-spherical ITO by tuning reaction time, temperature, or heating rate. This leaves the surfactant approach as the only alternative. Nearly all published synthetic methods for colloidal ITO nanocrystals use oleylamine and/or alkyl carboxylates as surfactants. However, less-traditional surfactants like oleyl alcohol (OLOH) or trioctylamine (TOA) have been used to produce faceted undoped indium oxide nanocrystals.^{240;263} Unfortunately, it proved impossible to synthesize ITO nanocrystals with good uniformity and LSPR properties using either OLOH or TOA alone. However, ITO cubes were successfully synthesized by using an equimolar mixture of OLOH and OLAM (the typical surfactant for ITO) along

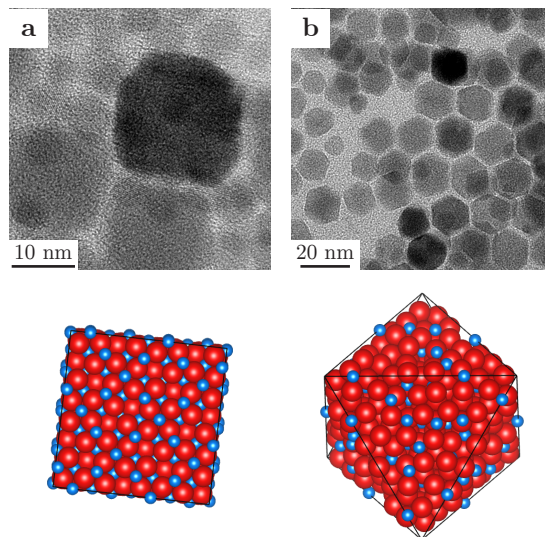


Figure 6.11: Faceted ITO nanocrystals. a: TEM micrograph and model of cubic shaped nanocrystals. b: TEM micrograph and model of octahedral shaped nanocrystals.

with a slow heating rate (Fig. 6.11a). It is also possible to form strongly faceted ITO octahedra (Fig. 6.11b) using an OLAM/OLOH mixture with higher precursor concentrations and faster heating rate, which are both expected to accelerate growth and amplify differences in surface energy between crystal facets. The ability to synthesize ITO nanocrystals with such facets should prove useful for future LSPR coupling and near-field studies. Furthermore, this strategy could be extended to new doped metal oxide formulations.

Chapter 7

Defect engineering in plasmonic metal oxide nanocrystals

“Crystals are like people: it is the defects in them which tend to make them interesting!”

— C.J. Humphreys, *Introduction to Analytical Electron Microscopy*

“Defects may tend to make crystals interesting, but they don’t always make them good.”

— Evan Runnerstrom

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Runnerstrom, E. L.; Bergerud, A.; Agrawal, A.; Johns, R. W.; Dahlman, C. J.; Singh, A.; Selbach, S. M.; Milliron, D. J. Defect Engineering in Plasmonic Metal Oxide Nanocrystals. *Nano Lett.* **2016**, 16, 3390–3398.

7.1 Introduction

Doped metal oxide nanocrystals display intriguing composition-dependent properties. Chief among these is near- to mid-infrared (NIR/MIR) localized surface plasmon resonance (LSPR), which is induced by n-type doping to generate free electrons that can participate in light-driven free carrier oscillation at tunable resonant frequencies. Colloidal synthesis has enabled the discovery of several doped metal oxide nanocrystals with LSPR over the past decade. Key examples include aluminum-doped zinc oxide (Al:ZnO),⁷⁷ indium-doped cadmium oxide (ICO),⁸¹ and tin-doped indium oxide (ITO or Sn:In₂O₃).⁷⁵ These materials have been studied as thin films for their transparent conductive properties, and the dielectric functions known from such studies are the basis for understanding the LSPR properties of the corresponding nanocrystals.

LSPR excitations are confined to the physical dimensions of nanocrystals and effectively concentrate light into volumes well below the diffraction limit. As a result, very intense local field “hotspots” are formed around the nanocrystals that can interact with nearby molecules or materials. This near field enhancement makes doped metal oxide nanocrystals good candidates for NIR and MIR near field optics and enhanced spectroscopies like surface enhanced infrared absorption spectroscopy (SEIRA). Efficient hot spot generation requires a high quality factor (Q , the ratio of the peak energy to the width of the LSPR peak), which implies longer plasmon lifetimes, weaker electronic damping, and stronger near field intensities. Thus, it is important to consider not only how dopants in metal oxides tune the LSPR frequency by changing the free carrier concentration, but also how their presence contributes to damping by scattering the oscillating free electrons. To create high- Q MIR plasmonic materials, strategies are needed to minimize scattering even as substantial concentrations of dopants are introduced.

To account for both free carrier concentration and electronic damping, the dielectric function of a doped oxide nanocrystal can be represented by the Drude model extended to include a frequency-dependent contribution to the damping of oscillating free carriers:

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma(\omega)} \quad (7.1)$$

$$\omega_p = \sqrt{\frac{ne^2}{m_e^*\varepsilon_0}} \quad (7.2)$$

where ε_∞ is the high frequency permittivity, $\Gamma(\omega)$ is the electronic damping function, ω_p is the plasma frequency, n is the free carrier concentration, m_e^* is the free carrier effective mass, and ε_0 is the permittivity of free space. The magnitude of Γ is critical because it determines the LSPR linewidth (i.e., Q) and its functional form reflects the frequency dependence of electronic scattering by charged point defects; such ionized impurity scattering acutely hampers electron transport and reduces mobility. This is particularly important for doped metal oxides, as aliovalent dopants are necessary for free carrier generation, and oxygen vacancies, as doubly ionized defects, scatter electrons four times more strongly than singly ionized defects.^{66;74;231} LSPR behavior therefore depends critically on how dopants influence defect chemistry, carrier scattering, and mobility. We recently demonstrated the importance of defects in determining LSPR properties by showing that Sn:In₂O₃ nanocrystals with surface-segregated tin display significantly narrower and more symmetric LSPR peaks compared to nanocrystals with homogenously distributed tin owing to a decrease in ionized impurity scattering.¹⁴³

Deliberate defect engineering—that is, rational dopant selection and minimization of vacancy concentration—has been explored in transparent conducting oxide thin films as a viable strategy to combat ionized impurity scattering. For example, Mo-doped In₂O₃ thin films have higher electron mobility than Sn:In₂O₃. Unlike Sn orbitals, Mo orbitals do not hybridize with the conduction band minimum (CBM), leading to stronger electrostatic screening of dopant potentials and reduced ionized impurity scattering.²⁶⁴ Likewise, Dy-

doped CdO thin films exhibit exceptional electronic mobility and large predicted plasmon quality factors because Dy dopants modify the defect equilibria to minimize oxygen vacancy concentration.²⁶⁵ Doping with Dy³⁺ also minimizes local strain and the associated electron-phonon scattering because it is a close match to Cd²⁺ in ionic radius.

Applying these strategies to indium oxide reveals cerium as a promising dopant. Cerium is significantly more electropositive than In and Sn, which implies that Ce states may lie within the conduction band of In₂O₃, limiting hybridization at the CBM and leading to remote screening of dopants as in Mo-doped In₂O₃. As an electropositive dopant, Ce may also be a more energetically stable electron donor than oxygen vacancies, which could modify the defect equilibria to inhibit oxygen vacancy formation. Finally, the six-coordinate crystal ionic radius of Ce⁴⁺ (101 pm) is a closer match to In³⁺ (94 pm) than is Sn⁴⁺ (83 pm),²⁶⁶ which implies that cerium doping may reduce lattice strain compared to Sn:In₂O₃ in a manner analogous to Dy in CdO. We therefore hypothesized that cerium-doped indium oxide (Ce:In₂O₃) nanocrystals would display higher electronic mobility and higher *Q* LSPR peaks compared to Sn:In₂O₃. The few literature accounts of Ce-doped In₂O₃ thin films report high mobility, which supports this hypothesis, though these studies used tin or hydrogen as co-dopants and did not study the microscopic mechanisms responsible for enhanced mobility.^{267;268}

7.2 Experimental procedures

7.2.1 Synthetic procedures

We synthesized, for the first time, colloidal Ce:In₂O₃ nanocrystals by adapting a typical procedure used to synthesize Sn:In₂O₃ nanocrystals.^{75;143} All chemicals were used as received without further purification. Indium acetylacetonate (In-acac, 99.99%), cerium (III) acetylacetonate hydrate (Ce-acac), cerium (III) acetate hydrate (Ce-acetate), cerium (IV) ammonium nitrate (C.A.N., 98.5%) and tin bis(acetylacetonate) dichloride (Sn(acac)₂Cl₂ 98 %) were purchased from Sigma Aldrich. Cerium (IV) tetramethylheptanedionate (Ce-TMHD, 97%) and cerium (III) acetate (Ce-acetate, 99.9%) were purchased from Strem. Oleylamine (OLAM, 80-90%) was obtained from Acros Organics. All synthetic procedures were carried out under inert nitrogen atmosphere with magnetic stirring using standard Schlenk line techniques and 50 mL three-neck round bottom flasks. For all syntheses, the molar ratio of metal precursor to OLAM was set at 1:12. Doping was achieved by adding the desired cerium and/or tin precursor while maintaining the total metal:OLAM ratio. For example, to synthesize 5.2% Ce-doped In₂O₃ nanocrystals, 0.85 mmol In-acac (350 mg) was combined with 0.045 mmol Ce-acac (20 mg) and 11 mmol OLAM (2.934 g). The solution was heated to 110°C for 10 minutes under nitrogen, then heated to 250°C for 2 hours to form colloidal Ce:In₂O₃ nanocrystals. The nanocrystals in the crude reaction mixture were purified by three cycles of flocculation with ethanol, centrifugation, and redispersion in hexane before finally being dispersed in hexane and filtered with a syringe filter.

7.2.2 Materials characterization

Transmission electron microscopy (TEM) was used to characterize size and shape of the synthesized nanocrystals, revealing that the synthesized nanocrystals were relatively uniform in size and shape and highly crystalline (Figure 7.1a-d and Figure A.1). TEM samples were prepared by diluting 10 microliters of the purified nanocrystal dispersion into 1 mL of toluene before dropcasting 10 microliters of the diluted toluene dispersion onto a copper TEM grid. TEM micrographs were collected using a JEOL 2010F TEM, with a Schottky field emission source, operated at 200 kV accelerating voltage. Low-resolution scanning TEM (STEM) micrographs were obtained using a Hitachi S5500 scanning electron microscope operating in STEM mode at 30 kV accelerating voltage.

X-ray diffraction (XRD, Figure 7.1e) confirms the crystallinity of $\text{Ce:In}_2\text{O}_3$ nanocrystals, which have the cubic bixbyite crystal structure typical of bulk In_2O_3 , without detectable impurity phases. XRD powder diffraction patterns were collected using a Rigaku MiniFlex 600 with a $\text{Cu K}\alpha$ X-ray source and a point detector, operating in Bragg-Bretano geometry. Rietveld refinement was performed using the TOPAS program, fitting the XRD patterns to the bixbyite crystal structure (space group Ia-3) while refining lattice parameter, sample displacement, peak profile, scale, and background function. Rietveld refinement (Figure 7.2) showed that the lattice parameter increased slightly with Ce doping along a trajectory well-fit by Vegard's law. Owing to the larger ionic radius of cerium, this lattice expansion signifies effective substitutional dopant incorporation. Cerium doping was confirmed and dopant concentration was quantified with inductively coupled plasma optical emission spectroscopy (ICP-OES). We prepared a doping series from 0% Ce to 11.1% Ce using cerium acetylacetonate (Ce-acac) as a dopant source, and we also evaluated other precursors, namely cerium tetramethylheptanedionate (Ce-TMHD), cerium ammonium nitrate, and cerium acetate. All dopant precursors produced colloiddally stable and highly crystalline nanocrystals with narrow MIR LSPR absorption, though LSPR peak shape and nanocrystal shape depended on the amount and type of cerium precursor used. For example, nanocrystals synthesized with Ce-acac tended to adopt cubic shapes with (100)-terminated facets, while those synthesized with Ce-TMHD were pseudospherical. As we show below, consistent with previously published simulations of ICO nanocrystals,¹⁴⁰ the synthesis of nanocrystals in shapes with defined corners and edges has positive implications for near field enhancement.

Optical spectra of the nanocrystal dispersions were measured using Fourier transform infrared spectroscopy (FTIR) in a liquid cell to characterize their LSPR properties. Because most organic solvents have strong molecular vibrations (e.g., C-H stretch) that would interfere with FTIR measurements, the nanocrystals were precipitated out of hexane and redispersed in a desired solvent for IR spectroscopy, such as tetrachloroethylene, taking care to remove as much hexane and ethanol as possible. The tetrachloroethylene nanocrystal dispersions were injected with a syringe into a liquid cell with IR transparent KBr windows, with a pathlength of 0.5 mm, for FTIR spectroscopy. The resulting spectra display remarkably narrow LSPR peaks that are air-stable (Figure 7.3a). The peak energy increases with Ce content, indicating donor dopant behavior.

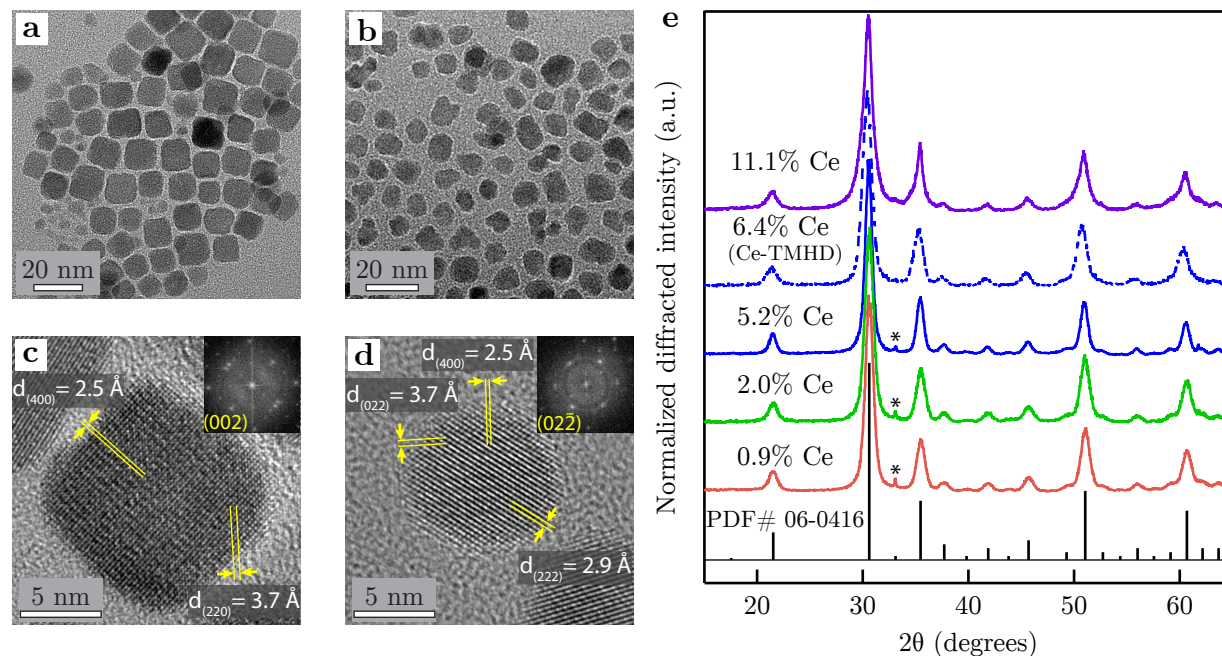


Figure 7.1: Physical characterization of $\text{Ce}:\text{In}_2\text{O}_3$ nanocrystals. a: TEM micrograph of cubic $\text{Ce}:\text{In}_2\text{O}_3$ nanocrystals doped with 5.2% Ce (from Ce-acac); b: TEM micrograph of pseudospherical $\text{Ce}:\text{In}_2\text{O}_3$ nanocrystals doped with 6.4% Ce (from Ce-TMHD); c: HRTEM image of cubic nanocrystal with FFT in inset; d: HRTEM of spherical nanocrystal with FFT in inset. e: Representative powder XRD patterns for $\text{Ce}:\text{In}_2\text{O}_3$ nanocrystals, confirming the indium oxide cubic bixbyite structure (reference PDF pattern shown at bottom). The sharp peaks marked with a (*) are due to the substrate.

The optical band gaps of the nanocrystals dispersed in hexane were measured using 1 cm path length quartz cuvettes and an Agilent Cary 5000 spectrophotometer. The UV optical bandgap shifts systematically to higher energy with increased doping (Figure 7.3b) as free conduction band electrons populate band edge states in accordance with observations of the Burstein-Moss effect in other doped oxide nanocrystals.^{77;81} Dispersing the nanocrystals in non-polar solvents with increasing refractive index results in a systematic red shift in LSPR peak position (Figure 7.3c). When the wavelength of the extinction peak is plotted vs. refractive index (Figure 7.3c inset), a linear trend is observed, consistent with the expected sensitivity of LSPR to the dielectric environment.

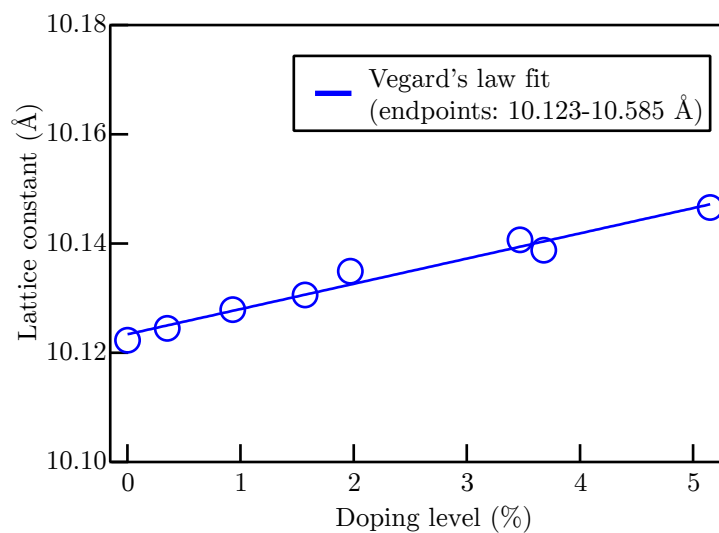


Figure 7.2: Lattice constant of Ce:In₂O₃ nanocrystals as calculated from Rietveld refinement of powder XRD patterns. The solid line is a fit of Vegard's law to the change in lattice parameter with doping level. The endpoints of the fit (i.e., 0% Ce extrapolated to 100% Ce) are listed in the legend.

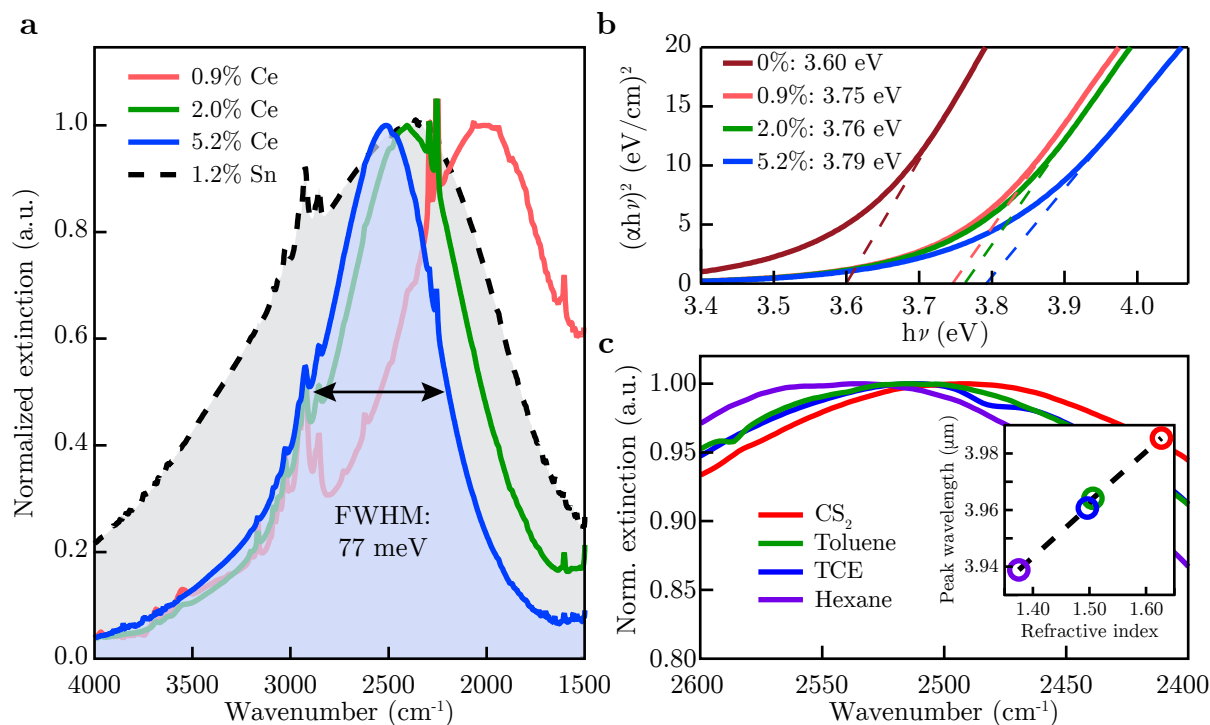


Figure 7.3: Optical properties of Ce:In₂O₃ nanocrystals. a: FTIR liquid cell spectra of Ce:In₂O₃ and Sn:In₂O₃ nanocrystals dispersed in tetrachloroethylene showing narrow and tunable MIR LSPR of Ce:In₂O₃. b: Tauc plot showing systematic increase of Ce:In₂O₃ optical bandgap with Ce content consistent with a Burstein-Moss shift. c: LSPR of 5.2% Ce-doped In₂O₃ dispersed in non-polar solvents with different refractive indices. Inset: LSPR peak wavelength vs. refractive index.

7.3 Analysis and Discussion

The LSPR peaks observed for the Ce:In₂O₃ nanocrystals above are exceptionally narrow and symmetric, especially compared to Sn:In₂O₃ nanocrystals with LSPR in the same spectral region (Figure 7.3a). The narrowest peak occurs for nanocrystals doped with 5.2% Ce, which display an LSPR peak at 2522 cm⁻¹ with a width of only 621 cm⁻¹ (77 meV) for a quality factor of 4.08. To our knowledge, this is higher than the Q values for gold nanostructures, nitrides, chalcogenides, and other doped metal oxide nanocrystals with LSPR in or approaching this spectral region.^{49;66;77;81;88;93;94;143;190;269–272} Furthermore, these peak widths are among the narrowest reported for any plasmonic nanoparticle, including single gold nanoparticles (120 meV),²⁷³ Sn:In₂O₃ (113 meV),¹⁴³ and ICO co-doped with fluorine (59 meV).¹⁹¹

Narrow and symmetric LSPR peaks indicate low levels of electronic damping and ionized impurity scattering.^{66;143} To quantify these electronic properties, we performed fits to the FTIR spectra with an extended Drude model using a MATLAB code developed by our group.^{28;143;224;229} In contrast to a simple Drude approximation, our model employs an empirical frequency-dependent damping function ($\Gamma(\omega)$ in Equation 1) to account for the frequency dependence of ionized impurity scattering:

$$\Gamma(\omega) = \Gamma_L - \frac{\Gamma_L - \Gamma_H}{\pi} \left[\tan^{-1} \left(\frac{\omega - \Gamma_X}{\Gamma_W} \right) + \frac{\pi}{2} \right] \quad (7.3)$$

where Γ_L is a low-frequency damping constant, Γ_H is a high-frequency damping constant, Γ_X is a crossover frequency between the low-frequency and high-frequency damping regimes, and Γ_W is the width of the crossover region.²³³ The magnitude of the low-frequency damping constant captures the influence of ionized impurity scattering, and when $\Gamma_L \gg \Gamma_H$, frequency-dependent ionized impurity scattering is a dominant LSPR damping mechanism. At sufficiently low frequencies, oscillating electrons effectively feel the same scattering potentials as they would under a DC field, so fits to the spectra can be used to calculate optical DC electronic mobility by the following relationships:¹⁴³

$$\sigma_{\text{opt}} = en\mu_{\text{opt}} = \frac{ne^2}{m_e\Gamma(0)} \quad (7.4)$$

where σ_{opt} is the optically-derived electronic conductivity, μ_{opt} is the optically-derived electron mobility, n is the free carrier concentration, m_e is the effective mass of an electron, and $\Gamma(0)$ is the value of the damping function (Equation 7.3) at zero frequency. Electronic properties derived optically by this method have been found to match physically measured properties, including mobility, in both dense thin films and electronically-connected nanocrystalline films.^{229;234;274;275}

We calculated the plasma frequency, electron concentration, damping constants, and electronic mobility for Ce:In₂O₃ nanocrystals and compared them to Sn:In₂O₃ nanocrystals containing 1 to 4% Sn. A representative fit and the salient fitting results are shown in Figure 7.4 and Table 7.1. The remaining Drude fits are shown in Figure A.2. In Ce:In₂O₃, the crossover frequencies are significantly blue shifted relative to the LSPR peak energy with

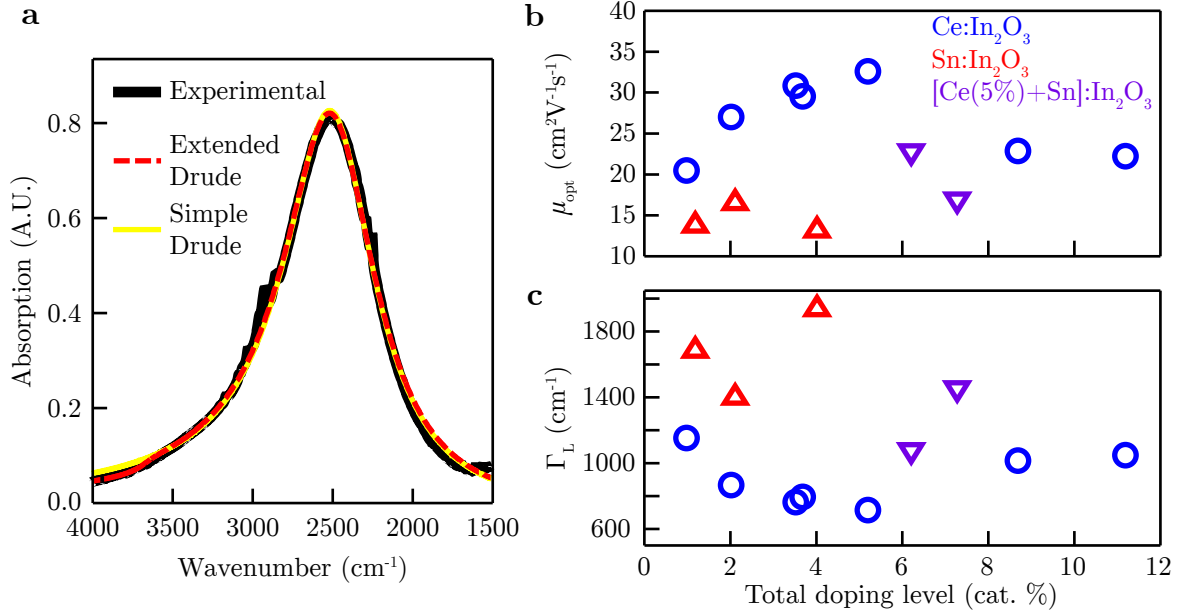


Figure 7.4: Drude modeling of LSPR in Ce:In₂O₃ nanocrystals. a: Example extended and simple Drude model fits to the FTIR spectrum of 5.2% Ce:In₂O₃ nanocrystals. b: Optically-calculated electronic mobility of Ce:In₂O₃ (blue circles), Sn:In₂O₃ (red triangles), and Ce/Sn-codoped In₂O₃ nanocrystals (purple, inverted triangles) vs. doping level. c: Low-frequency damping constant, calculated with the extended Drude model, for Ce:In₂O₃, Sn:In₂O₃, and Ce/Sn-codoped In₂O₃ nanocrystals vs. doping level.

narrow crossover widths and low Γ_L values. This is indicative of damping by a frequency-independent constant throughout the bandwidth of the LSPR peak and suppressed ionized impurity scattering.¹⁴³ When we fit the spectra using a simple Drude model with constant damping, the fits were nearly identical (Figure 7.4a, Table 7.1), supporting this conclusion.

Figures 7.3a and A.2 show a limited blue shift in the LSPR peak at doping levels higher than 5.2%, suggesting diminished donor character at higher Ce concentration. This is in contrast to Sn:In₂O₃, which has a stronger LSPR blue shift with Sn content. Comparing the electron concentrations determined by Drude analysis to Ce concentration reveals that a significant number of dopants are not activated as donors (Figure 7.5a), as is typical for degenerately doped metal oxides. X-ray absorption spectroscopy (XAS, Figure 7.5) revealed that a significant fraction of Ce dopants were not ionized, which is most likely a consequence of cerium's facile transition between the 3+ and 4+ oxidation states. We note that more complex defect chemistries are also possible and may be consuming free electrons, since the electron concentrations were generally lower than expected based on the Ce⁴⁺ fraction determined by XAS. For example, defect clustering between dopants and oxygen interstitials is a well-known phenomenon in bulk Sn:In₂O₃⁸⁹ and has been observed in plasmonic Sn:In₂O₃ nanocrystals.²⁷⁶ The latter study recognized that $(2\text{Sn}_{\text{In}}^{\bullet}-\text{O}_i^{\prime\prime})^{\times}$ defect clusters in-

Doping level (by ICP)	ω_p (cm ⁻¹)	Γ_L (cm ⁻¹)	Γ_H (cm ⁻¹)	Γ_X (cm ⁻¹)	Γ_W (cm ⁻¹)	n (cm ⁻¹)	μ_{opt} (cm ² /Vs)
0.9% Ce (acac)	5798 ± 5	1153 ± 12	422 ± 25	3425 ± 31	267 ± 46	1.50 × 10 ²⁰	20.5
2.0% Ce (acac)	6993 ± 0	867 ± 3	423 ± 8	3145 ± 11	141 ± 16	2.19 × 10 ²⁰	26.7
3.5% Ce (acac)	7416 ± 1	764 ± 3	421 ± 6	3261 ± 16	263 ± 17	2.46 × 10 ²⁰	30.9
3.7% Ce (acac)	7299 ± 1	795 ± 3	417 ± 7	3242 ± 15	232 ± 16	2.38 × 10 ²⁰	29.7
5.2% Ce (acac)	7362 ± 1	715 ± 2	468 ± 7	3679 ± 16	71 ± 12	2.42 × 10 ²⁰	32.7
8.6% Ce (acac)	7247 ± 2	1016 ± 3	625 ± 8	3886 ± 9	25 ± 6	2.35 × 10 ²⁰	23.0
11.1% Ce (acac)	7433 ± 2	1049 ± 3	594 ± 8	3735 ± 9	49 ± 7	2.47 × 10 ²⁰	22.3
6.4% Ce (TMHD)	7464 ± 3	1216 ± 7	617 ± 10	3581 ± 15	305 ± 27	2.49 × 10 ²⁰	19.4
4.8% Ce (acetate)	7322 ± 4	1059 ± 19	414 ± 26	3469 ± 39	492 ± 80	2.40 × 10 ²⁰	22.6
5.6% Ce (C.A.N.)	7561	2900	422	2519	1693	2.56 × 10 ²⁰	9.9
1.2% Sn	7190 ± 3	1692 ± 7	920 ± 15	3844 ± 27	361 ± 30	2.31 × 10 ²⁰	14.0
2.1% Sn	9300 ± 2	1407 ± 3	991 ± 8	4247 ± 25	184 ± 18	3.87 × 10 ²⁰	16.7
4% Sn	12997 ± 2	1935 ± 144	0	6030 ± 610	2009 ± 558	7.55 × 10 ²⁰	13.4
5.3% Ce + 1.0% Sn	8121 ± 3	1050 ± 5	685 ± 14	3974 ± 34	121 ± 25	2.95 × 10 ²⁰	22.3
5.2% Ce + 2.1% Sn	8722 ± 2	1426 ± 7	972 ± 7	3463 ± 16	226 ± 27	3.44 × 10 ²⁰	16.4

Table 7.1: Extended Drude model fitting results for LSPR in Ce:In₂O₃ and Sn:In₂O₃ nanocrystals. Reliable uncertainties could not be calculated for the 5.6% Ce (C.A.N.) sample.

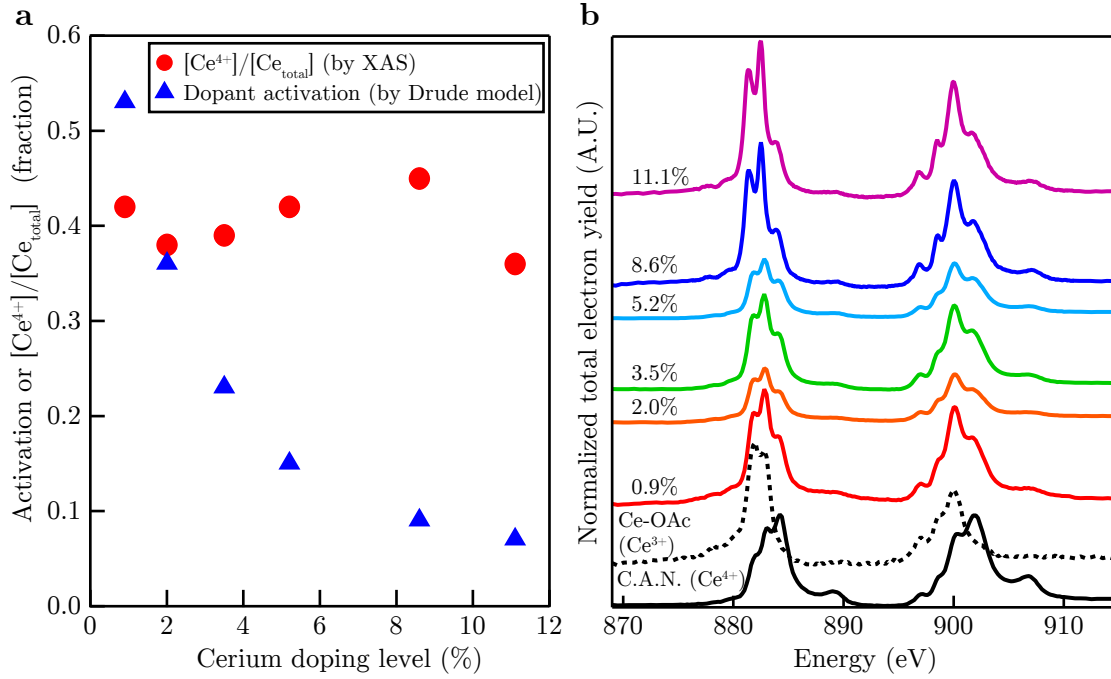


Figure 7.5: a: Fraction of activated dopants (blue triangles, calculated as the free electron concentration divided by dopant concentration) in Ce:In₂O₃ nanocrystals, and the fraction of ionized Ce^{4+} in the nanocrystals, calculated by XAS (red circles). b: XAS spectra of Ce:In₂O₃ nanocrystals at various doping levels, along with Ce^{4+} and Ce^{3+} reference compounds.

fluence LSPR in Sn-doped In₂O₃; similar $(2\text{Ce}_{\text{In}}^{\bullet}-\text{O}_i^{\prime\prime})^{\times}$ clusters and defect equilibria may contribute to limited activation at higher doping levels in Ce:In₂O₃ here. In an attempt to examine these possible defect equilibria, we performed a time-dependent aliquot study on a 5.4% Ce-doped sample (Figure 7.6), where we observed the emergence of LSPR over time, even though the Ce content measured by ICP-OES was essentially constant. This is further evidence for $(2\text{Ce}_{\text{In}}^{\bullet}-\text{O}_i^{\prime\prime})^{\times}$ clusters that dissociate into activated $\text{Ce}_{\text{In}}^{\bullet}$ and O₂ gas under low oxygen partial pressures, similar to the observations in Sn:In₂O₃ by Nag, *et al.*²⁷⁶

Turning back to the quantitative Drude modeling results, the values for μ_{opt} and Γ_{L} (Figure 7.4b,c) underscore the exceptional electronic properties of Ce:In₂O₃. Both the low- and high-frequency damping constants are significantly lower than for Sn:In₂O₃ nanocrystals, and the 2.0%-5.2% Ce-doped samples outperform our previously reported best performance from 6.4% Sn-doped In₂O₃ ($\Gamma_{\text{L}} = 913 \text{ cm}^{-1}$).¹⁴³ We also confirmed the deleterious effects of tin doping by preparing Ce/Sn-codoped samples: incorporation of only 1%-2% Sn significantly decreased mobility and increased both the low- and high-frequency damping constants (Figure 7.4b,c), but these nanocrystals nevertheless displayed enhanced properties relative to nanocrystals doped with tin only. In particular, the low Γ_{L} values quantitatively describe how ionized impurity scattering is suppressed in Ce:In₂O₃ compared to Sn:In₂O₃. Furthermore,

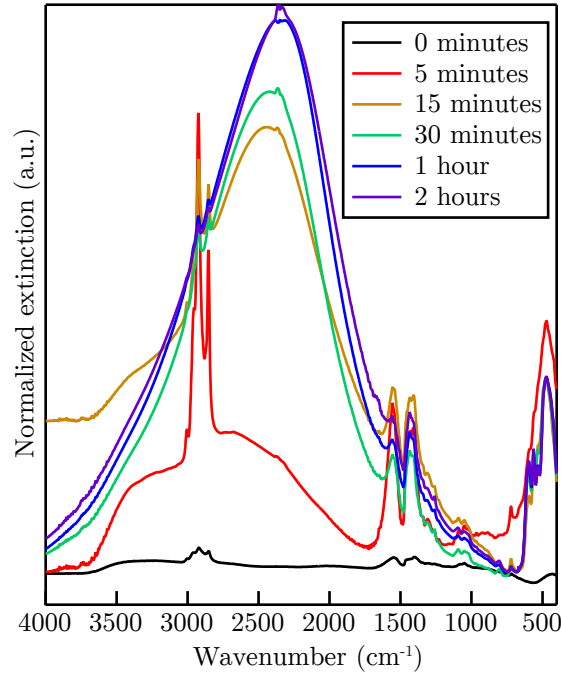


Figure 7.6: Aliquot study of LSPR in Ce:In₂O₃ nanocrystals changing during synthesis. The LSPR response gradually grows in with time even though Ce content is nearly constant, suggesting the dissociation of Ce-based defect clusters to yield free electrons. All spectra (except the 0 minutes spectrum) are normalized to the In-O phonon at around 500 cm⁻¹.

the extracted frequency-dependent damping functions translate to high electronic mobility as calculated by Equation 7.4; we calculated mobilities up to 33 cm²V⁻¹s⁻¹, twice what we observed for Sn:In₂O₃ nanocrystals.

The observed mobility trends suggest that cerium incorporation suppresses ionized impurity scattering by influencing crystal structure, electronic structure, or both. Furthermore, the electronic mobility in Ce:In₂O₃ actually increases substantially with doping level up to 5.2% Ce. These results are contrary to conventional models of ionized impurity scattering, which predict a decrease in mobility with doping.^{74;277} To evaluate the microscopic origins of the electronic property enhancements, we performed density functional theory (DFT) calculations using the Vienna *ab initio* simulation package (VASP) to simulate local strains, defect formation energies, and electronic structure in Ce:In₂O₃.^{278–281} In all calculations, doping was simulated by replacing a Wyckoff *8b* In site with Ce or Sn.

Using a GGA+U exchange correlation functional, we first calculated radial strains surrounding an oxygen vacancy, a substitutional Ce dopant, and a substitutional Sn dopant in a 80-atom In₂O₃ bixbyite unit cell, corresponding to a cation doping level of 3.1% (Figure 7.7).²⁸² The magnitude of the nearest neighbor strain around cerium ($\sim 4\%$) is slightly lower than tin ($\sim 5\%$). This slight decrease in lattice distortion is probably not the primary driver of high mobility, though it may be responsible for some decrease in frequency-independent

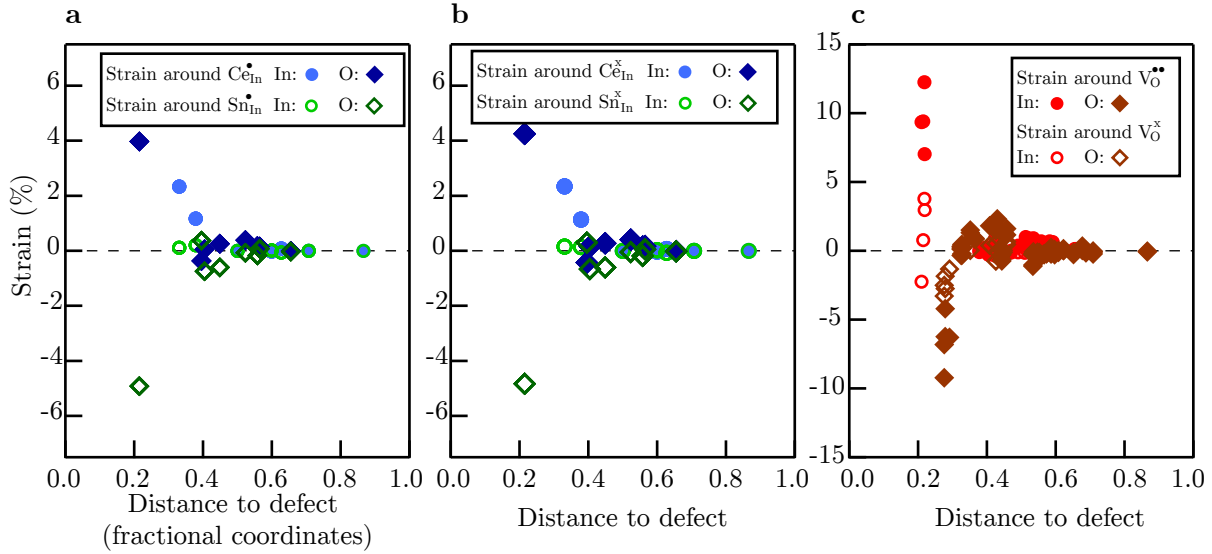


Figure 7.7: Radial strain from displacement of nearest neighbors in In_2O_3 (indium atoms denoted by circles, oxygen atoms denoted by diamonds) around a defect as calculated by DFT. a) Ionized Ce ($\text{Ce}_{\text{In}}^\bullet$, filled blue symbols) and Sn ($\text{Sn}_{\text{In}}^\bullet$, empty green symbols) dopants. b) Unionized Ce (Ce_{In}^x , filled blue symbols) and Sn (Sn_{In}^x , empty green symbols). c) Unionized and doubly-ionized oxygen vacancies (V_{O}^x , $\text{V}_{\text{O}}^{\bullet\bullet}$).

electron-phonon scattering. By contrast, the strain around an oxygen vacancy is up to three times greater and decays over a longer distance, which would cause strong electron-phonon scattering through lattice distortion. Furthermore, the ionized impurity scattering potentials from ionized oxygen vacancies are strongly felt by free electrons due to the significant contribution of oxygen orbitals to the conduction band.^{253;264}

Considering strong electron scattering by oxygen vacancies, the incorporation of Ce might suppress ionized impurity scattering by reducing the equilibrium concentration of oxygen vacancies. We therefore used DFT to calculate the defect formation energies for an oxygen vacancy, a substitutional cerium dopant, and a substitutional tin dopant in a bixbyite unit cell according to the following equation:

$$E_{\text{defect}}[X^q] = E_{\text{DFT}}[X^q] - E_{\text{DFT}}[\text{bulk}] - \sum_i n_i \mu_i + qE_F + E_{\text{corr}} \quad (7.5)$$

where $E_{\text{defect}}[X^q]$ is the formation energy of a defect X with charge q , $E_{\text{DFT}}[X^q]$ is the total energy of the defective cell calculated by DFT, $E_{\text{DFT}}[\text{bulk}]$ is the total energy of the perfect cell, n_i and μ_i are the number and chemical potential, respectively, of the atoms added or subtracted from the cell to form the defect, E_F is the Fermi level relative to the valence band maximum, and E_{corr} is a correction factor that accounts for potential alignment and image charges of the defect that arise during DFT calculations.²⁸³ This treatment captures the dependence of defect formation energies on the Fermi level as well as the chemical potential

of oxygen, allowing us to display these energies as a function of E_F under oxygen-poor and -rich conditions (see Section A.6 for a more detailed explanation). We note that the oxygen-poor case, corresponding to the minimum chemical potential of oxygen for which In_2O_3 is stable with respect to decomposition into indium metal and O_2 , likely matches our anaerobic synthetic environment more closely, especially considering the precipitation of bulk metal observed in some similarly performed nanocrystal syntheses.^{5;157;190}

We calculated defect formation energies for oxygen vacancies and substitutional tin in both the oxygen-poor (Figure 7.8a) and oxygen-rich (Figure 7.8b) limits, and they agree well with previous computational studies.^{254;284} Our calculations also indicate that under oxygen-poor conditions, the formation of substitutional Ce defects is significantly more energetically favorable than substitutional tin or oxygen vacancies, which have comparable formation energies. The energy difference between substitutional Ce and Sn arises primarily from the $E_{\text{DFT}}[X^q]$ term—the energy of a unit cell with one Ce defect is about 3.5 eV lower than a unit cell with one Sn defect—while the chemical potential and correction terms in Equation 7.5 differ by 0.5 eV or less between Ce and Sn doping. Incorporation of Ce or Sn donors increases the Fermi level, which consequently increases the formation energy of oxygen vacancies by over 3 eV as the Fermi level reaches the CBM. For a given electron concentration, it is much more energetically favorable to compensate free electrons with Ce donors as opposed to oxygen vacancies. In $\text{Sn}:\text{In}_2\text{O}_3$, the energy difference between substitutional Sn and oxygen vacancies is significantly smaller, so free electrons would more likely be compensated by a mix of both defects. Figure 7.8 also shows that neutral defects become favorable at higher Fermi levels, indicating the presence of both ionized and neutral dopants, which agrees with our observation of partial dopant activation. Overall, when comparing $\text{Ce}:\text{In}_2\text{O}_3$ and $\text{Sn}:\text{In}_2\text{O}_3$ at the same electron concentration, our results suggest that oxygen vacancies may be more prominent in the latter. This interpretation is consistent with our observations that the electronic mobility in $\text{Ce}:\text{In}_2\text{O}_3$ nanocrystals increases significantly with Ce concentration, while the electronic mobility in $\text{Sn}:\text{In}_2\text{O}_3$ nanocrystals does not increase with Sn doping.

The formation energies of Ce and Sn substitutional defects change progressively with oxygen chemical potential, eventually crossing over so that Sn is more favorable than Ce at oxygen-rich conditions (where the chemical potential of oxygen is set equal to the energy of O in an O_2 molecule, Figure 7.8b). This manifests at high oxygen activity because CeO_2 has a significantly lower chemical potential than SnO_2 (by about 5 eV, see tables A.2 and A.3); the chemical potentials of these two oxides set the oxygen-rich boundary conditions for Equation 7.5 and under these conditions, the chemical potential difference overwhelms the difference in the $E_{\text{DFT}}[X^q]$ term. Between these two extremes of oxygen chemical potential, substitutional Ce remains more favorable (Figure fig:cheetoS6). At the oxygen-rich extreme, the formation energy for all three defects is positive over nearly the whole range of Fermi levels, indicating that n-type doping would be difficult under these conditions. These conditions are unlikely to be encountered experimentally, and high oxygen partial pressures are associated with other deleterious effects in $\text{Sn}:\text{In}_2\text{O}_3$, such as defect clusters of tin and oxygen interstitials, which consume free electrons upon formation.⁸⁹

Finally, we considered electronic structure as an explanation for low ionized impurity

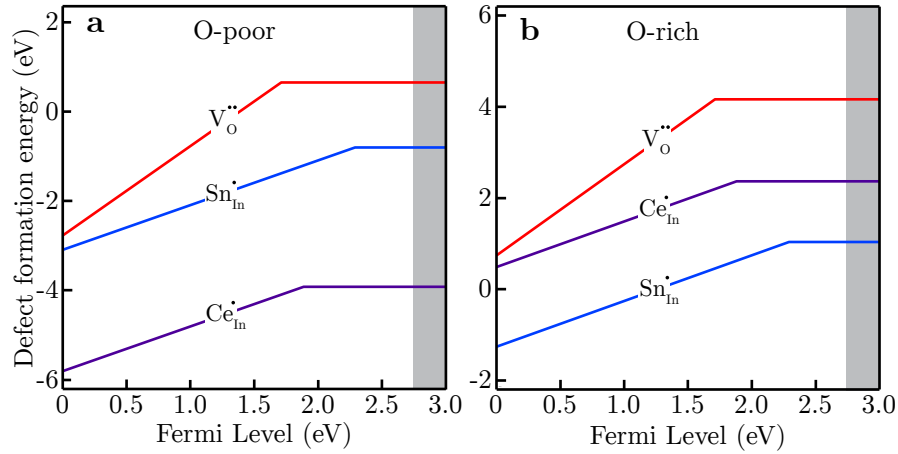


Figure 7.8: Defect formation energies in Ce:In₂O₃ and Sn:In₂O₃ calculated by DFT. a: Defect formation energies vs. Fermi level for oxygen vacancies ($V_O^{\bullet\bullet}$), substitutional tin dopants ($Sn_{In}^{\bullet}$), and substitutional cerium dopants ($Ce_{In}^{\bullet}$) under oxygen-poor conditions. The valence band maximum is set to 0 eV and the gray shaded region denotes the conduction band edge. The slope of the formation energy vs. Fermi level reflects the stable charge state of the defect at that Fermi level. b: Defect formation energies vs. Fermi level under oxygen-rich conditions.

scattering in Ce:In₂O₃. Because Ce is significantly more electropositive than In, hybridization between dopant orbitals and the states near the CBM should be limited. To test this hypothesis, we used DFT to calculate the electronic density of states (DOS) for a 40 atom primitive bixbyite unit cell with one substitutional Ce or Sn dopant, which corresponds to a doping level of 6.3% (Figure 7.9a, c). Here, we used the HSE06 hybrid functional to obtain a more accurate description of electronic structure, faithfully reproducing indium oxide's fundamental bandgap of 2.7 eV.^{253;285–287} We also calculated the DOS of Sn:In₂O₃ (Figure 7.9b, d) and stoichiometric In₂O₃ for comparison (Figure A.4). The partial density of states (PDOS) reveal that the bottom of the conduction band is primarily of In 5s and O 2s character, which implies a wide and dispersive conduction band that facilitates high electron mobility. The only dopant states that overlap in energy with the bottom of the conduction band are Ce 4f states, which are highly localized states that should resist mixing with s and p orbitals. The Ce 6s and 5p states, which could hybridize more strongly, contribute no PDOS to the CBM and only become significant about 1 eV above the band edge. By contrast, Sn 5s states are present at the CBM in our Sn:In₂O₃ calculations, and previous studies have shown strong hybridization between these and In 5s orbitals.^{252;264} Optical bandgap measurements (Figure 7.3b) suggest that the Fermi level for the 5.2% Ce-doped sample (with the highest mobility) is about 0.2 eV above the CBM, or about 2.9 eV above the valence band edge. Electrons near the Fermi level that contribute to conductivity and LSPR are thus unlikely to interact substantially with the Ce dopants, while they interact strongly with Sn dopants.

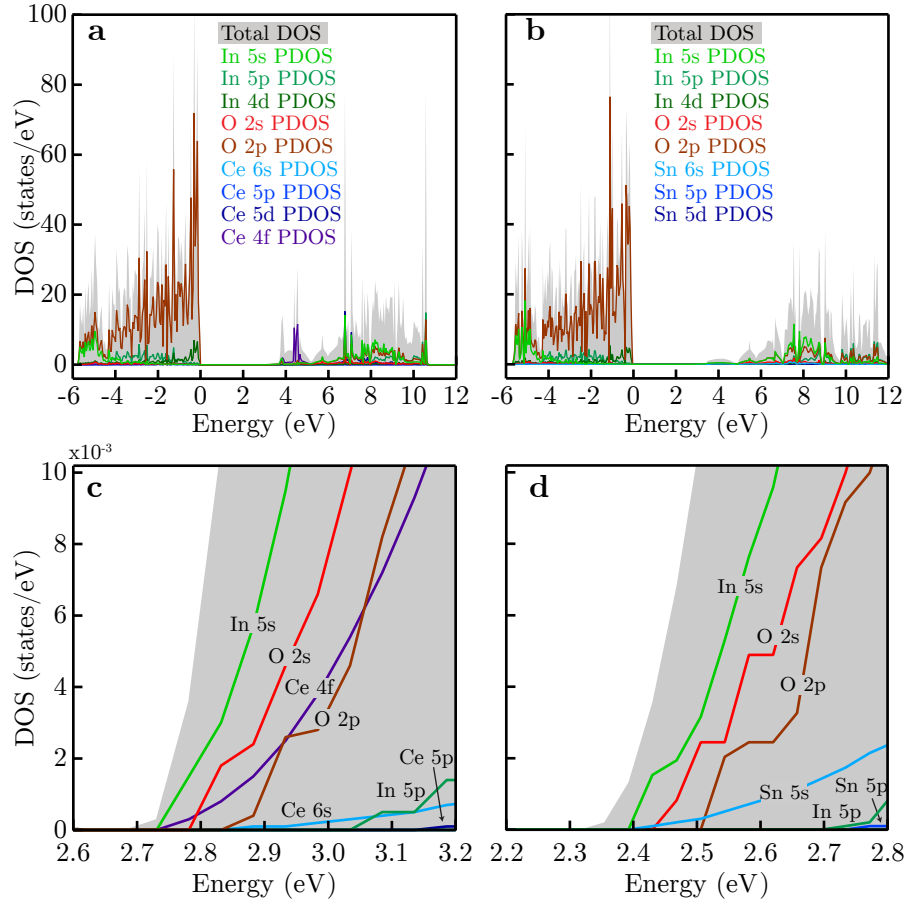


Figure 7.9: Density of states of Ce:In₂O₃ and Sn:In₂O₃ calculated by DFT. a: Total and partial density of states for a 40 atom primitive In₂O₃ unit cell containing one substitutional Ce dopant. The valence band maximum is set to 0 eV. b: Total and partial density of states for a 40 atom primitive In₂O₃ unit cell containing one substitutional Sn dopant. c: Detailed view of the total and partial DOS at the conduction band edge for Ce:In₂O₃. d: Detailed view of the total and partial DOS at the conduction band edge for Sn:In₂O₃.

In effect, the electronic structure of Ce:In₂O₃ is such that the dopant ions are effectively electrostatically screened and are not expected to strongly scatter free electrons. Moving electrons in Ce:In₂O₃ effectively experience the same electronic potentials as they would in intrinsic In₂O₃ due to this remote screening, limiting ionized impurity scattering in a manner analogous to modulation doping, where ionized dopants are spatially separated from conducting electrons.²⁸⁸ Here, the *electronic* separation in energy and/or orbital shape of dopant levels from the conduction states suppresses ionized impurity scattering and is likely the primary driver of enhanced mobility. Combined with our defect calculations, which suggest reduced oxygen vacancy concentrations with Ce doping, these electronic structure effects explain why we observe such narrow LSPR peaks and high electronic mobilities in Ce:In₂O₃ nanocrystals.

Based on their exceptional LSPR properties, we set out to evaluate the potential of Ce:In₂O₃ nanocrystals for near field enhancement applications. We measured absorption spectra of single nanocrystals using synchrotron infrared nano-spectroscopy (SINS, Figure 7.10a), which utilizes near field concentration of light by a metallic AFM tip positioned just above an isolated nanoscale object (Figure 7.10c) to collect an FTIR spectrum of that object.²⁸⁹ Our group has recently pioneered the use of this technique to interrogate single Sn:In₂O₃ and Al:ZnO nanocrystals in order to measure LSPR properties without the influence of ensemble peak broadening due to size, shape, or dopant heterogeneity.²²⁵ We collected SINS spectra (which can effectively correspond to absorption spectra)²⁹⁰ of several individual cubic-shaped Ce:In₂O₃ nanocrystals with average 5.2% Ce (Figures 7.10a, A.5) and observed linewidths as narrow as 479 cm⁻¹ (59 meV), corresponding to a quality factor of 5.5 for a single nanocrystal, compared to 4.08 for the ensemble, meaning that some peak broadening is the result of inhomogeneous broadening. This result highlights the plasmonic performance of Ce:In₂O₃ nanocrystals and the usefulness of SINS; the plasmonic damping in this material is actually nearly 25% less than ensemble measurements suggest.

To simulate near field enhancement around a nanocrystal, it is necessary to know its frequency-dependent dielectric function (Equation 7.1). Here, we use the SINS spectrum of a single, isolated nanocrystal to extract a materials-specific dielectric function free of effective medium complications and artifacts that would arise from ensemble peak broadening. Experimental SINS spectra contain the scattering and absorption properties of a coupled PtSi—Ce:In₂O₃—Au (tip-nanocrystal-substrate) system; to accurately generate a dielectric function for the Ce:In₂O₃ nanocrystal free of tip or substrate influence, we computationally solved Maxwell’s equations for this system using the finite element method (COMSOL multiphysics program) to discretize each component. Using our ensemble Drude model fit as an initial guess for the nanocrystal dielectric function, along with known dielectric functions for PtSi and Au, we simulated the SINS spectrum and iteratively adjusted the plasma frequency and damping functions in the dielectric function until the simulated spectrum matched the experimentally measured spectrum (Figures 7.10a, A.6). The dielectric function of the nanocrystal, estimated as such, allowed us to simulate the absorption, scattering, and near field properties of an isolated nanocrystal without tip or substrate influence.

We simulated the enhancement of incident light electric field intensity around a cubic

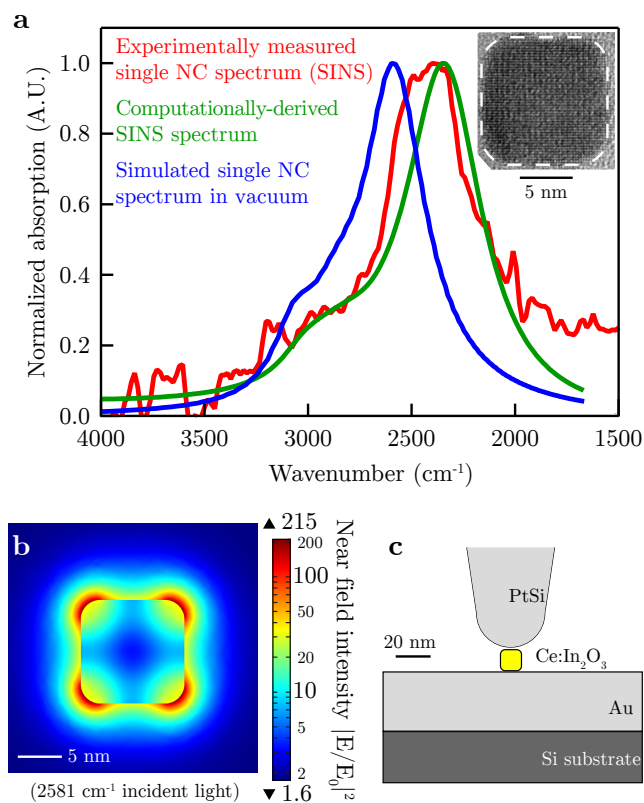


Figure 7.10: LSPR properties of $\text{Ce:In}_2\text{O}_3$ single nanocrystals. a: Experimentally collected SINS spectrum (red line) of a single cubic nanocrystal with 5.2% Ce, simulated SINS spectrum (green line) used to determine the dielectric function and simulate the absorption spectrum (blue line) of a single isolated nanocrystal. Inset: TEM of the nanocrystal used as a model. b: Simulated near field intensity map of the model nanocrystal illuminated at the LSPR peak frequency. c: Depiction of the geometry used to model and discretize the coupled substrate-nanocrystal-tip system in the SINS experiment (drawn to scale except for the thickness of the Si substrate).

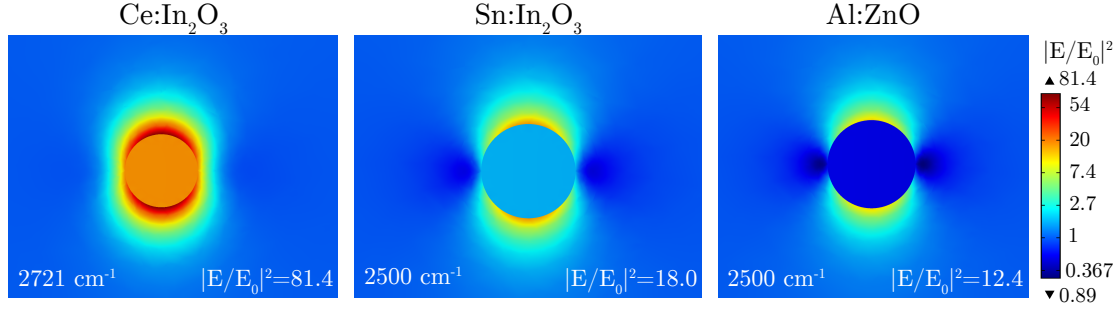


Figure 7.11: Simulated near field intensity maps of spherical Ce:In₂O₃ nanocrystals compared to Sn:In₂O₃ and Al:ZnO nanocrystals. The incident light frequency (chosen as the LSPR peak) is listed in the lower left of each panel, and the maximum near field intensity enhancement factor is listed in the lower right of each panel.

Ce:In₂O₃ nanocrystal by using the dielectric function to solve Maxwell's equations throughout the discretized nanocrystal (Figure 7.10b). Incident light, polarized along one of the cube axes and with a frequency of 2581 cm⁻¹, excites a dipolar LSPR mode with a maximum near field intensity enhancement factor of 215 relative to the incident intensity. The electric field and near field enhancement maps of other modes are shown in Figure A.7. The benefits of nanocrystal shape control are clear, as the near field enhancement is strongest near the cube vertices, and simulated near field enhancement factors around a spherical Ce:In₂O₃ nanocrystal reached only 81 (Figure 7.11). Overall, for an equivalent plasma frequency, Ce:In₂O₃ nanocrystals exhibit much stronger field enhancement than the other nanocrystals for which we have approximate dielectric functions to simulate near field enhancement, namely Sn:In₂O₃ and Al:ZnO (Figure 7.11). These simulations underscore the advantages of low loss Ce:In₂O₃ nanocrystals for field enhancement applications like SEIRA.

7.4 Conclusion

We have shown here that by purposefully choosing a dopant that minimizes ionized impurity scattering, doped metal oxide nanocrystals can exhibit high electronic mobilities, very narrow LSPR peaks, and strong near field enhancement. The predicted near field performance of Ce:In₂O₃ nanocrystals points to their potential for applications that rely on intense light concentration well below the diffraction limit. Ce:In₂O₃ nanocrystals would be good candidates for SEIRA substrates, where they could be tuned to resonantly couple to and enhance molecular vibration signals throughout the MIR for spectroscopy or sensing applications. From an application perspective, the colloidal nature of Ce:In₂O₃ provides a distinct advantage: many of the other recently-described systems with MIR plasmons, including nanostructured Sn:In₂O₃ thin films,²¹³ patterned graphene,²⁹¹ doped silicon nanowires,²⁹² or gold antenna arrays,²⁹³ require complex lithography or other nanostructuring techniques that limit options for their integration in different environments and effectively preclude

large scale applications. In contrast, colloidal nanocrystals are readily dispersed in fluid environments or on substrates and can be made to self-assemble into superlattices^{294–296} (with plasmonic hotspots between nanocrystals¹³⁹), and colloidal synthesis has been demonstrated as a scalable technique.¹⁰²

We hope that this report spurs additional research and development of Ce:In₂O₃, specifically. Based on our results, Ce:In₂O₃ offers a rich platform for studying the interplay between synthesis, defect chemistry, electronic properties, and performance. For example, Ce:In₂O₃ thin films would be particularly useful for transparent conductor applications that require low carrier concentration and high mobility, such as thin film photovoltaics.⁷⁴ Finally, the strategies incorporated here—rational dopant selection and defect engineering—could be applied to manipulate the electronic and plasmonic properties of any number of doped metal oxides. This suggestion comes at a time that growing efforts are underway to discover new transparent conductors incorporating unusual dopants,^{264;265} multiple elements,^{297;298} or correlated electron metals.²⁹⁹ To advance the understanding and control of LSPR in doped oxide nanocrystals, we plan to extend this strategy to study the influence of alternative dopants on the LSPR properties in other metal oxide hosts like TiO₂, ZnO, and SnO₂.

Part III

Nanocrystalline ceramics: ion transport at nanocrystal surfaces

Chapter 8

Intermediate temperature proton conduction in ceramic nanocrystal films

“Defects form the basis for diffusion and conductivity in crystalline solids.”

— Prof. T. Norby

Adapted from:

Runnerstrom, E.L.; Ong, G.K.; Gregori, G.; Maier, J.; Milliron, D.J. Colloidal Nanocrystal Films Reveal the Mechanism for Intermediate Temperature Proton Conductivity in Porous Ceramics, in preparation.

8.1 Introduction

Solid-state proton conduction is an important phenomenon with numerous consequences for electrochemical energy storage and conversion.^{300–304} Nonetheless, gaining a full understanding of and ability to manipulate proton transport in solids remains a pressing and interesting scientific and technological challenge. Proton-conducting membranes and solid electrolytes are critical components in many electrochemical devices and clean energy technologies, particularly fuel cells, and the performance of such devices is often limited by proton transport.^{300;305–308} Well-studied solid materials (Figure 8.1) that support proton conduction include polymers such as Nafion,^{300–304;306;308} solid acids such as CsHSO₄,^{309;310} and high-temperature proton-conducting ternary oxides such as BaZrO₃ and BaCeO₃.^{305;307;311} Despite the wealth of knowledge in this field, these materials have significant shortcomings. While proton exchange membranes can exhibit conductivities comparable to aqueous acid solutions ($\sigma > 10^{-1}$ S/cm),³⁰³ Nafion is expensive and has very poor conductivity at temperatures above 85–90°C due to dehydration.^{300;302;303;306} Meanwhile, the ceramic oxide-based proton conductors require high operating temperatures (350°C–800°C, with conductivity reaching 10^{-2} S/cm

only above 400°C) and can decompose under typical fuel cell operating conditions.^{303;305;307;311} Additionally, the performance and stability of ceramic proton conductors have lagged behind those of ceramic oxygen-ion conductors (i.e., yttria-stabilized zirconia and acceptor-doped ceria, with $\sigma > 1$ S/cm),^{303;307;311} favoring the development of high-temperature solid oxide fuel cells (SOFCs) based on said ceramics. Whether using ceramic proton or oxygen ion conductors, high-temperature fuel cell operation requires exotic and expensive electroceramic materials to connect multiple cells in series, induces thermal stresses and degradation, and requires large energy input to heat the cell up to operating temperature, all of which complicate operation, decrease efficiency, and increase costs.³⁰⁷ Hence, there is great interest in alternative proton conducting materials with the potential to enable fuel cell operation in the “gap” that currently exists at intermediate temperatures between 200°C and 500°C, which is a desirable range for energy conversion and electrochemical processes, and which would also enable advances in fuel cell power output and mobility.^{303;307;310}

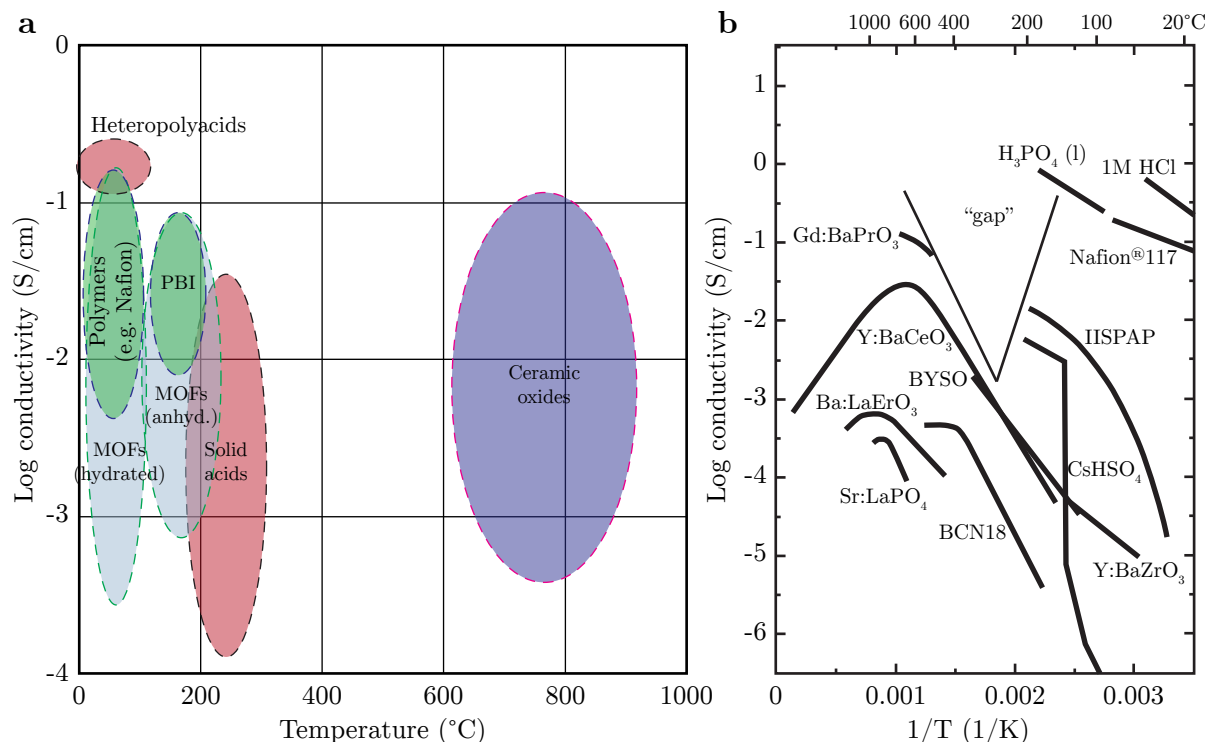


Figure 8.1: Temperature-dependent conductivities of common proton conductors. a) General proton conductors grouped by material types. b) Temperature-dependent conductivities of specific materials. Note the intermediate temperature conductivity “gap” in both panels. Panel (a) adapted with permission from Reference³¹², Copyright 2013 Wiley. Panel (b) adapted with permission from Reference³⁰³, Copyright 1999 Elsevier.

8.1.1 State of the literature

Unsurprisingly, research in this field has steadily grown over the past 10 years; motivated in part by the shortcomings of polymeric and solid oxide proton-conducting materials, significant advances have recently been made to understand proton transport through inorganic and hybrid organic-inorganic materials with high porosities and/or surface area-to-volume ratios. Such porosity and high specific surface area, which may be introduced through nanostructuring or may be intrinsic to the structure of these materials, has been found to bestow significant proton conductivity to these materials under humidified atmospheres. Some noteworthy examples include porous sol-gel silica glasses,³¹³ sol-gel anatase titanium dioxide (TiO₂) thin films,^{314;315} porous metal-organic frameworks,³¹² graphene oxide nanosheets,³¹⁶ and mesoporous networks of silica-phosphotungstic acid hybrids.³¹⁷ Interestingly, porous nanocrystalline ceramics, some of which are closely related to high-temperature oxygen ion conductors, have garnered significant attention for their proton conductivity at moderate temperatures. These include yttrium-stabilized zirconia (YSZ),^{318–325} samarium- and gadolinium-doped cerium oxide (SDC/GDC),^{319;326–329} and pure cerium oxide (CeO₂),^{328–330} which are all fluorite-type oxides that are most often studied as high-temperature oxygen ion conductors. All of these materials are poor proton conductors in their bulk form, yet nanocrystalline samples of these, as well as TiO₂,^{331;332} display significant proton conductivity at temperatures below 200°C in humidified atmospheres. A notable shared characteristic among these ceramics is a high concentration of extrinsic oxygen vacancies or the ability to support significant intrinsic oxygen vacancy concentrations at low oxygen activity.

In early work, Kim and coworkers observed intermediate-temperature proton conductivity in fine-grained YSZ under humid environments, publishing a series of papers between 2008 and 2010 demonstrating conductivities of $\sigma \sim 10^{-7}$ to 10^{-10} S/cm between room temperature and 120°C.^{319;320;322} The authors suggested that grain boundaries were the proton transport paths and attributed the conductivity to the high density of these defects in the sintered material. Subsequent work, however, suggested that proton conduction in nanocrystalline YSZ arises from residual open porosity that is typically present in nanocrystalline ceramics, owing to low sintering temperatures.^{324;325;328} Indeed, Pietrowski and coworkers, in 2012, observed water adsorption onto internal surfaces of nanocrystalline YSZ via infrared spectroscopy,³³³ and an interconnected porous network with surface-adsorbed water likely facilitates proton transport at intermediate temperatures.^{324;325;328} Conversely, fully dense films of nanocrystalline YSZ conduct only oxygen ions and do not support proton conduction, except along the sample surface at temperatures below 50°C.^{323;325}

In 2011, Shirpour and coworkers observed proton conduction at and below 250°C in nanocrystalline CeO₂ and GDC ($\sigma \sim 10^{-4}$ to 10^{-6} S/cm between 100°C and 250°C), and demonstrated that the mechanism likely involved adsorption of a water network into wedge-shaped, interconnected pores.³²⁸ Following up in 2013, the Maier group confirmed that only mesoporous CeO₂ exhibited proton conductivity under wet conditions, up to temperatures as high as 300°C, while dense films, whether nanocrystalline or not, did not conduct protons (Figure 8.2).³²⁹ These observations firmly established porosity, rather than grain boundaries,

as the central factor for proton transport through metal oxides at intermediate and low temperatures. Contemporary work by Oh and coworkers, studying proton conduction in CeO_2 thin films with nanoscale columnar grains, supported these conclusions by confirming that proton conduction occurs as a result of the adsorption of water inside of pores.³³⁰ That report also discussed some possible mechanisms, namely dissociative adsorption of water at CeO_2 surface oxygen vacancy sites. More recently, Tredici et al. examined low- and intermediate-temperature proton conductivity in nanocrystalline TiO_2 of various grain sizes and porosity using solid-state NMR.³³² They found that both physisorbed water and chemisorbed hydroxyl moieties contributed to proton conduction at low and intermediate temperatures, respectively. Other recent work includes that by Ding et al., who used time-resolved Kelvin probe force microscopy to interrogate water splitting and charge transport in a nanostructured CeO_2 -based electrochemical device, and Jiang and Hertz's study on intermediate proton conduction on the surface of YSZ ultra thin films. Both of these studies strongly suggest that oxygen defects in nanocrystalline ceramics play an important role in proton transport.^{334;335} Nevertheless, the mechanism for proton generation and conduction in porous oxides is still not fully understood since the studies reported to date have examined only singular material compositions without systematic control over structural parameters such as pore dimensions, oxygen activity and defect equilibria, or surface chemistry.

8.1.2 Motivation

Taken together, the results of the past few years imply that proton transport in nanocrystalline oxides is enabled by: 1) porosity, pore size, and specific surface area, which influence water adsorption, and 2) the interactions between adsorbed water and metal oxide surfaces. It is likely that the latter not only mediates proton diffusion at surfaces or through adsorbed water layers, but may also be responsible for generating protonic charge carriers in the first place. Because physical fabrication processes, such as sintering, were typically used to fabricate these nanocrystalline films in the past, fine control over crystallite size, exposed surface area, and pore size and shape has not been possible and the effects of these variables on proton conduction at intermediate temperatures have not been systematically revealed. Here, we address this problem by using colloidal ceramic nanocrystals of CeO_2 and TiO_2 that are synthesized with controlled size. By processing the nanocrystals into continuous films and removing their native surface-bound ligands, we generate microporous nanocrystalline thin films with well-defined crystallite size, pore size, and exposed surface area. Conductivity measurements using AC impedance spectroscopy in a controlled temperature and gas environment with controlled humidity revealed proton conduction in both CeO_2 and TiO_2 films at intermediate temperatures. Furthermore, we found that the proton conductivity was strongly modulated by the partial pressure of oxygen, as samples under humid oxygen displayed orders of magnitude reduction in conductivity compared to samples under argon, a phenomenon that appears to be general but has not been previously reported for nanocrystalline ceramics. Based on these new observations and consistencies across the literature,

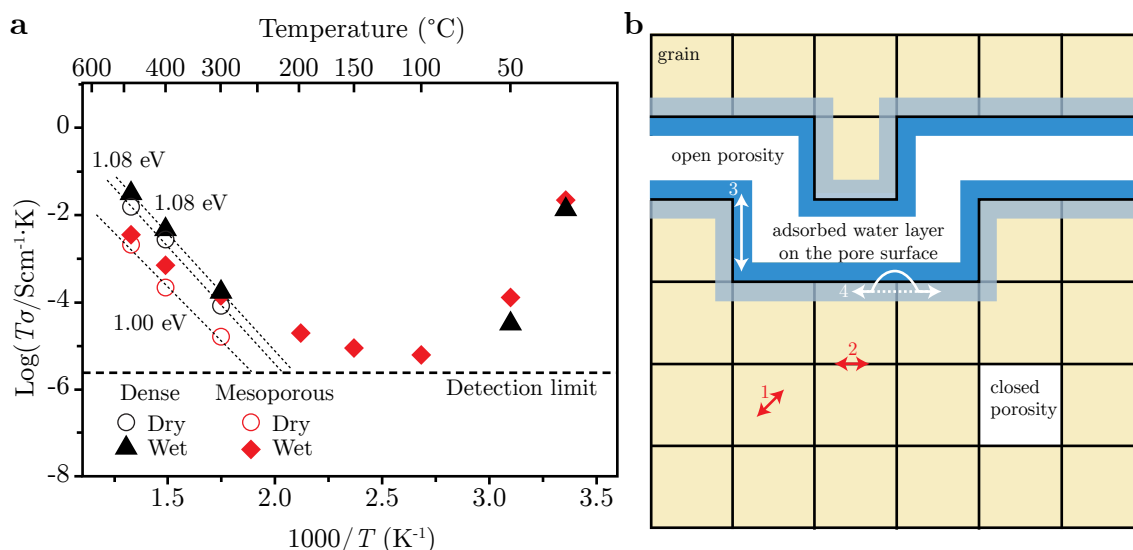


Figure 8.2: Previously published results from the Maier group measuring proton conductivity in dense and mesoporous nanocrystalline CeO_2 thin films. a) Arrhenius plot showing evidence of intermediate temperature proton conductivity in mesoporous nanocrystalline ceria under wet conditions (red diamonds), while the dense nanocrystalline ceria film (black triangles) does not exhibit proton conductivity, except for at the sample surface at 50°C. b) Previously proposed proton conduction mechanisms: 1) transport within the bulk; 2) transport along grain boundaries; 3) transport through water adsorbed onto open pore walls; 4) proton injection and transport into a proton-enriched layer below the pore surface. Figure adapted with permission from Reference³²⁹, Copyright 2013 Wiley.

we conclude that proton conduction in nanocrystalline metal oxides arises from dissociative water adsorption and interface-mediated transport at active surface defect sites.

8.2 Experimental

8.2.1 Synthetic methods

We synthesized CeO_2 and TiO_2 colloidal nanocrystals using adaptations of published literature methods.^{200;336} Cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \bullet 6\text{H}_2\text{O}$, 99.99%), titanium (IV) butoxide ($\text{Ti}(\text{OBu})_4$, 97%), oleic acid (OLAC, 90%), octadecylamine (ODAM, 90%), 1-octadecene (ODE, 90%), 200 proof ethanol, octane (98%) formic acid (reagent grade), and acetonitrile (ACN, ACS grade) were purchased from Sigma Aldrich. Oleylamine (OLAM, 80-90%) was purchased from Acros Organics. Hexane (ACS grade), chloroform (CHCl_3 , ACS grade) and denatured ethanol (EtOH, ACS grade) were purchased from BDH. Ultra-pure water was obtained using an EMD Millipore Milli-Q water purification system.

To synthesize 3.9 nm CeO_2 nanocrystals, 2 mmol $\text{Ce}(\text{NO}_3)_3 \bullet 6\text{H}_2\text{O}$ was combined with 24 mmol OLAM and 5 mL ODE in a 50 mL round bottom flask under inert nitrogen atmosphere. Under constant magnetic stirring, the temperature of the reaction mixture was raised to 80°C for 30 minutes, and then the temperature was raised to 250°C for 2 hours to nucleate and grow the nanocrystals. After the reaction, the nanocrystals were purified by four cycles of flocculation with EtOH, centrifugation, and redispersion in hexane. Finally, the nanocrystals were dispersed in a 1:1 volumetric mixture of hexane:octane at a concentration of 33 mg/mL and filtered with a 0.2 micron poly(tetrafluoroethylene) syringe filter.

To synthesize 9.9 nm CeO_2 nanocrystals, 15 mmol ODA, 15 mmol OLAM, and 5 mL ODE were combined in a 50 mL round bottom flask under inert nitrogen atmosphere. Under constant magnetic stirring, this mixture was heated to 70°C to melt the ODA, upon which 10 mmol $\text{Ce}(\text{NO}_3)_3 \bullet 6\text{H}_2\text{O}$ and 0.725 mL ultra-pure water were added to the flask. The mixture was then slowly heated to 175°C over 30 minutes to homogenize the solution before raising the temperature further to 230°C to nucleate and grow the nanocrystals. After about 2 minutes at 230°C, the reaction was complete when a large amount of smoke was released (presumably NO_2 gas) and the solution instantaneously became optically clear and a deep brown color. The nanocrystals were purified by the same methods as the 3.9 nm CeO_2 nanocrystals, except that this sample was additionally subjected to three rounds of size-selective precipitation to improve uniformity. Finally, the nanocrystals were dispersed in 1:1 hexane:octane at a concentration of 37 mg/mL and filtered. DANGER: without adequate ventilation or pressure relief, this reaction is prone to over-pressurization as the nitrate precursor violently decomposes to liberate large volumes of NO_2 gas.

To synthesize 6.7 nm TiO_2 nanocrystals, 5 mmol $\text{Ti}(\text{OBu})_4$, 30 mmol OLAC, 20 mmol OLAM, and 100 mmol 200 proof ethanol were combined and stirred for 30 minutes before being transferred into a 40 mL Teflon cup. The cup was placed inside a 100 mL Teflon-lined stainless steel autoclave, which contained 19.8 mL of 200 proof ethanol and 0.8 mL of ultra-pure water. The autoclave was then sealed and placed into a 180°C oven for 18 hours. After the reaction, the nanocrystals were purified by four cycles of precipitation with EtOH, centrifugation, and redispersion in hexane, before finally being dispersed in 1:1 hexane:octane by volume and filtered.

Transmission electron microscopy (TEM) was performed using a Zeiss Libra 120 operating at 120 kV accelerating voltage. Particle size analysis was performed on TEM micrographs using ImageJ to measure the diameters of at least 320 nanocrystals from each sample. Powder and thin film X-ray diffraction (XRD) was performed on a Bruker AXS D8 Discover X-ray diffractometer equipped with a GADDS area detector in Bragg-Bretano geometry, using Cu $K\alpha$ radiation.

8.2.2 Film fabrication and conductivity measurements

We fabricated the nanocrystal-based thin films by spincoating the 1:1 hexane:octane dispersions onto 1x1 cm ultrasonically-cleaned (Hellmanex detergent, acetone, isopropanol) quartz substrates. Following spincoating, we employed a ligand exchange and removal procedure previously developed in our laboratory to generate open microporosity within the films by removing the organic ligands surrounding each nanocrystal.^{28;337} This method replaces the native OLAM or OLAC ligands on the nanocrystal surfaces with formic acid, which is volatile and easily baked off leaving no detectable residue. The films were soaked in a 0.1 M solution of formic acid in acetonitrile for 10 minutes, rinsed four times with an equal mixture of ACN/ CHCl_3 , and baked in air for 10 minutes on a hot plate held at 300°C. The entire procedure was repeated two more times to generate films with desired thicknesses close to 300 nm for transport measurements.

For conductivity measurements, we prepared samples on quartz substrates and deposited two 400 nm thick, 4.5 mm by 10 mm area parallel platinum electrodes onto the top surface of the nanocrystal film using an Edwards Auto 306 sputtering system (60W, 30 minutes), leaving a 1 mm by 10 mm uncoated region between them. In situ conductivity measurements were performed with the sample in a controlled environment measurement cell, depicted in Figure 8.3. This cell allowed us to vary temperature, carrier gas (grade 5.0 Ar or O_2), and humidity; wet atmospheres were achieved by bubbling the carrier gas through a water bubbler held at 17°C ($p\text{H}_2\text{O} = 20$ mbar). To measure conductivity, we used AC impedance spectroscopy (Novocontrol Alpha-A impedance analyzer) over a frequency range of 1 MHz to 1-10 Hz, with a voltage amplitude of 0.12 V, and allowed the samples to equilibrate with the surrounding environment for at least 2 hours at each temperature before recording the reported conductivity values.

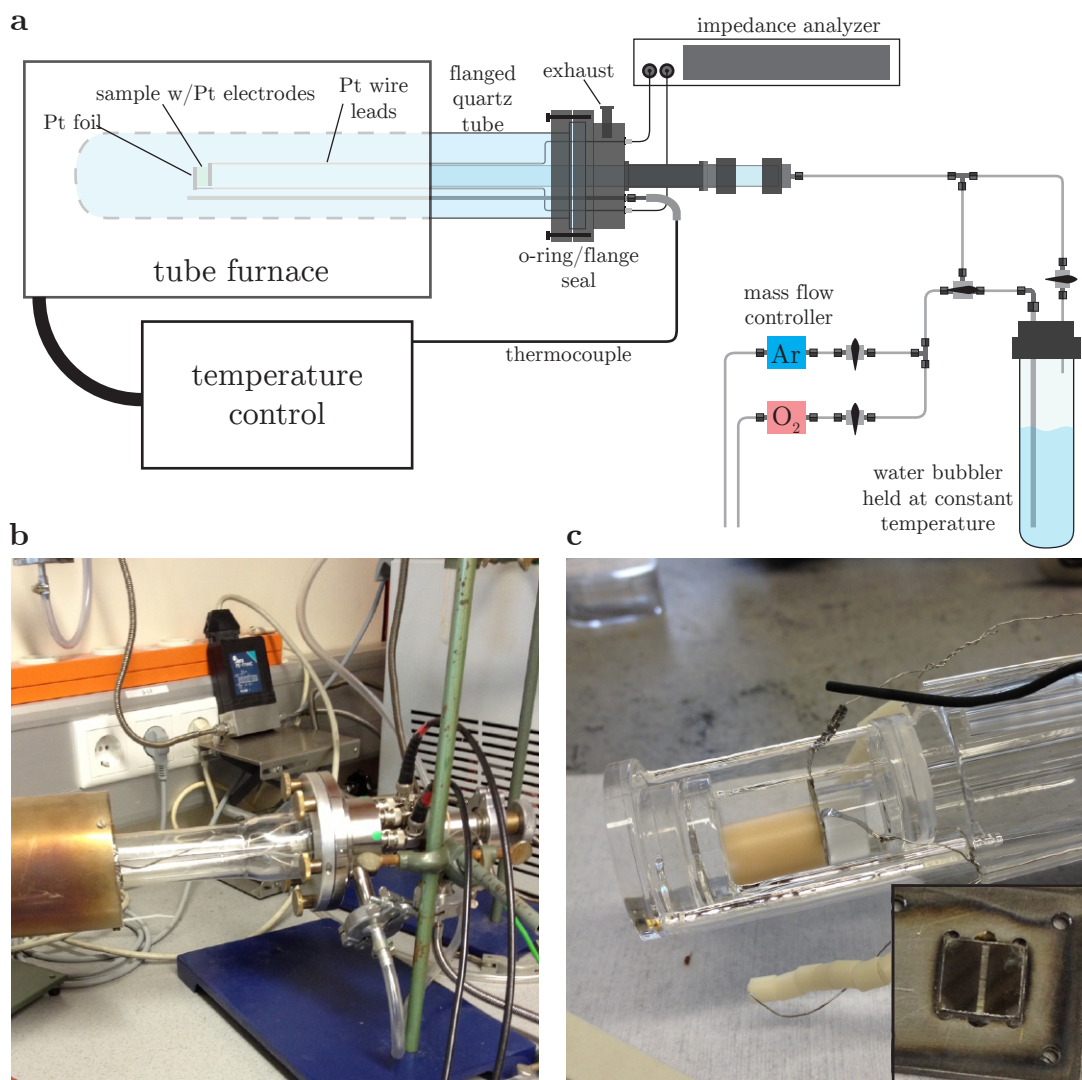


Figure 8.3: Variable temperature and environment measurement cell. a: Schematic of setup. b: Photograph of measurement cell and supporting instrumentation. c: Detail photograph of sample seated in the measurement cell. Inset: detail photograph of sample with deposited Pt contacts.

8.3 Results and discussion

8.3.1 Physical characterization

The TEM micrographs displayed in Figure 8.4 show that the nanocrystals used in this study are relatively uniform with distinct and tunable size, which allows us to controllably study the influence of grain size and porosity on proton conduction. Particle size analysis confirms

that the samples have well-defined grain sizes with respect to each other. The standard deviations in diameter for the 3.9 nm CeO₂, 9.9 nm CeO₂, and 6.7 nm TiO₂ nanocrystals were 0.6, 1.2, and 0.8 nm, respectively. The powder XRD (Figure 8.5) patterns for both CeO₂ samples matched that of the fluorite CeO₂ crystal structure, while the XRD pattern for the TiO₂ sample was indexed to the anatase phase.

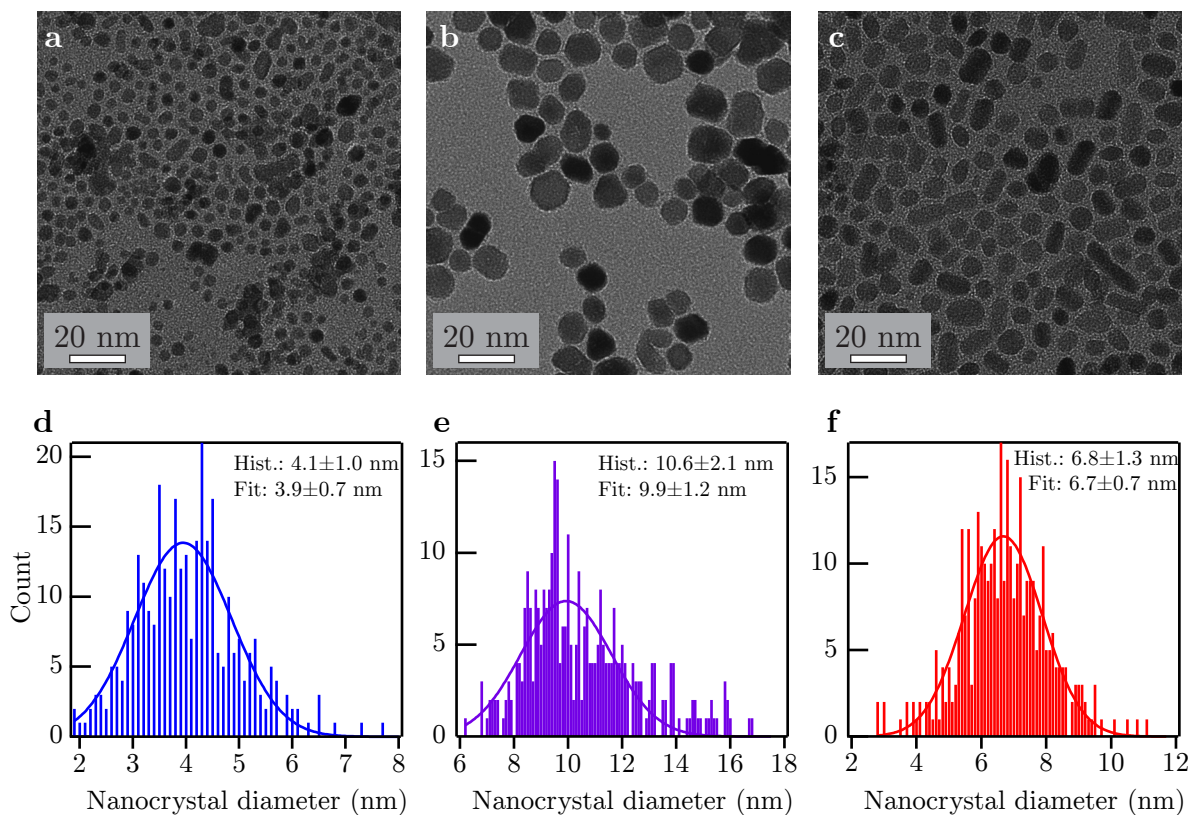


Figure 8.4: TEM characterization of colloidal CeO₂ and TiO₂ nanocrystals. a: TEM micrograph of CeO₂ with average diameter of 3.9 nm. b: TEM micrograph of CeO₂ with average diameter of 9.9 nm. c: TEM micrograph of TiO₂ with average diameter of 6.7 nm. d-f: Size distribution histograms for the nanocrystals used in this study. The average size and standard deviation is listed in each panel for both the histogram and the Gaussian fit to the histogram. d: 3.9 nm CeO₂. e: 9.9 nm CeO₂. f: 6.7 nm TiO₂.

During nanocrystal film fabrication, we tracked the ligand exchange process using Fourier transform infrared spectroscopy (FTIR, Figure 8.6) at room temperature and under ambient conditions. FTIR allows us to monitor the alkyl C-H stretching modes between 2800-2900 cm⁻¹ for films deposited on double-polished, undoped silicon. The films as deposited display strong C-H peaks, indicating the presence of organic ligands at the nanocrystal surfaces. After the formic acid soak and rinse, the C-H stretch is strongly diminished in intensity, indicating that the long alkyl chain ligands have been displaced and washed out of the film.

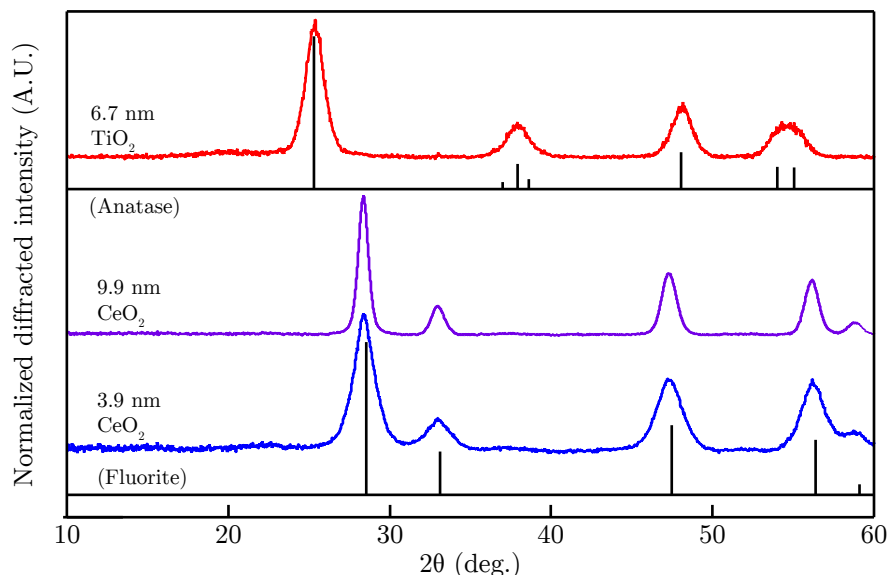


Figure 8.5: Powder XRD patterns of CeO_2 and TiO_2 nanocrystal samples. The CeO_2 samples are indexed to the cubic fluorite structure (reference pattern from PDF card no. 01-081-0792) and the TiO_2 sample is indexed to the tetragonal anatase structure (reference pattern from PDF card no. 01-075-2547).

Finally, after the film is baked and returned to room temperature under ambient conditions, the C-H stretch is eliminated, indicating the complete removal of organics from the film and the generation of open porosity. FTIR also confirms that this process works over multiple deposition cycles to build up thick, porous films. The appearance of a broad O-H peak at around 3400 cm^{-1} after the baking step confirms that the films are porous and adsorb water vapor from the atmosphere. We note that the 3.9 nm CeO_2 appears to adsorb significantly more water than either the 9.9 nm CeO_2 or 6.7 nm TiO_2 samples, the last of which appears to adsorb the least amount of water. These differences in water vapor uptake at room temperature presage differing abilities to conduct protons within the pores, which will be discussed below.

To confirm the open porosity and nanocrystalline character of our films, we imaged them with scanning electron microscopy (SEM). To ensure that the conditions for measuring proton transport would not coarsen the films or collapse their porosity, we further annealed samples deposited on silicon at 500°C for two hours under argon. Representative top-down and cross-sectional SEM images (Figure 8.7) of these samples reveal that the films maintain their porosity and nanocrystalline character, and Scherrer analysis of XRD patterns before and after annealing confirms that the grain size did not increase appreciably (Figure 8.8).

We also performed ellipsometric porosimetry (EP) to measure the pore size and distribution of our films deposited on undoped silicon.^{338–340} The EP data were acquired using a Semilab PS-1100R ellipsometric porosimeter, with toluene as the adsorbant, and the results

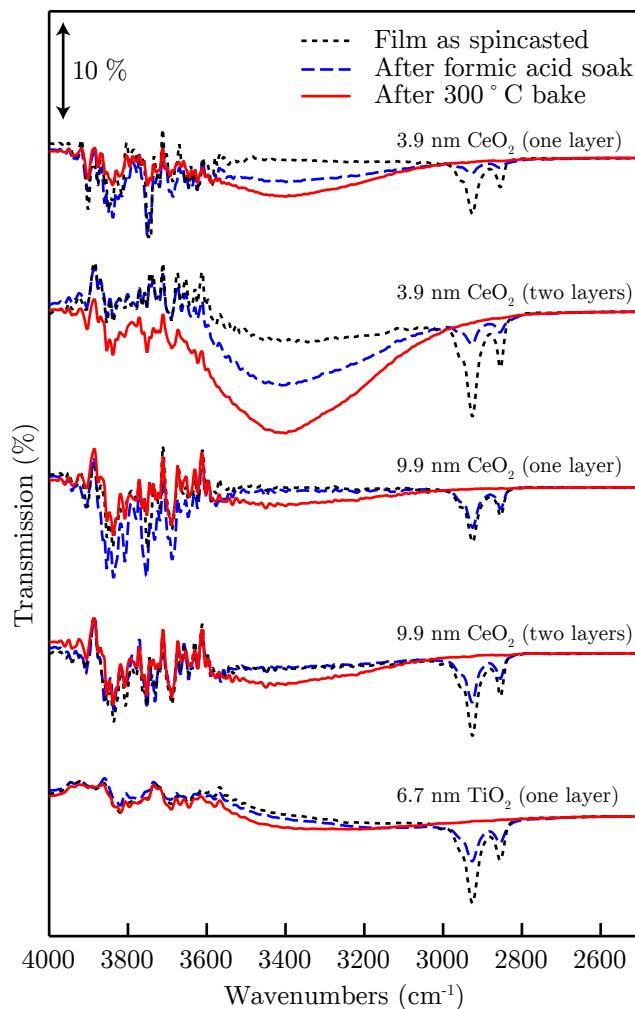


Figure 8.6: FTIR spectroscopy tracking ligand exchange process of CeO_2 and TiO_2 nanocrystal films on undoped silicon. The spectra displayed, which are offset for clarity, are of the films after spincoating (small black dashed lines), after the formic acid soak and rinse (larger blue dashes), and after the 300°C bake (solid red), confirming the removal of organics from the film by the disappearance of the C-H stretching bands at $\sim 2800\text{--}2900\text{ cm}^{-1}$. The sharp peaks between 3900 and 3600 cm^{-1} are instrumental noise.

were analyzed using the Semilab SEA software for ellipsometry fitting at different pressures (Figure 8.9). EP allows for a direct measurement of porosity and pore size distribution in our films by measuring how the refractive index changes with solvent partial pressure as the film takes up solvent.

The EP results for the nanocrystal films, including the porosity isotherm, mesopore size distribution, and micropore size distribution (for pore radii $<1\text{ nm}$, calculated using the Dubinin-Raduchkevish model)^{341;342} are shown in Figure 8.10, and summarized in Table 8.1.

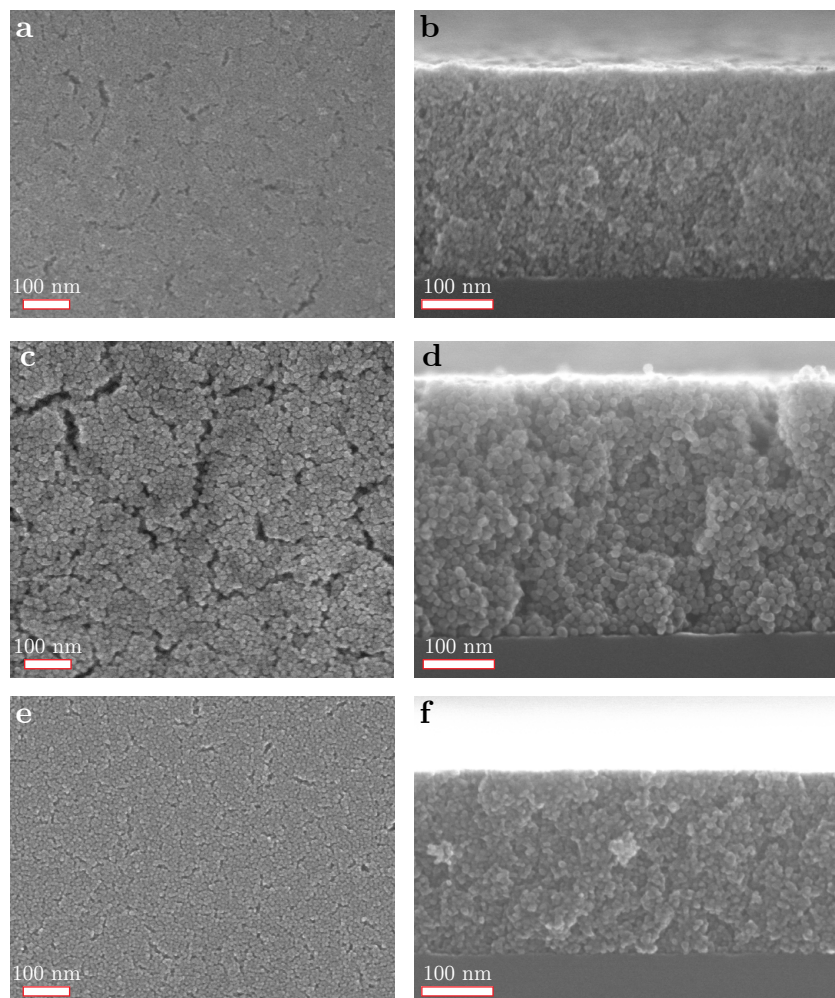


Figure 8.7: SEM characterization of porous nanocrystal films. a: Top-down SEM micrograph of a film made from 3.9 nm CeO_2 nanocrystals after annealing at 500°C for two hours. b: Cross-section SEM micrograph of same film. c: Top-down SEM micrograph of a film made from 9.9 nm CeO_2 nanocrystals after annealing at 500°C for two hours. d: Cross-section SEM micrograph of same film. e: Top-down SEM micrograph of a film made from 6.7 nm TiO_2 nanocrystals after annealing at 500°C for two hours. f: Cross-section SEM micrograph of same film.

The hysteresis in the adsorption and desorption curves at intermediate pressures (Figure 8.10a, d, g) is characteristic of open and accessible mesopores throughout the film. The hysteresis occurs because the radius of curvature of the liquid meniscus within the pores is different during adsorption than during desorption, leading to different critical pore radii for capillary condensation and evaporation during the adsorption and desorption steps, respectively. Additionally, the significant solvent uptake and lack of hysteresis at low pressures

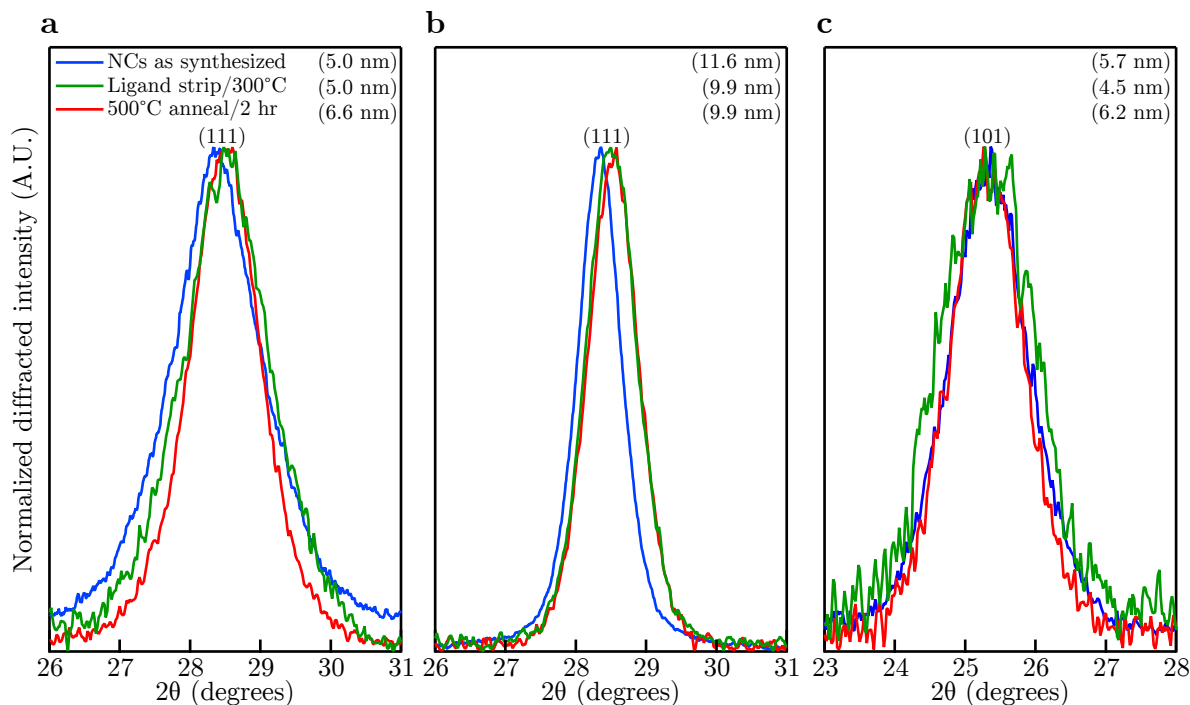


Figure 8.8: Thin-film XRD patterns ($\theta - 2\theta$ scans) of nanocrystal films after annealing at 500°C for two hours under Ar. Scherrer grain size analysis was performed on the main diffraction peak (listed above the peak). The calculated grain size is listed in the upper right corner of each panel. a) 3.9 nm CeO₂. b) 9.9 nm CeO₂. c) 6.7 nm TiO₂.

indicates the presence of significant microporosity within the film. Finally, the shape of the hysteresis loop (broader on adsorption, steeper during desorption) is indicative of approximately spherical or cylindrical pores connected by smaller cylindrical pore necks in an “ink bottle” geometry.³⁴³ This effect arises from solvent in the larger pores being unable to evaporate at the partial pressure associated with the critical pore radius, because the partial pressure is still too high for the adsorbed solvent in the smaller pore necks or interconnections to undergo capillary evaporation. Ultimately, once the pressure is low enough to evacuate the smaller pore necks, the solvent evaporates from the large and small pores simultaneously, leading to the sharper drop in the desorption curve.³⁴³ While the 9.9 nm CeO₂ nanocrystal film presents a higher overall porosity and larger mesopore size, visual examination of the SEM micrographs indicates that these differences arise mostly from some small cracks and voids in the film. The 3.9 nm CeO₂ and 6.7 nm TiO₂ nanocrystal films present nearly identical morphologies with respect to porosity and pore size; this similarity means that differences in proton transport will result from material, rather than morphological, differences. This will prove valuable when we compare the proton transport characteristics of both films, below. Notably, the micropore radii for all three samples are very similar.

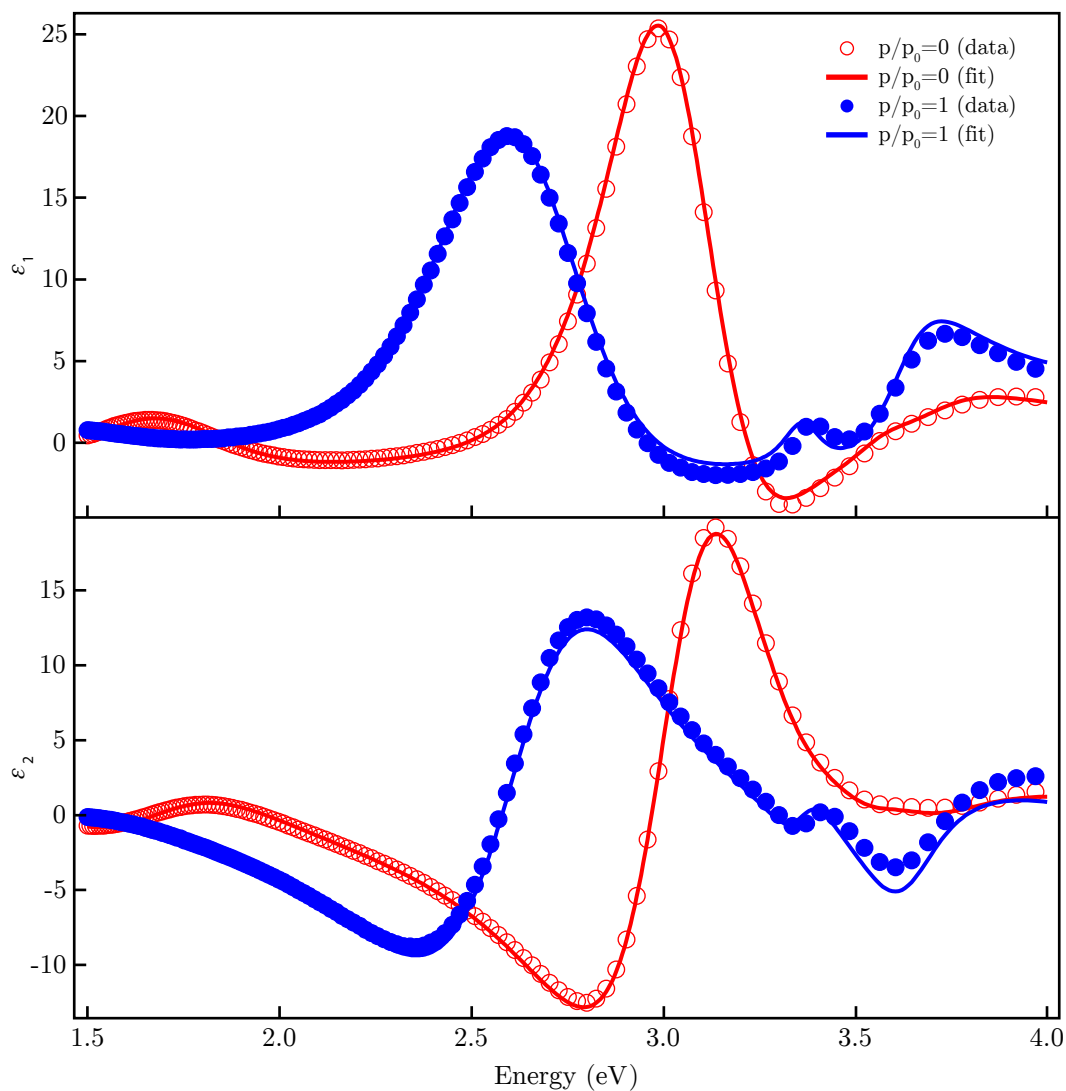


Figure 8.9: Example ellipsometric porosimetry of a film of 9.9 nm CeO_2 nanocrystals. The ellipsometry data and the corresponding fits using the Semilab SEA software are displayed in terms of the real (ϵ_1 , top panel) and imaginary (ϵ_2 , bottom panel) dielectric functions of the material. Data and fits are shown for the two extremes in partial pressure of the toluene adsorbent: zero partial pressure (red), and saturation (blue).

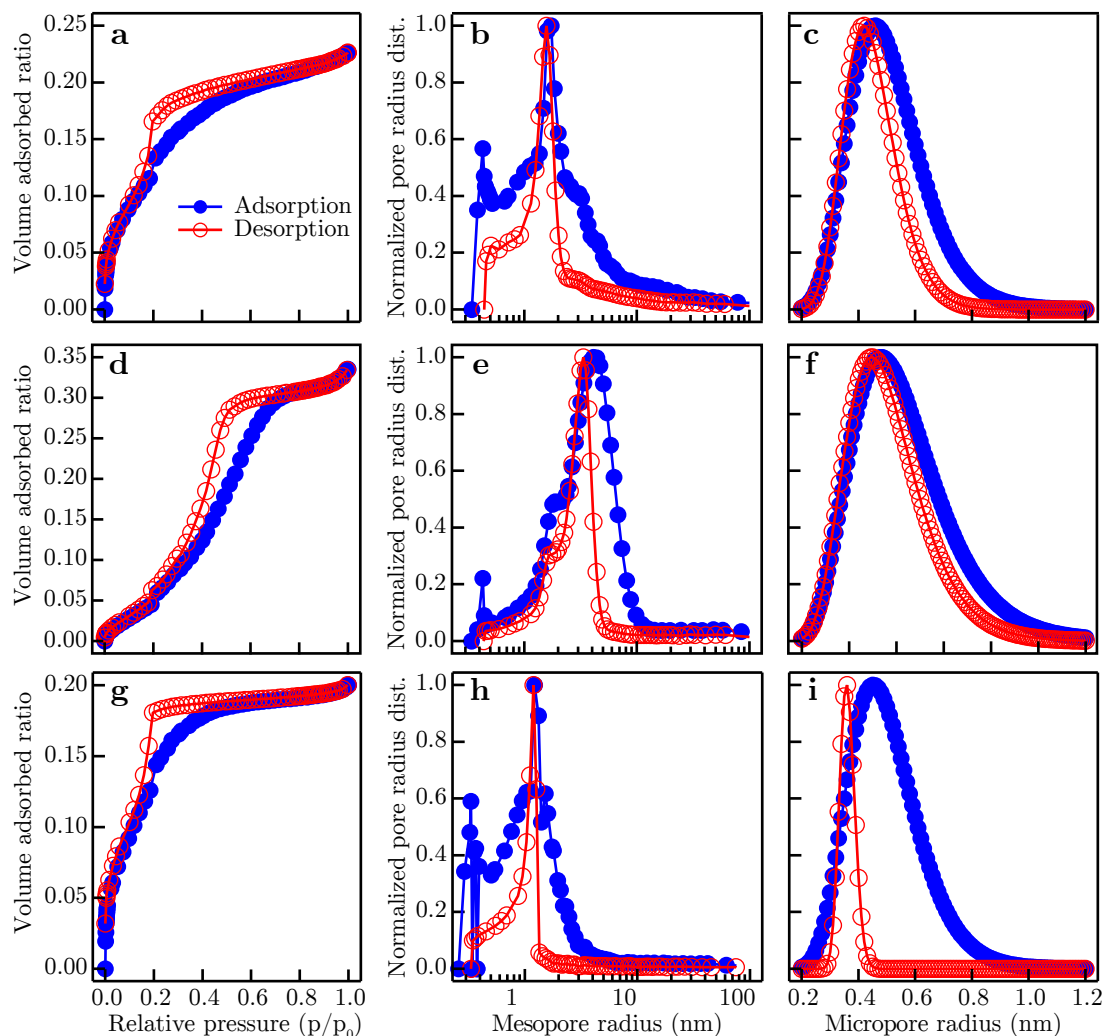


Figure 8.10: Ellipsometric porosimetry data for nanocrystal films. a: Volume adsorption and desorption isotherm (for toluene) of a film made from 3.9 nm CeO_2 nanocrystals. b: Normalized mesopore radius distribution for the same film derived from EP. c: Derived micropore radius distribution for the same film. d-f: Adsorption/desorption isotherm, mesopore radius distribution, and micropore radius distribution for a 9.9 nm CeO_2 nanocrystal film. g-i: Adsorption/desorption isotherm, mesopore radius distribution, and micropore radius distribution for a 6.7 nm TiO_2 nanocrystal film.

8.3.2 Film conductivity

We used impedance spectroscopy to evaluate the conductivity of nanocrystal films at different temperatures and under different gas and humidity environments. To determine conductivity values, we fitted the Nyquist impedance plots using ZView software and extrapolated a

Nanocrystal size	Porosity	Avg. mesopore radius (adsorption/desorption)	Avg. micropore radius (adsorption/desorption)
3.9 nm CeO ₂	22.6%	1.7 nm/1.6 nm	0.46 nm/0.42 nm
9.9 nm CeO ₂	33.2%	4.1 nm/3.3 nm	0.53 nm/0.50 nm
6.7 nm TiO ₂	19.7%	1.6 nm/1.6 nm	0.45 nm/0.36 nm

Table 8.1: Summary of porosity results for the samples used in this study as measured by EP.

semicircle to the real axis to obtain a low-frequency intercept. In some cases, a model with two time constants/semicircles provided a better fit, though the low-frequency intercept was always used to calculate conductivity. Reliable capacitance values for the film could not be determined, due to the stray capacitance between the two electrodes on the top surface of the film. Representative Nyquist plots and fits for the conductivity of a 290 nm thick film of 3.9 nm CeO₂ nanocrystals under humidified Ar are shown in Figure 8.11.

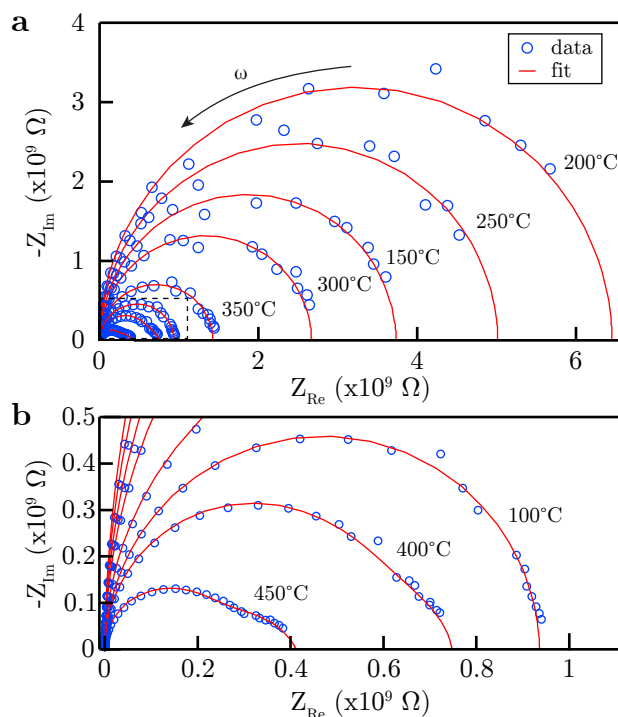
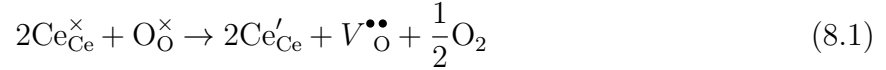


Figure 8.11: a: Nyquist plots showing the AC impedance response of a 290 nm thick film of 3.9 nm CeO₂ nanocrystals exposed to humidified Ar at different temperatures, and fits to the data. b: Zoomed in view of lower left region of part a.

Under a dry Ar atmosphere, 3.9 nm CeO₂ nanocrystals exhibit electronic conductivity that increases with temperature (Figure 8.12a), with an activation energy of 0.76 eV. This trend is expected based on the defect chemistry of CeO₂, in which oxygen vacancies are

generated at low partial pressures of oxygen (here, about 10^{-5} atm) according to the following defect equation (using Kroger-Vink notation):



The electrons liberated by this reaction localize onto cerium ions (Ce_{Ce}') and form small polarons, which can then conduct electricity by thermally activated hopping transport.³⁴⁴ The activation energy for electronic conduction observed here (0.76 eV) is rather low compared to bulk and porous nanocrystalline CeO_2 ,^{328;329;345–348} which, assuming that the activation energy for electron hopping is not strongly changed in nanocrystals, indicates that the enthalpy of formation for oxygen vacancies in this material is suppressed. It is well known that CeO_2 with very small crystallite sizes displays significantly enhanced oxygen vacancy concentration and electronic conductivity.^{345;346;349} This is due to the high specific surface area associated with nanocrystalline ceria, which causes the defect chemistry of the material to be dominated by surfaces and interfaces. The oxygen vacancy formation energy is lower at surfaces because the lattice strain associated with forming Ce^{3+} is much more easily accommodated at a surface or grain boundary.³⁵⁰ Decreasing particle size, and the associated increase in specific area, is therefore naturally accompanied by a significant increase in the thermodynamic concentration of oxygen vacancies and polarons in nanocrystalline ceria.³⁵¹

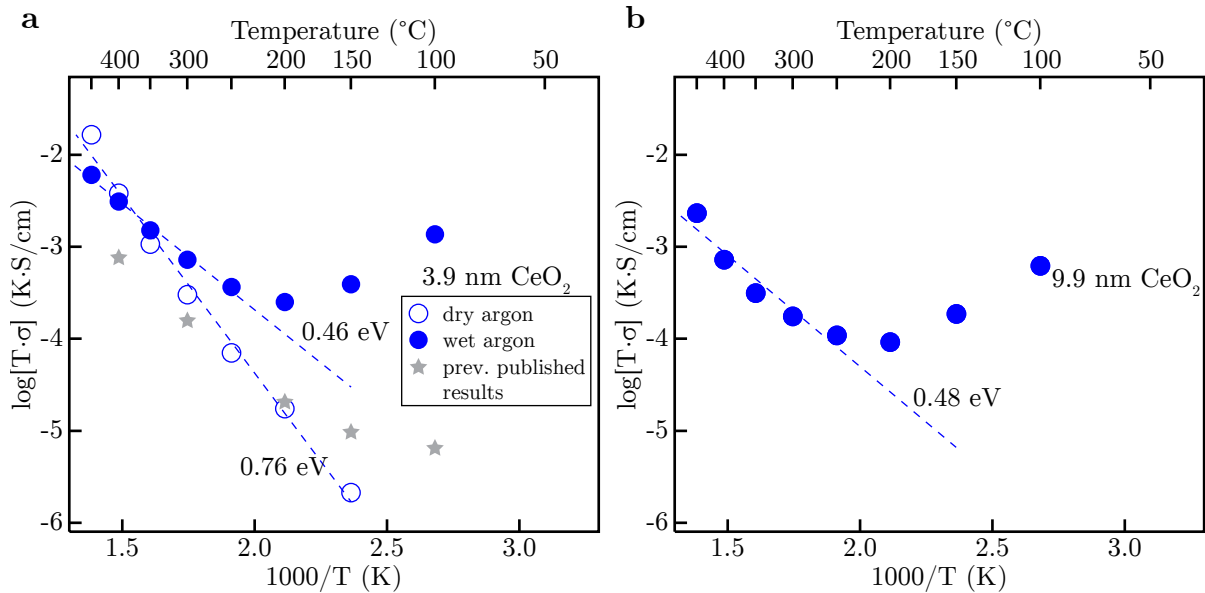


Figure 8.12: Arrhenius plots of the conductivity of CeO_2 nanocrystals under wet and dry Ar. a: Conductivity of a 290 nm thick film of 3.9 nm CeO_2 nanocrystals under dry and wet Ar. The grey stars are results from Reference³²⁹ for comparison. b: Conductivity of a 360 nm thick film of 9.9 nm CeO_2 nanocrystals under wet Ar.

Indeed, X-ray absorption spectroscopy (XAS) measurements at the Ce M-edge (Figure 8.13)³⁵² reveal that, even as synthesized, the 3.9 nm CeO_2 nanocrystals are significantly

enriched in Ce^{3+} compared to the 9.9 nm nanocrystals: the fraction of Ce^{3+} (calculated using XAS in surface-sensitive total electron yield mode) at the surface of the 3.9 nm nanocrystals is about 30%, while it is about 20% for the 9.9 nm nanocrystals. By contrast, total fluorescence yield XAS shows that the Ce^{3+} content is reduced in the nanocrystal cores, and the difference between the two samples is also reduced (22% for 3.9 nm vs. 17% for 9.9 nm). This indicates that the smaller nanocrystals support higher intrinsic concentrations of oxygen vacancies and n-type polarons, and underlines the importance of surfaces in dictating the defect behavior of nanocrystalline CeO_2 .

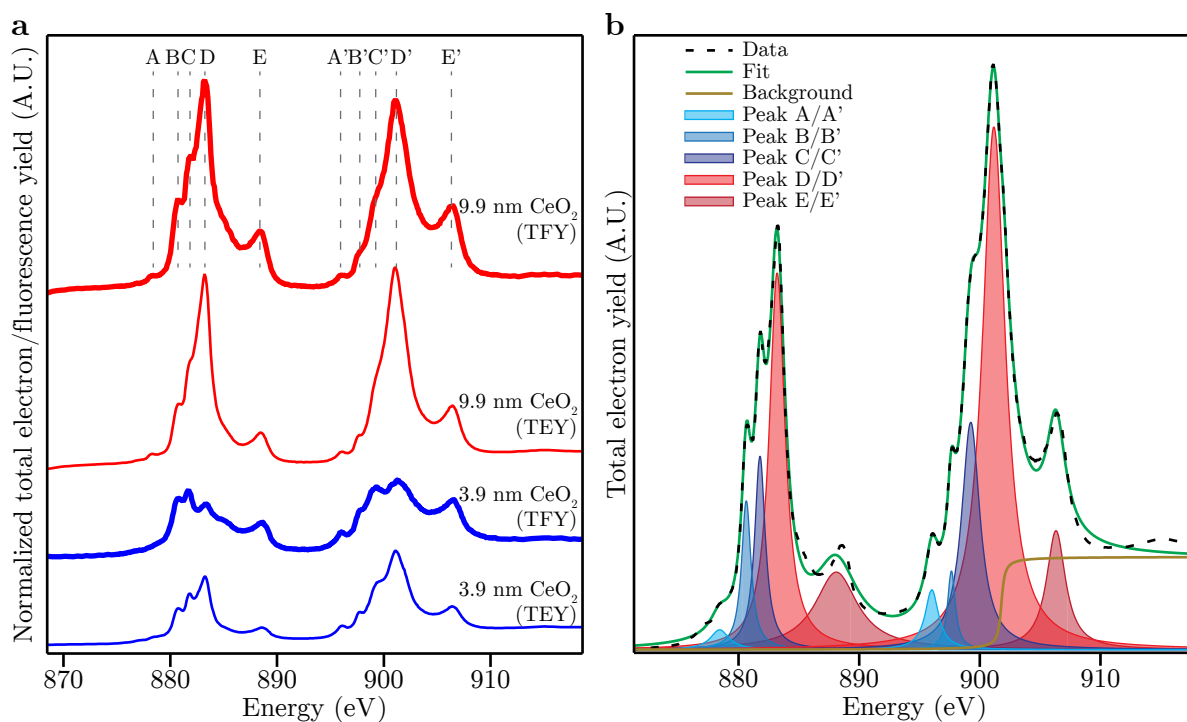


Figure 8.13: X-ray absorption spectroscopy (XAS) of 3.9 nm and 9.9 nm CeO_2 nanocrystals at the Ce M4,5-edge. a) Normalized total electron yield (TEY) and total fluorescence yield (TFY) XAS spectra. The ten total M5 (A-E) and M4 (A'-E') peaks are annotated; peaks A/A', B/B', and C/C' are associated with Ce^{3+} , while peaks D/D' and E/E' are associated with Ce^{4+} . b) Example peak deconvolution for the TEY spectrum of 3.9 nm CeO_2 nanocrystals.

When the impedance measurements are repeated under humidified Ar ($p_{\text{H}_2\text{O}}=20$ mbar) at the same temperatures (Figure 8.12a), the high temperature conductivity is similar or slightly smaller than under dry Ar, indicating that electronic conductivity is dominating at higher temperatures. However, beginning at 350°C, and especially at lower temperatures, the sample exhibits a strong conductivity enhancement under humidified conditions, and a

much lower activation energy. Furthermore, the conductivity begins to increase again at 150°C. These observations are consistent with previous reports, and the difference between conductivity in wet and dry atmosphere can be attributed to proton conduction.^{328;329} The proton conductivities here, however, are also significantly higher than in the previous study on mesoporous nanocrystalline CeO₂, which we attribute to the much smaller grain sizes used here (3.9 nm vs. 20 nm). In agreement with this hypothesis, the proton conductivities in a film of 9.9 nm CeO₂ nanocrystals are 2-4 times smaller than in the 3.9 nm nanocrystal film (Figure 8.12b).

8.3.3 Analysis

The difference in conductivity between the two CeO₂ samples is particularly intriguing, especially considering that the micropore radius of the 9.9 nm CeO₂ sample is only 0.7 larger (Table 8.1). On the other hand, the conductivity difference could arise from the higher porosity or the larger mesopore radius in the 9.9 nm CeO₂ sample compared to the 3.9 nm sample (4.1 nm vs. 1.7 nm). Prior reports suggested that proton transport is enabled by sufficiently small mesopores filled with liquid water via capillary condensation.³²⁹ The critical pore radius-dependence of capillary condensation may account for the substantial conductivity difference between our samples. To evaluate this hypothesis, we solved the Kelvin equation for our experimental conditions:

$$\frac{1}{r} = \frac{RT}{\gamma V_m} \ln \left(\frac{p}{p_0} \right) \quad (8.2)$$

where r is the critical pore radius for capillary condensation, R is the gas constant, T is the temperature, γ is the surface tension of water, V_m is the molar volume of water, p is the vapor pressure of water (constant here at 20 mbar), and p_0 is the saturated vapor pressure of water. Note that γ , V_m , and p_0 are all temperature-dependent quantities. The result of this analysis (Figure 8.14) shows clearly that capillary condensation is not possible in our films and it therefore cannot explain the proton conductivity we observe. The maximum temperature for which we can expect wholesale capillary condensation into the pores of our CeO₂ nanocrystal films is about 50-60°C, based on a micropore radius of 0.46 nm. Considering that the normalized micropore radius distribution vanishes for pore radii 0.2 nm and smaller (Figure 8.10c, f, i), capillary condensation can be considered as essentially non-existent in our films at temperatures above 100°C (Figure 8.14). Furthermore, if capillary condensation into mesopores were responsible for proton conductivity, then conductivity differences between the 3.9 nm and 9.9 nm nanocrystals would only manifest near room temperature. Capillary condensation cannot explain the significant proton conductivity in either sample at and above 250°C, where condensation would require pore radii less than 0.3 Å (more than 1 Å smaller than the radius of a water molecule), nor can it explain the significant decrease in proton conductivity when the nanocrystal size is increased from 3.9 nm to 9.9 nm.

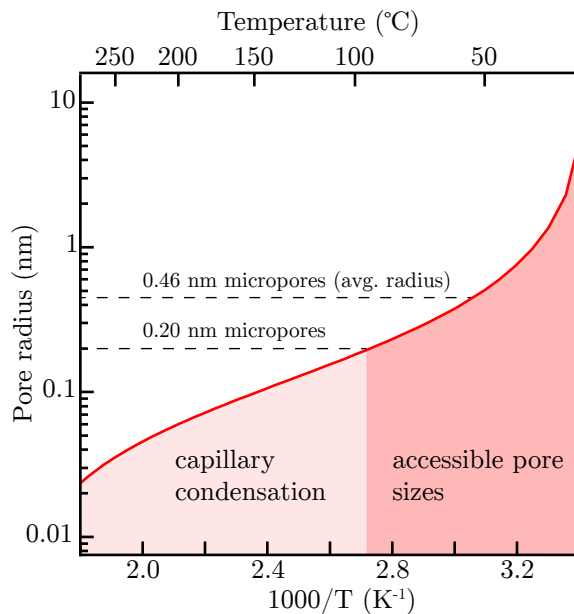


Figure 8.14: Solution to the Kelvin equation for our experimental conditions. The shaded area depicts the temperatures and pore radii where capillary condensation is expected. The deeply shaded region shows the temperatures for which capillary condensation is possible in our samples.

We instead propose that the proton conductivity depends on nanocrystal size through the associated changes in specific surface area and the size-dependent surface chemistry and defect equilibria. The surface area-to-volume ratio of a 3.9 nm nanocrystal is about two times that of a 9.9 nm nanocrystal. Coincidentally, our XAS results (Figure 8.13) show that the surface fraction of Ce^{3+} (and oxygen vacancy concentration) in 3.9 nm CeO_2 is about 1.5 times greater than in 9.9 nm CeO_2 at room temperature, and it is possible that this difference would be exaggerated at elevated temperatures. This is on the same order of the difference in conductivity between the two samples and strongly suggests that surface defects are playing a significant role in proton conduction here.

To further investigate the relationship between proton conductivity and defect chemistry at the surface, we again measured the conductivity of 3.9 nm CeO_2 nanocrystals under humid conditions while using pure oxygen, rather than argon, as the carrier gas (Figure 8.15). It is immediately apparent that the conductivity under wet O_2 is dramatically lower than under wet Ar, and that the activation energy is higher. Furthermore, there is a much less pronounced uptick in conductivity between 200°C at 100°C. Based on the defect equilibrium described by Equation 8.1, the equilibrium concentration of oxygen vacancies and polarons is described by the equilibrium constant:

$$K = (p\text{O}_2)^{1/2} [V^{\bullet\bullet}\text{O}] [\text{Ce}'_{\text{Ce}}]^2 \quad (8.3)$$

The electroneutrality condition ($2[V^{\bullet\bullet}\text{O}] = [\text{Ce}'_{\text{Ce}}]$) can be invoked to show that the concentra-

tion of oxygen vacancies and polarons is proportional to $(pO_2)^{-1/6}$. A change in atmosphere from pure Ar ($pO_2 \sim 10^{-5}$ to 10^{-6} atm) to pure O_2 ($pO_2 \sim 1$ atm) will then change the equilibrium concentration of both defects by about one order of magnitude. If the concentration of oxygen vacancies or polarons has an effect on water adsorption or proton transport, then this concentration change should correspond to a significant change in conductivity. Indeed, we observe a very large decrease in the intermediate temperature proton conductivity when pure oxygen is used as a carrier gas. Under wet O_2 , the proton conductivity decreases by a factor of 5 (at 300°C) to 64 (at 100°C).

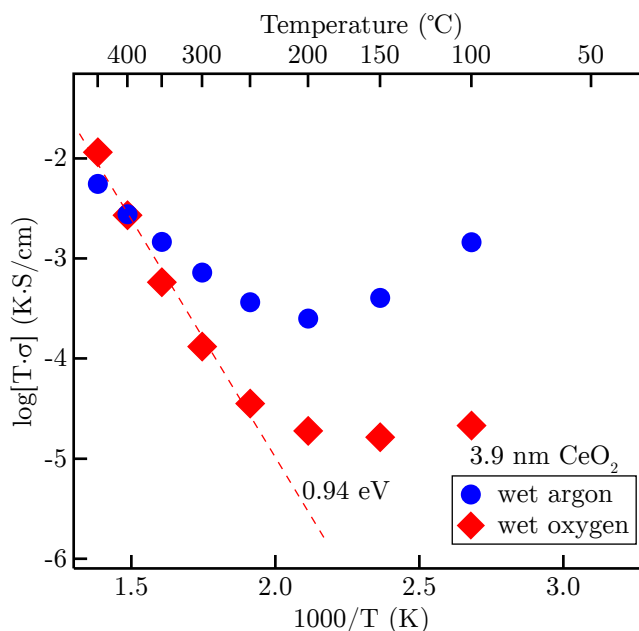


Figure 8.15: Arrhenius plot of the conductivity of a 290 nm thick film of 3.9 nm CeO_2 nanocrystals under wet oxygen. (Wet argon results included for comparison).

This drastic decrease in proton conductivity under O_2 atmosphere further rules out capillary condensation as a major contributor to conductivity because changing the carrier gas would not change the critical pore radius in Equation 8.2. The self-dissociation of water into hydronium and hydroxide ions also cannot describe our conductivity results; the self-dissociation constant at 100°C is only 5.4×10^{-13} (5.2×10^{-12} at 200°C), and the conductivity of pure water at 100°C is only 7.6×10^{-7} S/cm (3×10^{-6} S/cm at 200°C).³⁵³ By contrast, the proton conductivities in our films are two to four times higher despite the majority of their volume being crystalline ceramic, meaning that protons must be generated by some other mechanism.

Instead, this strong suppression of proton conductivity by O_2 indicates that surface oxygen vacancies play a critical role generating protons in nanocrystalline CeO_2 . Previous studies have shown that the amount of water adsorbed to ceria surfaces and the dissociative binding enthalpy increases at chemically reduced and defective ceria surfaces.^{337;354} To

understand how oxygen vacancies and cerium oxidation state influence water uptake in our nanocrystals, we performed thermogravimetric analysis (TGA) on 3.9 nm CeO₂ nanocrystals with their surface ligands removed in an alumina crucible (Figure 8.16). After equilibrating under dry Ar at 450°C to generate oxygen vacancies, the temperature was reduced to 150°C to stabilize for 2 hours. Then, the nanocrystals were exposed to humidified Ar ($p_{\text{H}_2\text{O}}=20$ mbar) inside the TGA furnace. The mass of the sample (corrected for buoyancy and water adsorption by running an equivalent experiment with an empty crucible) subsequently increased as the nanocrystals adsorbed water. The experiment was then repeated using 25% O₂. Under dry conditions, the sample mass was higher, indicating a decrease in the oxygen vacancy concentration. Furthermore, the mass gained upon switching to a humid oxygen atmosphere at 150°C was significantly diminished. Comparing the time-averaged sample mass over one hour before switching between a dry and wet environment to the time-averaged sample mass over one hour after exposure to moisture (averaged to improve precision) reveals that the sample under pure Ar gained 62 times more mass than the one in an oxidative environment. This confirms that oxygen vacancy concentration directly influences water adsorption in CeO₂ nanocrystals, and in porous nanocrystal films, the pore surfaces determine the chemistry of water adsorption and how much water adsorbs to the pore walls.

We hypothesize here that mobile protons are generated in situ by dissociative adsorption of water at surface oxygen vacancies. Oxygen vacancies serve as active or catalytic sites for water dissociation at CeO₂ surfaces, generating two protonic defects according to the following reaction:^{321;330;355}



The hypothesized dissociation process, also shown schematically in Figure 8.17a-b, is well supported by atomistic simulations reported in the literature, as well as experimental scanning tunneling microscopy and X-ray photoelectron spectroscopy studies showing that OH_O[•] defects saturate surface oxygen vacancies in reduced CeO₂ under humid conditions.^{337;354;356–358} In fact, this is the very process by which ceramic high temperature proton conductors such as ternary oxides like BaCeO₃ generate mobile protons.^{311;355} Once the protonic defects are formed, proton conduction may follow a few different pathways, such as proton hopping along neighboring adsorbed surface hydroxide defects,³¹⁸ which may be facilitated by partial solvation from adsorbed water (Figure 8.17c), or the proton may be exchanged between the surface protonic defect and physisorbed water molecules in the pores (Figure 8.17d),^{318;321} followed by proton conduction within this adsorbed water layer either via diffusion or the Grotthuss mechanism.³²⁵ We do not have sufficient experimental evidence to determine which transport process is dominant, although recent studies on proton conduction in TiO₂ and YSZ, which used solid-state NMR,³³² in situ FTIR,³⁵⁹ and ultrathin YSZ films,³³⁵ indicate that the surface hopping mechanism is dominant at higher temperatures (300+°C), where there is little physisorbed water. At intermediate temperatures, conduction through the “ice-like” chemisorbed water layer is likely dominant, while hydronium ion conduction within adsorbed water is dominant at lower temperatures where the physisorbed water layer is thicker.^{332;359} We note that extracting a proton from the surface defect will result in a

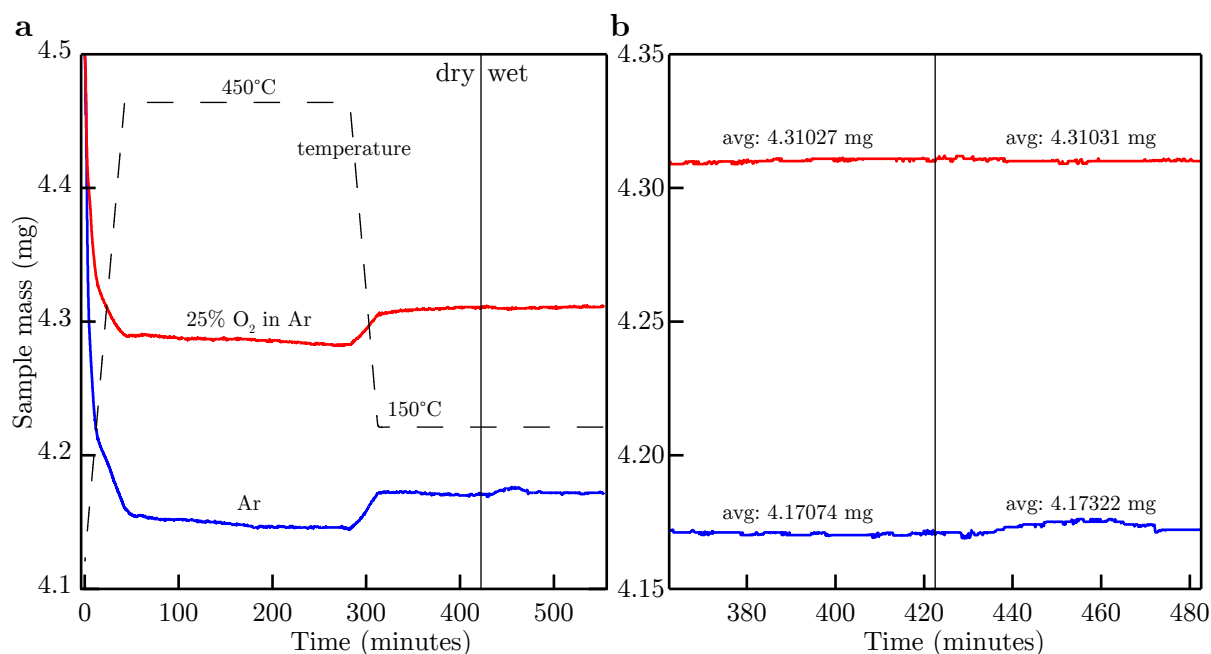


Figure 8.16: Thermogravimetric analysis (TGA) of 3.9 nm CeO₂ nanocrystal powder with surface ligands removed, in an Al₂O₃ crucible, after blank curve subtraction. a) Sample mass vs. time under both Ar atmosphere (blue line) and 25% O₂ atmosphere (red line) in both dry and wet ($p\text{O}_2=20$ mbar) conditions, with the switch from dry to wet conditions delineated by a vertical line. The temperature profile is shown as a dashed line. b) Zoomed-in display of the sample mass vs. time for one hour before and after switching (vertical line) from dry to wet conditions. The one-hour time averaged sample mass before and after the switch is listed above each curve.

charged nanocrystal, due to the presence of the polarons that originally compensated the oxygen vacancies and now the protonic defects. Thus, if the proton is conducted within the water layer, it is likely confined to the near-surface region, where, coincidentally, diffusivity and other transport characteristics can be enhanced.

The hypothesis of oxygen vacancy-mediated dissociative adsorption of water can explain the observed differences in conductivity as a consequence of the change in the number of protonic charge carriers that are generated for a given nanocrystal size, temperature, and gaseous environment. Increasing the nanocrystal size from 3.9 nm to 9.9 nm results in a lower intrinsic concentration of oxygen vacancies at a given equilibrium, due to the decreased surface-to-volume ratio. Based on our XAS results, this decrease is expected to be about 1.5 to 2. The decrease in oxygen vacancy concentration corresponds to a decrease in proton conductivity of the same order, because fewer mobile protons are generated. It is also clear from the O-H vibrations in our FTIR data (Figure 2) that the film of 9.9 nm CeO₂ nanocrystals adsorbs significantly less water under ambient conditions, supporting our hypothesis. Finally, using pure oxygen as a carrier gas, which corresponds to a $p\text{O}_2$ increase

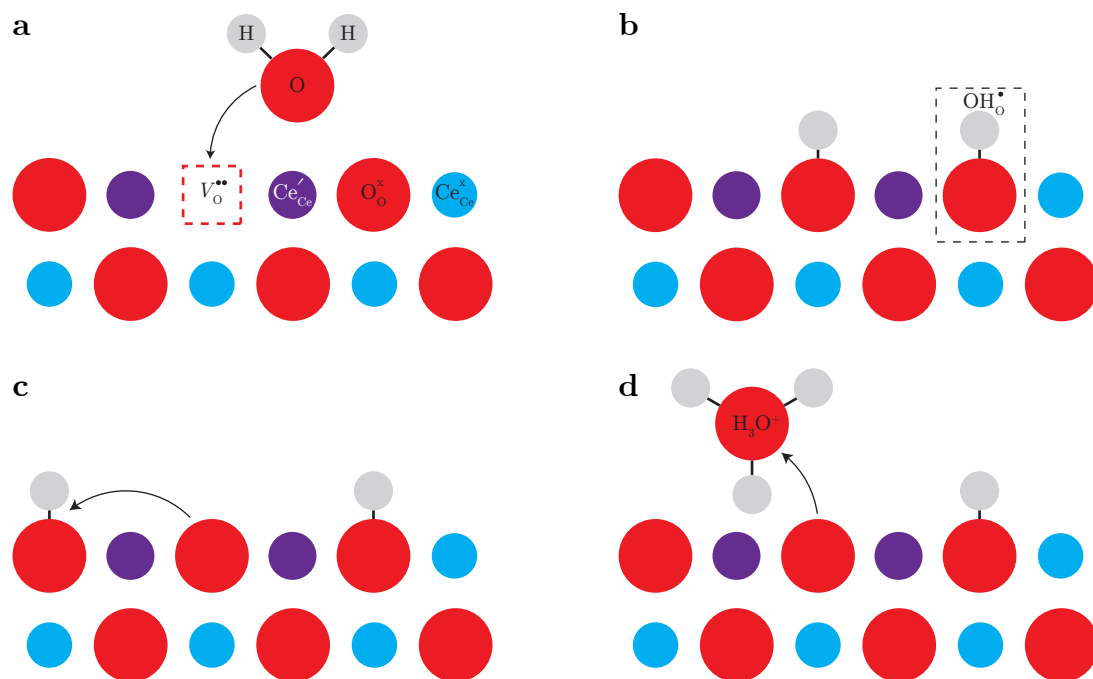


Figure 8.17: Proposed mechanism for surface-mediated proton transport in nanocrystalline CeO_2 . a: An oxygen vacancy serves as the active site for dissociative water adsorption, forming b: two protonic defects. c: Proton conduction can occur by hopping along the oxide surface, or by d: Exchange with adsorbed water at the surface.

of 10^5 - 10^6 atm, reduces the oxygen vacancy concentration by about an order of magnitude, and our TGA results confirm that the amount of water adsorbed also decreases by over an order of magnitude. The corresponding drop in proton conductivity under these conditions is, correspondingly, about an order of magnitude or greater.

To evaluate the generality of proton conduction in porous nanocrystal films, and the generality of our hypothesized mechanism, we measured the conductivity of a thin film consisting of 6.7 nm TiO_2 nanocrystals under dry Ar, humidified Ar, and humidified O_2 (Figure 8.18). Note that, based on our EP data (Table 8.1), the pore morphology of this sample is nearly equivalent to the 3.9 nm CeO_2 nanocrystal sample: the mesopore and micropore radii are identical within the precision of the analysis, and the overall porosity is comparable. Any observed changes in proton conductivity should then arise mainly from differences in the surface chemistry of TiO_2 compared to CeO_2 . Indeed, both the high temperature electronic conductivity (under both dry and wet Ar) and the intermediate temperature proton conductivity (under wet Ar) are significantly lower in the TiO_2 nanocrystal film. This is easily explained by the higher energy required to form an oxygen vacancy in TiO_2 compared to CeO_2 : e.g., 3.2 eV at a TiO_2 (110) surface vs. 1.8 eV at a CeO_2 (111) surface.³⁵⁰ As a result, for a given temperature and $p\text{O}_2$, TiO_2 is less reducible than CeO_2 and is expected to have significantly fewer oxygen vacancies and polarons. This is undoubtedly why TiO_2 has a

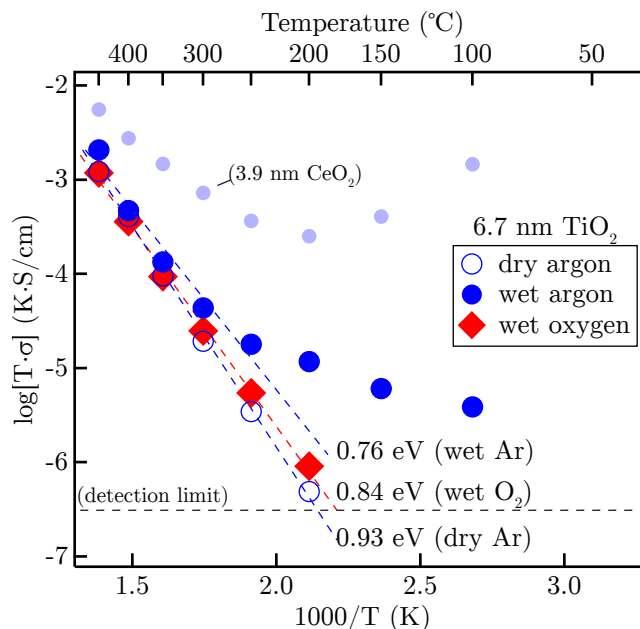


Figure 8.18: Arrhenius plot of the conductivity of a 265 nm thick film of 6.7 nm TiO_2 nanocrystals under dry argon, wet argon, and wet oxygen. (Conductivity of 3.9 nm CeO_2 nanocrystals under wet argon included for comparison).

decreased electronic conductivity under dry Ar. Based on our proposed mechanism, a lower oxygen vacancy concentration also explains why TiO_2 displays a lower proton conductivity at intermediate temperatures. Finally, we also observed that the proton conductivity in the TiO_2 nanocrystal film is strongly diminished under humidified oxygen. These results further support our assertion that water dissociatively adsorbs at oxygen vacancies to form mobile protonic defects. Ultimately, while previous studies firmly established the fact that open porosity is a critical requirement for proton conduction in nanocrystalline ceramics, we have found here that defect equilibria and surface chemistry play an additionally critical role.

8.4 Conclusion

We have shown here how systematic control over grain size and surface chemistry can be used to shed light on the proton conduction mechanism in nanocrystalline ceramics. By utilizing and manipulating colloidal CeO_2 and TiO_2 nanocrystals, we were able to achieve enhanced proton conductivity in nanocrystal films under humid atmospheres, particularly for small (3.9 nm) CeO_2 nanocrystals. From both scientific and application perspectives, colloidal nanocrystals offer an attractive route to generate nanocrystalline ceramic films with engineered and controlled porosity and grain size that is not typically achievable with sintering or other physical fabrication methods. Achieving these small grain sizes also enabled us to easily manipulate their surfaces and defect chemistries in situ. In turn, these manipulations

revealed the strong influence of defect chemistry on proton transport in nanocrystalline oxides, allowing us to conclude that dissociative water adsorption into oxygen vacancies is the likely source of mobile protons. Our observation of surface-mediated proton transport in both CeO_2 and TiO_2 suggests that this may be a general phenomenon for nanocrystalline metal oxides, particularly for reducible oxides that easily form oxygen vacancies.

Chapter 9

Epilogue: conclusions and suggested future work

Studying the fundamental relationships between the materials science of metal oxides and charge transport is crucial if the unique properties of metal oxides are to be successfully used in real-world applications. I have hopefully convinced the reader that such studies are unique and equally critical when it comes to colloidal metal oxide nanocrystals. This dissertation has shown how materials science, materials chemistry, and colloidal chemistry can be leveraged to control and manipulate charge transport in nanoscale systems.

The tenants of solution processing and colloidal stability were used to create ITO-polymer nanocomposites and manipulate their morphology. This control over morphology was shown to influence the electronic and ionic conductivity of ITO-polymer nanocomposites. The lessons learned here were, in turn, successfully applied to understand electrochemical charge generation and transport in electrochromic devices. Ultimately, this allowed the creation of solid state electrochromic devices which could dynamically modulate the transmittance of near-infrared light.

Controlling electronic charge transport within nanocrystals was also shown to have a very strong impact on their optical properties based on localized surface plasmon resonance. Developing connections between materials science of defects in metal oxides and electron transport made it possible to understand how these processes work in nanocrystalline oxides. Colloidal chemistry was then used to tune the location of tin dopants within ITO nanocrystals and their shape for additional control over electronic charge transport and LSPR properties. This trajectory of study led to the discovery of a new type of plasmonic nanocrystal, $\text{Ce:In}_2\text{O}_3$, with exceptional LSPR properties. This advance was a direct result of the new ability, partially developed in this dissertation, to understand and manipulate defect chemistry and the associated electronic charge transport within nanocrystals.

Finally, the connections made throughout the dissertation were applied to proton-conducting ceramic metal oxide nanocrystals. The well-developed connections between metal oxide nanocrystal synthesis, processing, defect chemistry, and charge transport made previously provided excellent context for this system, where defect chemistry was used to control the

generation and electrochemical charge transport of protons. Developing this knowledge and understanding of charge transport is an important step towards the real world applications of these nanomaterials in real world devices.

9.1 Future work

Despite being the culmination of nearly six years of work, this dissertation only begins to add to humanity's understanding of charge transport in metal oxide nanocrystals. In some ways, the results presented here may raise more additional questions than they have answered. There are probably too many possible next steps to reasonably list here. Below are a few suggested future research directions that are immediately apparent.

9.1.1 Polymer-nanocrystal composites

The following paragraph is partly adapted from Reference¹⁴:

Runnerstrom, E. L.; Llordes, A.; Lounis, S. D.; Milliron, D. J. Nanostructured Electrochromic Smart Windows: Traditional Materials and NIR-Selective Plasmonic Nanocrystals. *Chem. Commun.* **2014**, *50*, 10555–10572.

As mentioned at the end of Chapter 4, solid state electrochromic devices based on ITO nanocrystals and polymer electrolytes are a promising development, but a number of device integration issues must be overcome for them to realize their potential. Device integration challenges include development of counter-electrode materials and charge balancing. The ideal counter-electrode material for plasmonic electrochromic devices would be p-type TCO nanocrystals, which would theoretically display anodic coloration in the NIR upon capacitive charging. Unfortunately, due to limitations in oxide band structure and defect chemistry, p-type TCOs are not readily achievable in bulk form, much less in nanocrystal form. Nevertheless, some p-type plasmonic nanocrystals, such as Cu_{2-x}S ⁴⁹ and Cu_{2-x}Se ,⁵⁰ do exist, and other transparent p-type materials, such as Cu-doped ZnS ,³⁶⁰ have recently been synthesized as thin films. If these materials can be adapted for use in plasmonic nanocrystal devices, they would likely greatly enhance the optical contrast and overall coloration efficiency. In any case, it is important to achieve charge balance between the counter electrode and the active electrode for optimum device performance.^{19;21;23} Charge balance will require careful evaluation of the charge capacities of the active ITO and counter CeO_2 or p-type nanocrystal electrodes, in addition to the polarization and charge transport behavior of the electrolyte. Additional flexibility in device fabrication and electrochemical charge generation may also be possible if a sacrificial redox agent is added to the electrolyte and/or the nanocomposite electrodes. Such an agent would ideally be easily oxidized to provide free electrons to

nanocrystals in the device, allowing for easier break in procedures and avoiding problems associated with oxidizing components of the polymer electrolyte.

The characterization and synthesis techniques developed in Chapter 3 can and should also be applied to other nanocrystal materials that may be relevant for electrochemistry, batteries, or solar cells. For example, manipulating morphology and mixed conduction in nanocomposites of TiO_2 nanocrystals may provide new tunability for dye-sensitized solar cells. TiO_2 nanocrystals are also relevant for battery and electrochromic applications.^{103;361} Additionally, the role of aspect ratio has not yet been considered in these mixed conducting composites, though it is expected to have a strong effect. Electronic percolation can be achieved in composites containing high aspect ratio fillers at filler fractions as low as 1 vol.% or less.³⁶² Thus, electrochromic nanocrystals with variable aspect ratios, such as tungsten oxide and cesium-doped tungsten oxide,^{93;363} may prove that nanocrystal aspect ratio provides an additional way to tune electronic and ionic conductivity in composites of nanocrystals and solid polymer electrolytes.

9.1.2 Plasmonic nanocrystals

Chapter 7 demonstrated that alternative dopants for In_2O_3 nanocrystals can have profound effects on their LSPR properties. Alternative dopants that have been explored in thin films of In_2O_3 for high mobilities and/or low resistivities include molybdenum, titanium, and zirconium.^{264;364–366} These dopants may also decrease ionized impurity scattering, and synthetic methods for producing these doped materials in nanocrystal form would advance our understanding of the relationships between dopant identities, electronic properties, defect properties, and LSPR in doped metal oxides. Additionally, nanocrystals of other TCOs with exceptionally high mobilities, like dysprosium-doped cadmium oxide,²⁶⁵ may show remarkable LSPR properties if they can be synthesized successfully.

One clear next step for applying the plasmonic properties of doped metal oxide nanocrystals is to couple LSPR excitations with other optical transitions, such as the infrared vibrational signatures of molecules. Enhancing detection of vibrational spectroscopic signatures via the interaction between high local fields and molecular vibrations is the fundamental phenomenon behind Surface Enhanced Raman Spectroscopy (SERS) and Surface Enhanced Infrared Absorption (SEIRA).^{62;138;139;145;146;213;367–371} Depending on the relative ratio between radiative and non-radiative damping of the LSPR, coupling between LSPR and dipolar vibrational transitions can either lead to enhanced vibrational absorption or induced transparency at the vibrational resonance frequency, which can be useful for sensing or other advanced photonic devices. This makes TCO nanocrystals with high quality tunable LSPR prime candidates to study near field enhancement of light at near-infrared and mid-infrared frequencies. Coupling between doped metal oxide nanostructures and dipolar vibrational transitions has been demonstrated, as lithographically fabricated ITO nanorods couple with infrared vibrations of an over-coated polymer (PMMA) layer (Figure 9.1).²¹³ However, use of nanofabrication to explore coupling phenomena limits the tunability of materials chemistry that is more easily accessed with the colloidal nanocrystals studied here

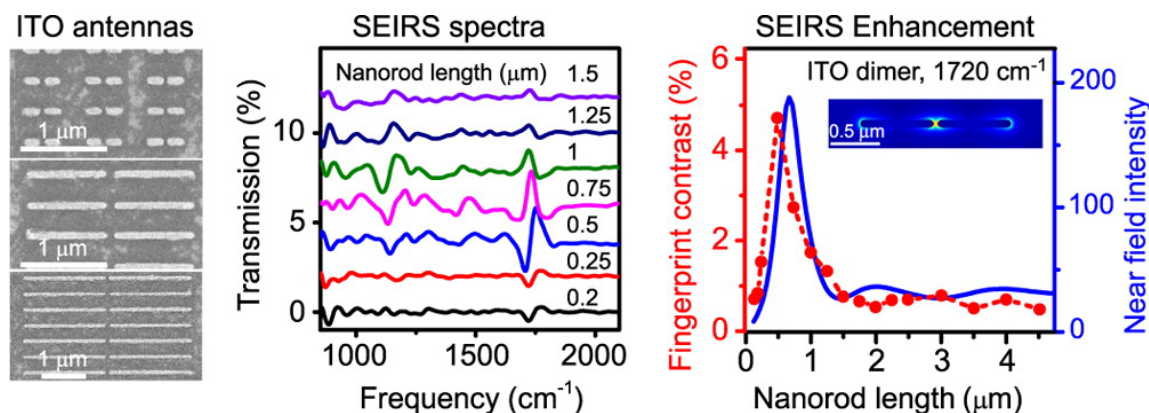


Figure 9.1: Coupling between ITO nanostructures and infrared vibrational absorption. SEIRA spectra (center) of PMMA showing derivative shaped C=O vibration due to coupling with underlying ITO antennae (left) via inter-nanorod hot spots (right). Figure reprinted with permission from Reference²¹³, Copyright 2014 American Chemical Society.

(dopant distributions, composition, faceting). Nanocrystals additionally offer the ability to create well-defined plasmonic hot spots that are expected to couple more strongly in self-assembled superlattices. Even randomly structured thin films are expected to contain hot spots distributed throughout based on inter-particle interactions, as has been studied for gold nanoparticle films.^{62;372} More controlled assemblies, made by arranging highly uniform plasmonic nanocrystals into supercrystalline lattices,^{62;81;294;296} will give rise to better-defined hot spots,¹³⁹ and ligand length can be varied by ligand exchange before or after assembly³⁷³ to tune the inter-nanocrystal coupling responsible for these hot spots. Ultimately, the coupling properties of TCO nanocrystals could be made dynamic and amenable to modulation by external chemical or electrochemical stimuli, in a clear parallel with the electrochromic devices studied in Part I. Specifically, the nanocrystal LSPR mode will change strength and its resonant energy as electrons are added or removed, while the vibrational modes will remain relatively unaffected, allowing for tunable coupling and perhaps the development of new active infrared sensing and spectroscopic platforms.

9.1.3 Proton conducting nanocrystalline ceramics

Chapter 8 showed that proton conduction may be a general effect in ceramic nanocrystal films of reducible metal oxides. Iron oxide, Fe_3O_4 , is another transition metal oxide that can be prepared with highly uniform nanocrystal sizes ranging from at least 3-15 nm in diameter.³⁷⁴ Systematic proton conductivity studies on iron oxide nanocrystals would further establish the generality of the observations made regarding the impact of pore size and surface oxygen vacancies on proton transport. Future work is also needed on CeO_2 and TiO_2 nanocrystal films to further study and manipulate surface-mediated proton transport, especially if this phenomenon is to be eventually exploited for electrochemical devices like

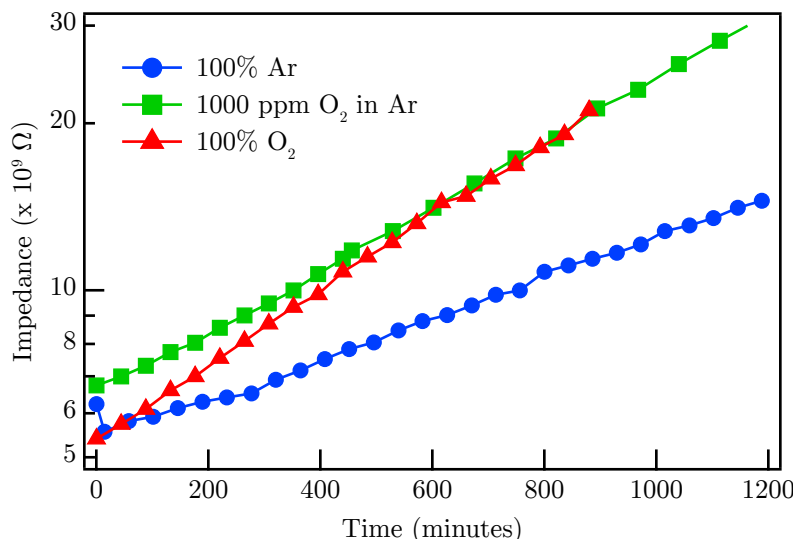


Figure 9.2: Change in resistance of a film of 9.9 nm CeO_2 nanocrystals over long times at $150^\circ C$. Note that the rate of change is greater for higher oxygen partial pressures.

proton-exchange membrane fuel cells. When nanocrystal films were exposed to wet conditions at $150^\circ C$ (20+ hours), the conductivity slowly, but significantly, decreased over time (Figure 9.2). This decline could be a result of protons and polarons reacting to form H_2 gas, thus diminishing the number of protonic charge carriers.³⁵⁷ It could alternatively be the result of contaminants poisoning the nanocrystal surface, e.g., carbon monoxide oxidation to formate or carbonate.³⁵⁰ The conductivity did decrease more quickly with higher pO_2 , which implicates adventitious contaminants. In either case, this effect warrants further study, particularly if these materials are to be used in electrochemical devices.

Additionally, the results reported here will hopefully motivate deeper examinations into the mechanism for proton transport in colloidal nanocrystal films and other micro- and mesoporous ceramics. Techniques like solid-state NMR could elucidate whether surface proton hopping or proton transport in the adsorbed liquid layer dominate the conductivity, or if different processes dominate at different temperatures.

Finally, our results suggest that deliberate attempts to maximize oxygen vacancy concentration could maximize proton conductivity in nanocrystalline ceramics. This could be accomplished either by choosing a material with a low oxygen vacancy formation energy, or by extrinsic generation of high oxygen vacancy concentrations by acceptor doping. For example, Gd-doping of CeO_2 nanocrystals is expected to fix the oxygen vacancy concentration, as Gd'_{Ce} would be compensated by oxygen vacancies. Deliberate and controlled acceptor doping may then enable systematic tuning and maximization of proton conductivity in nanocrystalline GDC. Additionally, nanocrystals of materials that exhibit fast proton conduction at high temperatures, such as $BaCeO_3$, may also show high proton conductivities at intermediate temperatures when they are processed into porous nanocrystal films.

One additional hypothesis that has not yet been explored is that the Lewis acidity of the metal cation could influence the activity of the corresponding metal oxide toward the water dissociation and proton transport processes described above. Considering that water and hydroxide ions are hard Lewis bases, they are expected to bind strongly to hard Lewis acids and weakly to soft Lewis acids. Ce^{4+} ions are hard Lewis acids, so which motivates the study of metal oxide nanocrystals with softer Lewis acid cations, such as zinc oxide (ZnO , Zn^{2+} is an intermediate Lewis acid) and copper (I) oxide (Cu_2O , Cu^+ is a soft Lewis acid). By fixing oxygen vacancy concentration in the materials using controlled oxygen partial pressures, it should be possible to isolate the effects of nanocrystal Lewis acidity on water adsorption and proton conductivity. Depending on the exact mechanism of proton transport in these materials, surface acidity may also influence how easily protons hop between adjacent surface sites or are exchanged between surface sites and adsorbed water. In fact, decreasing Lewis acidity may impose competing effects on proton conductivity by suppressing the ability of the surface to generate mobile protons on the one hand, while increasing proton mobility on the other.

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Appendix A

Supporting information for Chapter 7

A.1 Additional TEM micrographs

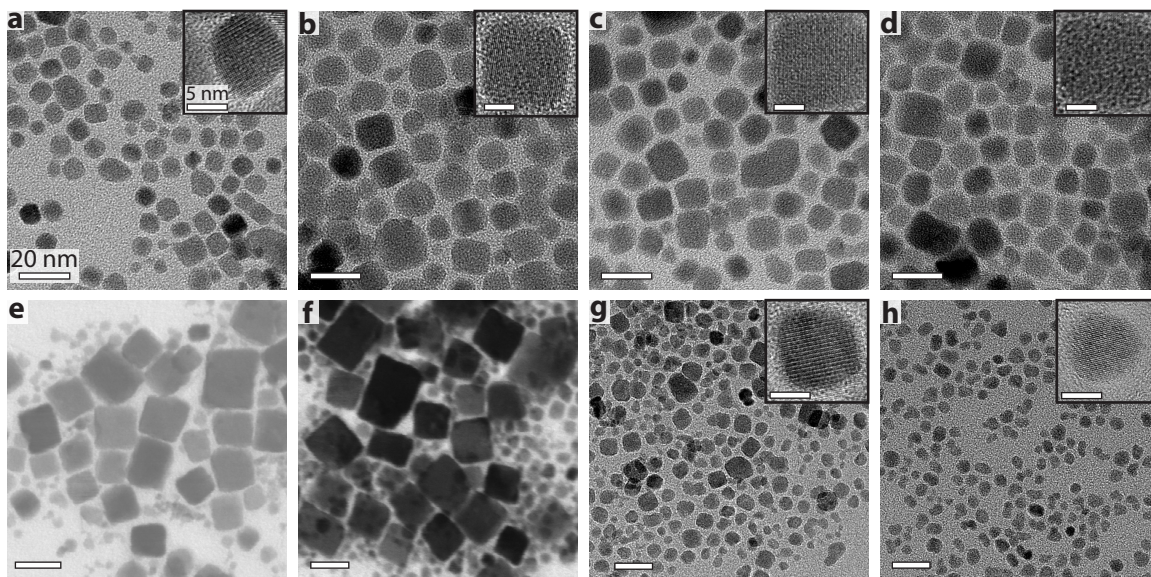


Figure A.1: TEM images (high resolution images in insets) of $\text{Ce:In}_2\text{O}_3$ nanocrystals. The cerium precursors used were Ce-acac (a-f), Ce-acetate (g) and C.A.N. Panels (e) and (f) are low-resolution STEM images. Ce doping levels: (a) 0.93%; (b) 1.97%; (c) 3.47%; (d) 3.68%; (e) 8.64%; (f) 11.14%; (g) 4.79%; (h) 5.60%. All scale bars are 20 nm, 5 nm for inset images.

A.2 Drude modeling

The Drude model can be used to fit optical LSPR spectra and extract quantitative information about the optoelectronic properties of the nanocrystals under study. A material's optical response depends on its frequency dependent dielectric function; for an isolated, conductive nanocrystal, this is primarily the Drude contribution:

$$\varepsilon_{\text{particle}}(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma(\omega)} \quad (\text{A.1})$$

where ε_{∞} is the high frequency permittivity of the material, $\Gamma(\omega)$ is a frequency-dependent electronic damping function, and ω_p is the bulk plasma frequency, given by:

$$\omega_p = \sqrt{\frac{ne^2}{m_e^* \varepsilon_0}} \quad (\text{A.2})$$

where n is the free carrier concentration, m_e is the free carrier effective mass, and ε_0 is the permittivity of free space. The frequency-dependent damping component Γ is given by the empirical function:

$$\Gamma(\omega) = \Gamma_L - \frac{\Gamma_L - \Gamma_H}{\pi} \left[\tan^{-1} \left(\frac{\omega - \Gamma_X}{\Gamma_W} \right) + \frac{\pi}{2} \right] \quad (\text{A.3})$$

where Γ_L is a low-frequency damping constant, Γ_H is a high-frequency damping constant, Γ_X is a crossover frequency between the low-frequency and high-frequency damping regimes, and Γ_W is the width of the crossover region.

Because the nanocrystals are dispersed in solvent at appreciable concentrations for the liquid cell FTIR measurements, we employ the Maxwell-Garnett effective medium approximation (EMA) to account for far-field interactions between nanocrystals and for dielectric interactions between the nanocrystals and the solvent. The EMA is:

$$\frac{\varepsilon_{\text{effective}} - \varepsilon_{\text{solvent}}}{\varepsilon_{\text{effective}} + 2\varepsilon_{\text{solvent}}} = f_v \left(\frac{\varepsilon_{\text{particle}} - \varepsilon_{\text{solvent}}}{\varepsilon_{\text{particle}} - \varepsilon_{\text{solvent}}} \right) \quad (\text{A.4})$$

where $\varepsilon_{\text{effective}}$ is the effective dielectric function of the nanocrystal-solvent dispersion, $\varepsilon_{\text{solvent}}$ is the dielectric constant of the dispersing solvent, $\varepsilon_{\text{particle}}$ is the dielectric function of an isolated nanocrystal in vacuum (see above), and f_v is the volume fraction of nanocrystals dispersed in the solvent. Once $\varepsilon_{\text{effective}}$ is determined, it can be used to calculate the absorption of the nanocrystal dispersion. Our MATLAB code combines the above four equations to perform a least-squares fit to the collected spectra and extract the free parameters f_v , ω_p , Γ_L , Γ_H , Γ_X , Γ_W . Using an effective mass of $0.4m_e$ (the effective mass of Sn:In₂O₃), the electron concentration and the optically-derived DC mobility can be further determined.

We also fit the FTIR spectra using a simple Drude model utilizing a frequency-independent (i.e., scalar) damping term γ , in which case equation 1 in chapter XX becomes:

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \quad (\text{A.5})$$

Doping level (by ICP)	ω_p (cm ⁻¹)	γ (cm ⁻¹)	n (cm ⁻¹)	μ_{opt} (cm ² /Vs)
0.9% Ce (acac)	5814	1015	1.51×10^{20}	22.9
2.0% Ce (acac)	6983	777	2.18×10^{20}	30.1
3.5% Ce (acac)	7410	691	2.45×10^{20}	33.7
3.7% Ce (acac)	7290	716	2.38×10^{20}	32.5
5.2% Ce (acac)	7359	696	2.42×10^{20}	33.6
8.6% Ce (acac)	7400	979	2.33×10^{20}	23.9
11.1% Ce (acac)	7226	968	2.45×10^{20}	23.6
6.4% Ce (TMHD)	7425	1072	2.46×10^{20}	21.8
4.8% Ce (acetate)	7294	884	2.38×10^{20}	26.4
5.6% Ce (C.A.N.)	7550	1232	2.55×10^{20}	18.9
1.2% Sn	7175	1507	2.30×10^{20}	15.4
2.1% Sn	9282	1325	3.85×10^{20}	17.7
4% Sn	13009	1355	7.56×10^{20}	17.2
5.3% Ce + 1.0% Sn	8107	990	2.94×10^{20}	23.6
5.2% Ce + 2.1% Sn	8774	1239	3.44×10^{20}	18.8

Table A.1: Simple Drude model fitting results for LSPR in Ce:In₂O₃ nanocrystals.

and the optical mobility is calculated from the relations:

$$\sigma_{\text{opt}} = en\mu_{\text{opt}} = \frac{ne^2}{m_e\gamma} \quad (\text{A.6})$$

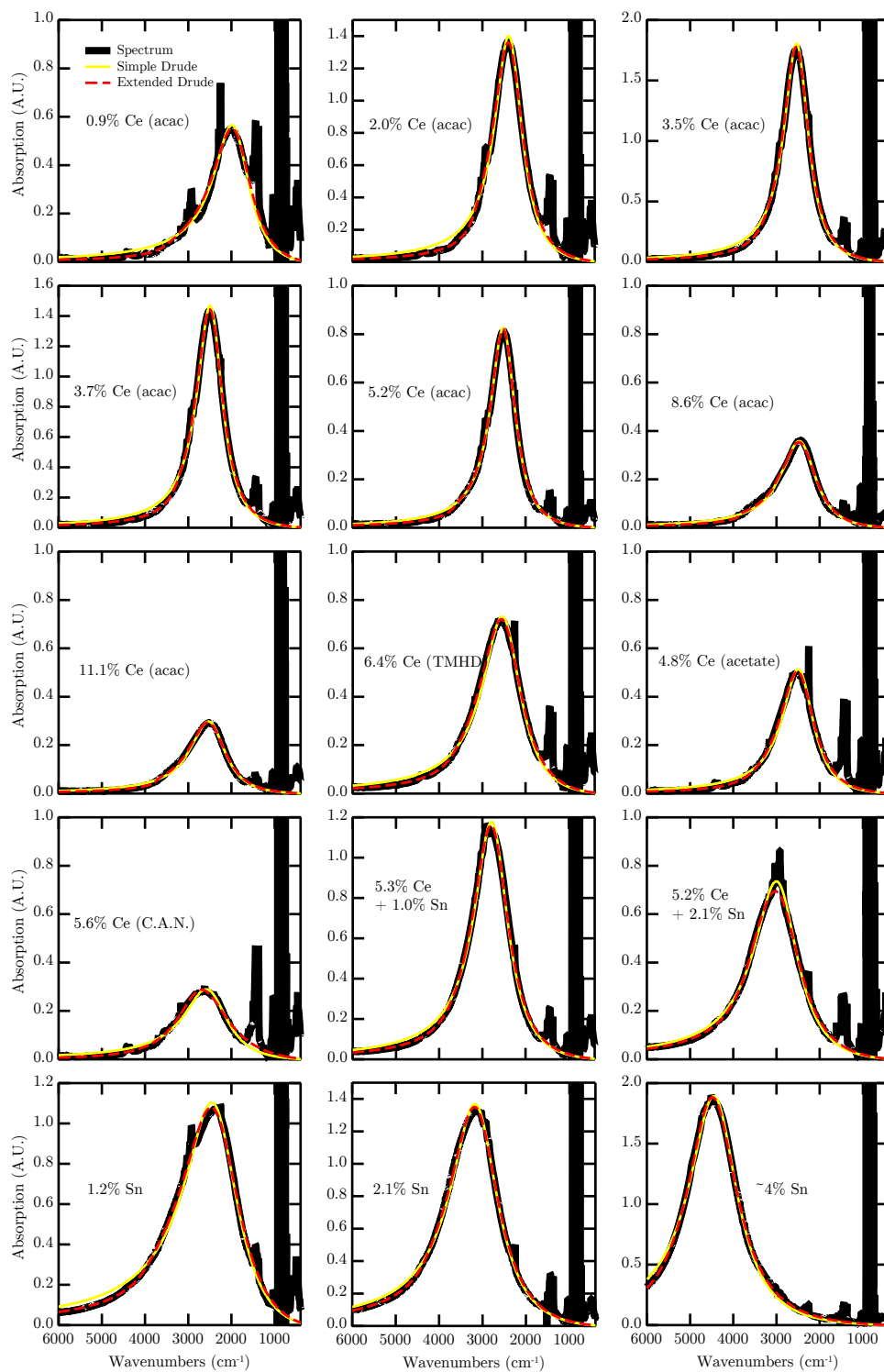


Figure A.2: Liquid cell FTIR spectra of the nanocrystals used in this study along with simple Drude and extended Drude optical fits.

A.3 X-ray absorption spectroscopy (XAS) experimental details

Synchrotron X-ray absorption spectra at the Ce $M_{4,5}$ -edge we collected at beam line (BL) 8.0.1 and 6.3.2 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, Berkeley, CA. Samples were prepared either by dropcasting hexane dispersions of the nanocrystals onto doped silicon substrates, or by spincoating concentrated nanocrystal dispersions in 1:1 hexane:octane. In general, the dropcasted samples gave better total fluorescence yield (TFY), and the spincoated samples gave better total electron yield (TEY). Analysis of Ce oxidation state was performed using TEY spectra. The pre-edge signal was background subtracted using the software from ALS BL 10.3.2 with an edge + elastic fitting algorithm with a quadratic function tailored to the Ce M_5 edge. The spectra were all normalized to the post-edge step background.

The Ce $M_{4,5}$ -edge has complex multiplet structure that changes with oxidation state. The reference spectra displayed in Figure 7.5 show the qualitative differences between Ce^{3+} and Ce^{4+} , and comparison with the $Ce:In_2O_3$ spectra indicates that a significant portion of Ce dopants in the nanocrystals is in the Ce^{3+} oxidation state. The first three peaks in both the M_5 and M_4 edges (at approximately 879, 882, 883 eV, and 897, 898.5, 900 eV, respectively) are associated with the 3+ oxidation state, while the fourth and fifth peaks in both edges (884, 888.5 eV, and 902, 907 eV) are associated with the 4+ oxidation state. Dividing the areas of all four peaks associated with Ce^{4+} by the sum of the areas of all 10 peaks in the $M_{4,5}$ -edge gives the approximate fraction of Ce^{4+} relative to the total Ce content. Multi peak fitting was performed using IGOR Pro software. While the accuracy of this method can be increased by accounting for local Ce coordination environments, we did not perform those corrections for the purpose of this analysis.

A.4 Density functional theory (DFT) simulations

DFT^{1,2} calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) with a plane-wave basis set expanded up to a cutoff energy of 550 eV.^{3,4} Projector augmented wave (PAW) potentials were used, treating 13 valence electrons for indium ($4d^{10}5s^25p^1$), 14 for tin ($4d^{10}5s^25p^2$), 12 for cerium ($5s^25p^64f^15d^16s^2$), and 6 for oxygen ($2s^22p^4$).^{5,6} Brillouin zone integration was done on a 3x3x3 Monkhorst-Pack k-point mesh. Lattice parameters and atom positions were relaxed until residual forces became less than 0.01 eV/Å. Radial lattice strain and defect formation energy calculations were performed using the 80-atom bixbyite unit cell (space group $Ia-3$) and the PBE+U exchange-correlation functional,⁷ where a U value of 4 eV was applied to indium 4d, tin 4d, and cerium 4f states. For a more accurate description of electronic structure, density of states calculations were performed on the 40-atom primitive cell using the HSE06 hybrid functional, with $\alpha = 25\%$ exact nonlocal Hartree-Fock exchange.^{8,9} A cutoff energy of 450 eV was used for all hybrid functional calculations with lattice parameter and atomic positions fixed to those obtained via PBE+U method. The

Species (structure)	Energy calculated by DFT (eV)	Formula units per unit cell	Chemical potential (eV)
In ₂ O ₃ (80-atom cubic)	-454.05	16	$\mu_{\text{In}_2\text{O}_3, \text{bulk}} = -28.38$
SnO ₂ (6-atom tetragonal)	-39.38	2	$\mu_{\text{InO}_2, \text{bulk}} = -19.69$
CeO ₂ (12-atom cubic)	-98.64	4	$\mu_{\text{CeO}_2, \text{bulk}} = -24.66$
In metal (2-atom tetragonal)	-4.69	2	$\mu_{\text{In}, \text{bulk}} = -2.34$
Sn metal (4-atom tetragonal)	-15.28	4	$\mu_{\text{Sn}, \text{bulk}} = -3.82$
Ce metal (FCC)	-17.35	4	$\mu_{\text{Ce}, \text{bulk}} = -4.34$
O ₂ (oxygen molecule)	-8.77	2	$\mu_{\text{O}} = -4.38$

Table A.2: Bulk DFT-calculated chemical potentials used for defect energy calculations by Equation 7.5 in Chapter 7.

partial densities of states were projected onto spheres centered around the atom positions with radii of 1.68, 1.57, 1.32 and 0.82 Å for In, Sn, Ce and O, respectively.

Defect formation energies were calculated as a function of electron chemical potential ($\text{VBM} \leq \mu_e \leq \text{CBM}$), with CBM determined by the more accurate, hybrid functional band gap, and the chemical potential of the species added and/or removed. The chemical potentials of the atomic species added or removed are limited to a range of obtainable chemical potentials, and they are necessarily related to each other. For the O-poor, metal-rich limiting condition, the chemical potential of the metallic species is set to the energy of atoms in the pure metal, μ_{metal} , and the chemical potential of oxygen is $\mu_{\text{O}} = 1/3\mu_{\text{In}_2\text{O}_3} - 2/3\mu_{\text{In}}$. For the O-rich, metal-poor limiting condition, the chemical potential of oxygen is the energy of an oxygen atom in an oxygen molecule, $\mu_{\text{O}} = 1/2\mu_{\text{O}_2}$, and the chemical potential of the metallic species is given by $\mu_{\text{metal}} = \mu_{\text{metal oxide}} - \mu_{\text{O}}$. The calculated chemical potentials are listed in Table A.2 while the $\sum_i n_i \mu_i$ terms used to account for added and removed atoms the calculation of defect formation energy are shown in Table A.3.

The correction factor E_{corr} in Equation 7.5 (Chapter 7) accounts for finite size effects in charged crystals and includes a potential alignment and image charge correction term. The potential alignment correction ($q\Delta V$) accounts for the compensating background charge introduced for charged cell calculations and was determined from the difference in atomic potential of atoms far from the defect in defective and perfect cells.¹⁰ The Makov-Payne correction scheme, as applied by Oba et al., was used to account for electrostatic interactions between charged defects.^{11,12}

Defect	Limit	$\sum_i n_i \mu_i$	Value (eV)
Sn_{In}	O-rich	$\mu_{\text{SnO}_2, \text{bulk}} - 1/2 \mu_{\text{In}_2\text{O}_3, \text{bulk}} - 1/2 \mu_{\text{O}}$	-3.31
	O-poor	$\mu_{\text{Sn, bulk}} - \mu_{\text{In, bulk}}$	-1.48
Ce_{In}	O-rich	$\mu_{\text{CeO}_2, \text{bulk}} - 1/2 \mu_{\text{In}_2\text{O}_3, \text{bulk}} - 1/2 \mu_{\text{O}}$	-8.28
	O-poor	$\mu_{\text{Ce, bulk}} - \mu_{\text{In, bulk}}$	-2.00
V_{O}	O-rich	$-\mu_{\text{O}}$	4.38
	O-poor	$-[1/3 \mu_{\text{In}_2\text{O}_3, \text{bulk}} - 2/3 \mu_{\text{In}}]$	7.90

Table A.3: $\sum_i n_i \mu_i$ terms used to calculate defect formation energy for different defect species and limiting conditions.

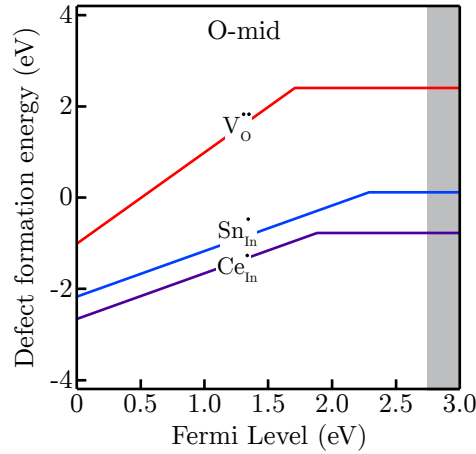


Figure A.3: Defect formation energies vs. Fermi level for oxygen vacancies ($\text{V}_{\text{O}}^{\bullet\bullet}$), substitutional tin dopants ($\text{Sn}_{\text{In}}^{\bullet}$), and substitutional cerium dopants ($\text{Ce}_{\text{In}}^{\bullet}$) under conditions with an intermediate chemical potential of oxygen. All chemical potentials in this case are taken as the average chemical potential between the O-poor and O-rich extremes. The valence band maximum is set to 0 eV and the gray shaded region denotes the conduction band edge as determined by the band gap calculated via the hybrid functional. The slope of the formation energy vs. Fermi level reflects the stable charge state of the defect at that Fermi level.

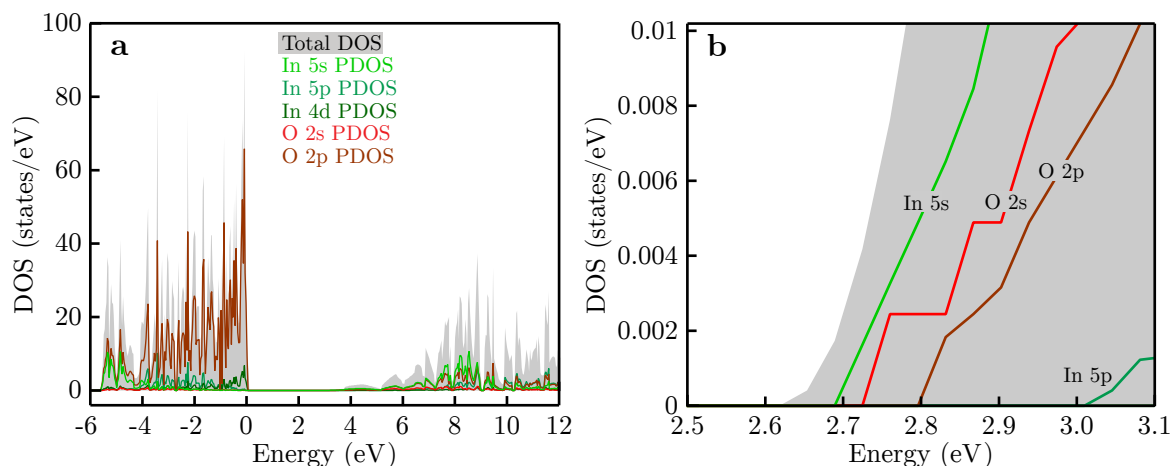


Figure A.4: Total and partial density of states calculated by DFT for stoichiometric In_2O_3 . The valence band maximum is set to 0 eV. Panel b is a detailed view of the conduction band edge of stoichiometric In_2O_3 .

A.5 Synchrotron infrared nano spectroscopy (SINS) single nanocrystal spectra

Single nanocrystal absorption measurements¹³ were performed using a modified atomic force microscope (AFM) at the Advanced Light Source in order to perform synchrotron infrared nano-spectroscopy (SINS).¹⁴ This technique couples light to the near field in the space between an AFM tip and substrate and the scattered light is then collected to measure the complex infrared scattering function of the material that sits beneath the AFM tip with roughly 20 nm spatial resolution. Through the extraction of the real and imaginary portion of this function both the particle light absorption and scattering can be ascertained. Lock-in amplification of scattered light was collected at the second harmonic of the AFM tip resonance frequency in order to isolate signal exclusively from the nanocrystal's infrared response. In order to perform SINS on single nanocrystals, dilute dispersions of nanocrystals were spin cast onto gold-coated silicon substrates leading to isolated particles that were sufficiently spaced to eliminate the possibility of inter-particle LSPR coupling. Backgrounds were collected from nearby, empty portions of the substrate to minimize spurious far field contamination of the signal. Single particle scans displayed as absorption represent the imaginary component of the background-subtracted complex scattering function.¹⁵ These scans were performed on several particles to account for particle to particle variations.

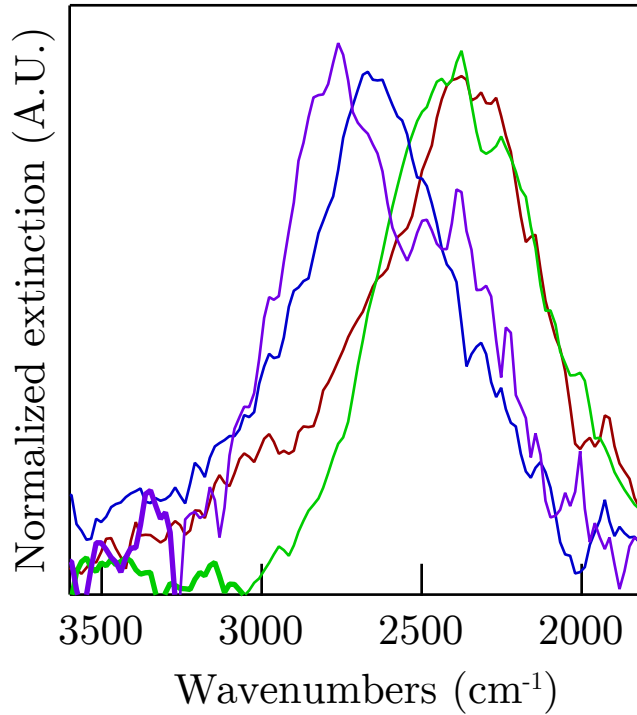


Figure A.5: Additional SINS spectra collected from multiple single $\text{Ce:In}_2\text{O}_3$ nanocrystals. The blue spectrum has a FWHM of 479 cm^{-1} at a peak location of 2644 cm^{-1} , corresponding to a quality factor of 5.5.

A.6 Near field simulations

Frequency-dependent dielectric functions are typically extracted optically via the measurement of transmission and reflection of thin film samples. In the case of nanocrystal films, these optical data are usually convoluted with nanocrystal shape/size/interface effects, making the extraction of an accurate dielectric function difficult.

In our work, we use SINS to measure the optical properties of single, isolated nanocrystals to evaluate their dielectric functions. A SINS measurement yields the scattering and absorption characteristics of a coupled tip-nanocrystal-substrate system. To extract a dielectric function from SINS data, one can opt to use analytical methods such as extended finite dipole theory, which has been done previously to calculate the dielectric function of poly(methyl methacrylate) with high spatial resolution.¹⁶ Another option is to use computational methods, which are more flexible. Here, we computationally solve Maxwell's equations for our system of interest, namely the coupled PtSi AFM tip- $\text{Ce:In}_2\text{O}_3$ cubic nanocrystal-Au substrate system. Using the COMSOL multiphysics program, the finite element method can be used to discretize each component of the system so that their geometry is accurately represented in solving Maxwell's equations.

The dielectric function of the nanocrystal was determined iteratively. The initial guess

for the dielectric function of the cubic nanocrystal was taken from the Drude fit to the ensemble spectrum, while the dielectric functions for PtSi and Au are known. These dielectric functions, along with the finite element method, were then used to simulate the absorption spectrum of the entire coupled structure. Depending on deviations between the simulated spectrum and the experimentally collected SINS spectrum, the plasma frequency and frequency-dependent damping function could be iteratively adjusted to change the dielectric function of the nanocrystal to achieve a match between the experimental and simulated spectra. The flowchart in Figure A.6 graphically summarizes this process. After matching the spectra, the dielectric function of the Ce:In₂O₃ nanocrystal was extracted and used to simulate the absorption and near field properties of a single, isolated nanocrystal free of substrate and tip coupling effects.

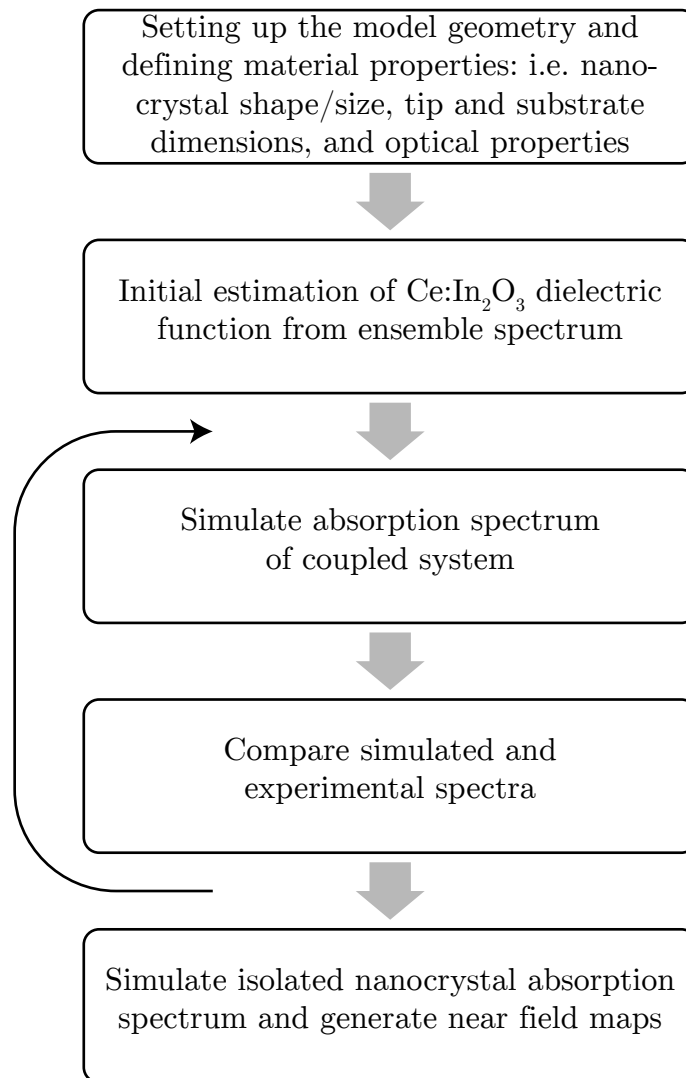


Figure A.6: Flowchart depicting process for determining the dielectric function of a Ce:In₂O₃ nanocrystal from an experimental SINS spectrum.

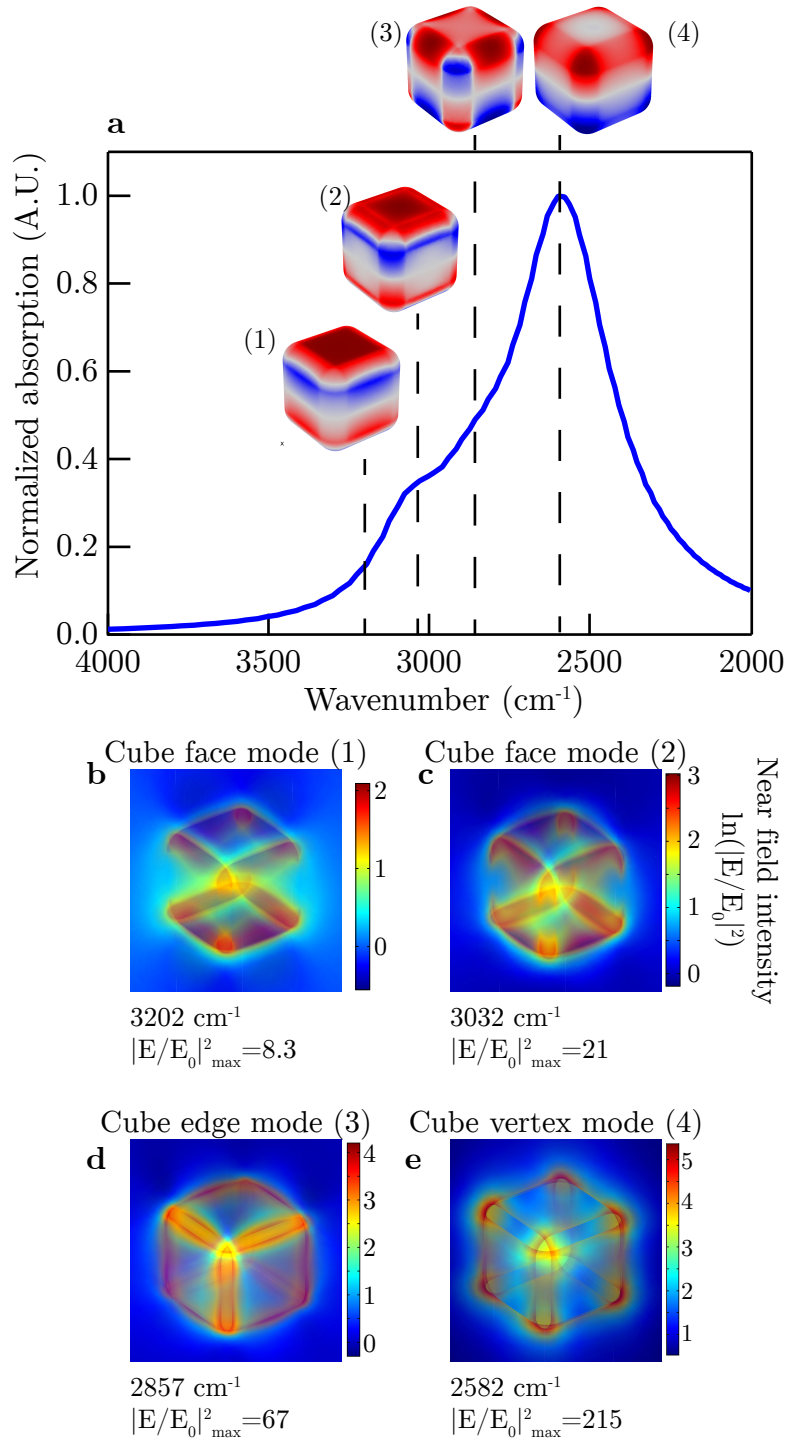


Figure A.7: Electric charge density maps (a) and electric near field intensity maps (b-e) of simulated LSPR modes of a Ce:In₂O₃ cubic nanocrystal.

A.7 Appendix References

Below are the references that are specifically pertinent to this Appendix:

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16. Govyadinov, A. A.; Amenabar, I.; Huth, F.; Carney, P. S.; Hillenbrand, R. Quantitative Measurement of Local Infrared Absorption and Dielectric Function with Tip-Enhanced Near-Field Microscopy. *J. Phys. Chem. Lett.* **2013**, *4*, 1526–1531.

Appendix B

Drude model Matlab code and documentation

B.1 extended_drude_fit.m documentation

Run this script to fit a solution spectrum with the extended Drude model

This script loads and initializes everything and it calls a function to perform the fitting. That fitting function utilizes the extended Drude script to properly fit the spectra

Contents

- Initialize global variables for fitting
- Load data
- Simple Drude Model (frequency independent damping)
- Extended Drude Model (frequency dependent damping)
- Create vectors for plotting the fits
- Generate/append CSV file with summary of results and a CSV file with curves
- Plot results and save plot

Initialize global variables for fitting

```
clear all
close all
global epsilonNC epsilonSolvent epsilonLigand pathLength
epsilonNC=4; % Dielectric constant of nanocrystal
epsilonSolvent=1.505^2; % TCE Host/solvent Dielectric Constant
epsilonLigand=1.46^2; % Dielectric constant of ligand shell
diameter=7.5e-7; % Nanocrystal diameter in cm
```

```

pathLength=.05;           % Optical path length in cm
% Low and high frequency fitting cutoffs (wave numbers)
lowFreqCutoff=1500;
hiFreqCutoff=6000;

```

Load data

The data should be in a text file named "spectrum_to_fit" and they should be formatted so that wave numbers are in the first column and absorption values are in the second column

```

[filename, pathname]=uigetfile('spectra/*.txt',...
    'Select the file you want to fit');
spectrum=dlmread([pathname filename],'\t',2,0);
[spectrumLocation, sampleName, extension]=fileparts(filename);

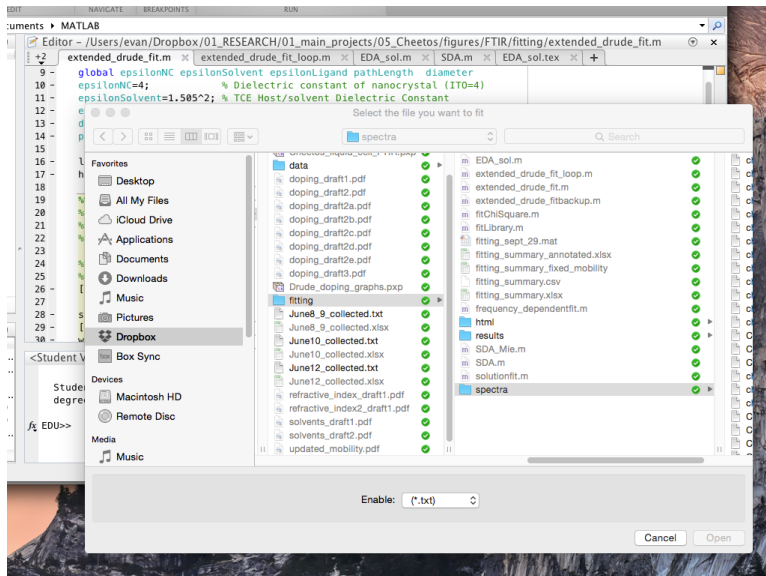
%load regular frequency values in wave numbers
wavenumbers=spectrum(:,1);

%load absorption values
absorption=spectrum(:,2);

% set fitting range
% set limits of fitting and grab indices
limits=find(wavenumbers>lowFreqCutoff,...
    &wavenumbers<hiFreqCutoff);

%extract frequencies
reducedFrequency=wavenumbers(limits);
%extract absorption values over desired range
reducedAbsorption=absorption(limits);

```

Simple Drude Model (frequency independent damping)

```

disp('$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$')
disp('Simple Drude_Mie')
figure
op = optimset; % Default optimization options
op.Display='on';
op.Plot=1; %display plot with fitting results
op.ErrorsUnknown = 1; %set to 1 if measurement uncertainties
%are unknown
%Increase #of function evals. for convergence
op.MaxFunEvals=1e12;
op.TolX=1e-12; %Smallest variable step tolerance
op.TolFun=1e-12; %Smallest function change tolerance
op.MaxIter=3e4; %Maximum iterations possible
%set to 1 to get fit uncertainties for each parameter
op.FitUncertainty=[1 1 1];

%Perform the simple Drude fit to the data by calling SDA.m
[paramsIT0,dParamsIT0,gofIT0,stddevIT0]=fitChiSquare,...
    (reducedFrequency,reducedAbsorption,@SDA,...
    [1 3000 800],[[]],[[]],op);

disp('Calculated value for n in cm^-3')

```

```

disp('effective mass 0.3m, 0.4m, 0.5m')
% take (normal) plasma frequency in cm^-1 convert to
% angular frequency rad/s to calculate n
omega_pSDA=paramsIT0(2)*3*10^10*2*pi;
mstar=[0.3 0.4 0.5]*9.109e-31; %effective mass in kg
echarge=1.6022e-19; %electron charge in coulombs
epsilon0=8.85e-12; %permittivity of free space(SI)

```

```

% display electron density n in cm^-3
nSDA=(omega_pSDA).^2*mstar*epsilon0/echarge^2/10^6
$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$

```

```

Simple Drude_Mie
Fitting function parameters...

```

```

Finding parameter 1 lower bound
Finding parameter 1 upper bound
Finding parameter 2 lower bound
Finding parameter 2 upper bound
Finding parameter 3 lower bound
Finding parameter 3 upper bound
Parameter 1 = 184.433 + 0.258709 - 0.258488
Parameter 2 = 7359.48 + 1.39927 - 1.39915
Parameter 3 = 695.65 + 1.31905 - 1.31653
Reduced chi-square = 1.000000
Calculated value for n in cm^-3
effective mass 0.3m, 0.4m, 0.5m

```

```

nSDA =

```

```

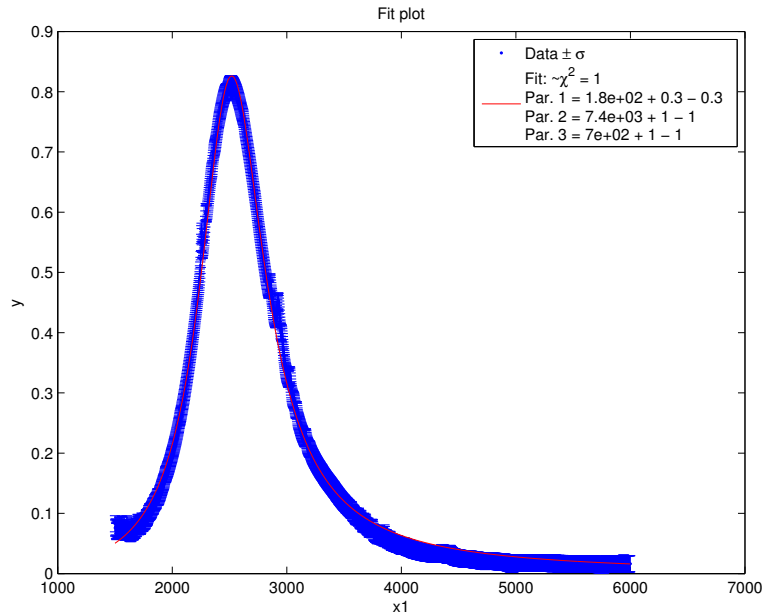
1.0e+20 *

```

```

1.8130    2.4173    3.0217

```



Extended Drude Model (frequency dependent damping)

```

disp('$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$')
disp('Extended Drude')

op=optimset;
op.Display='on';
op.Plot=1;           %display plot with fitting results
figure
op.ErrorsUnknown = 1;           %set to 1 if measurement
                               uncertainties
                               %are unknown

op.MaxFunEvals=1e15;
op.TolX=1e-15;         %Smallest step tolerance
op.TolFun=1e-15;       %Smallest function change tolerance
op.MaxIter=1e6;        %Maximum iterations possible
%set to 1 to get uncertainties for each parameter
op.FitUncertainty = [1 1 1 1 1 1];

% volFraction, omega_p, Gamma_L, Gamma_H, Gamma_X, Gamma_W
op.LowerBound = [1 1000 50 0 1000 1];
initialGuess = [500 10000 1400 1000 4000 200];
op.UpperBound = [10000 100000 5000 5000 100000 2000];

```

```

%Perform extended Drude fit to the data by calling EDA_sol.m
[paramsIT0_ed,dParamsIT0_ed,gofIT0_ed,stddevIT0_ed]=...
    fitChiSquare(reducedFrequency,reducedAbsorption, ...
    @EDA_sol,initialGuess,[],[],op);

disp('Calculated value for n in cm^-3')
disp('effective mass 0.3m, 0.4m, 0.5m')

% take (normal) plasma frequency in cm^-1 convert to
% angular frequency rad/s to calculate n
omega_pEDA=paramsIT0_ed(2)*3*10^10*2*pi;
mstar=[0.3 0.4 0.5]*9.109e-31; %effective mass in kg
echarge=1.6022e-19; %electron charge in coulombs
epsilon0=8.85e-12; %permittivity of free space(SI)

% display electron concentration n in cm^-3
nEDA= (omega_pEDA).^2*mstar*epsilon0/echarge^2/10^6

$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$

```

Extended Drude

Fitting function parameters...

```

Finding parameter 1 lower bound
Finding parameter 1 upper bound
Finding parameter 2 lower bound
Finding parameter 2 upper bound
Finding parameter 3 lower bound
Finding parameter 3 upper bound
Finding parameter 4 lower bound
Finding parameter 4 upper bound
Finding parameter 5 lower bound
Finding parameter 5 upper bound
Finding parameter 6 lower bound
Finding parameter 6 upper bound
Parameter 1 = 186.895 + 0.220753 - 0.220416
Parameter 2 = 7362.33 + 1.10592 - 1.10575
Parameter 3 = 714.811 + 1.62516 - 1.5791
Parameter 4 = 467.757 + 6.9922 - 7.08818
Parameter 5 = 3678.65 + 15.6993 - 15.634
Parameter 6 = 71.4351 + 12.145 - 11.2423
Reduced chi-square = 1.000000

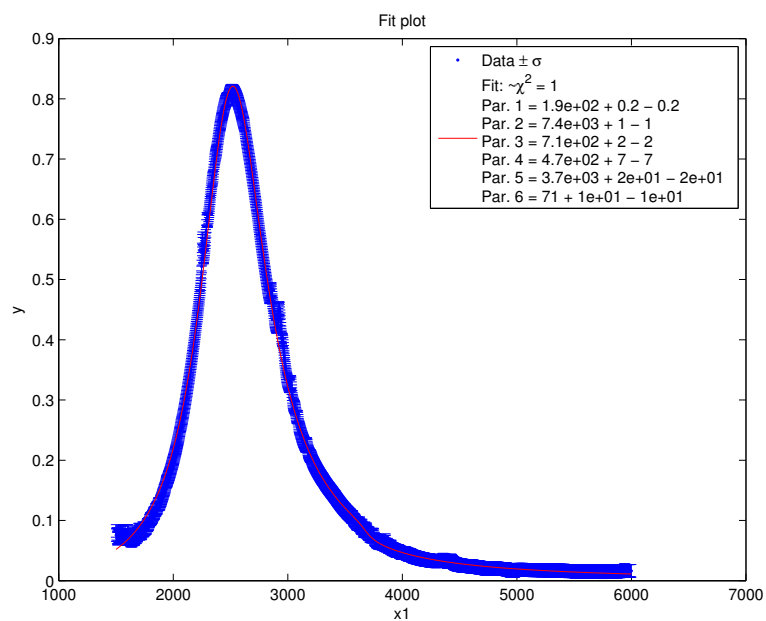
```

Calculated value for n in cm^{-3}
 effective mass 0.3m, 0.4m, 0.5m

nEDA =

1.0e+20 *

1.8144 2.4192 3.0240



Create vectors for plotting the fits

```
absorptionSDA=SDA(paramsITO,[max(wavenumbers):-2:...
    min(wavenumbers)]');
absorptionEDA=EDA_sol(paramsITO_ed,[max(wavenumbers):-2...
    :min(wavenumbers)]');
```

%Determine the mean square error of each fit

```
MSE_SDA=mean((reducedAbsorption-SDA(paramsITO,...
    reducedFrequency)).^2)
MSE_EDA=mean((reducedAbsorption-EDA_sol(paramsITO_ed,...
    reducedFrequency)).^2)
```

MSE_SDA =

```
1.7891e-04
```

```
MSE_EDA =
```

```
1.0857e-04
```

Generate/append CSV file with summary of results and a CSV file with curves

```
% Generate a CSV file containing the data and fit curves
% *no spaces in file header*
fileHeader = {'Wavenumbers' 'Absorption' 'SDA_fit' 'EDA_fit'};
fileData=[wavenumbers absorption absorptionSDA absorptionEDA];
fileContents=array2table(fileData, 'VariableNames',fileHeader);
writetable(fileContents,...
    strcat(['results/' sampleName '_fits'], '.csv'));

% Append fitting parameters to a summary CSV file
SDA_results = {'simple Drude:' 'SDA f_v' ...
    'SDA \omega_p (cm^-1)' 'SDA \gamma (cm^-1)'};
SDA_results = [SDA_results; {sampleName, paramsITO(1)*1e-6, ...
    paramsITO(2), paramsITO(3)}];
SDA_results = [SDA_results; {'SDA n (cm^-3) for m^*=.3m_e; ...
    .4m_e; .5m_e', nSDA(1), nSDA(2), nSDA(3)}];
EDA_results = {'Extended Drude:' 'EDA f_v' ...
    'EDA \omega_p (cm^-1)' 'EDA \Gamma_L (cm^-1)' ...
    'EDA \Gamma_H (cm^-1)' 'EDA \Gamma_X (cm^-1)' ...
    'EDA \Gamma_W (cm^-1)'};
EDA_results = [EDA_results; {sampleName, ...
    paramsITO_ed(1)*1e-6, paramsITO_ed(2), ...
    paramsITO_ed(3), paramsITO_ed(4), ...
    paramsITO_ed(5), paramsITO_ed(6)}];
EDA_results = [EDA_results; {'EDA n (cm^-3) for ...
    m^*=.3m_e; .4m_e; .5m_e', ...
    nSDA(1), nSDA(2), nSDA(3), '', '', ''},];

fid = fopen('fitting_summary.csv','a');
```

```

fprintf(fid, '%s, %s, %s, %s\n', SDA_results{1,:});
fprintf(fid, '%s, %f, %f, %f\n', SDA_results{2,:});
fprintf(fid, '%s, %f, %f, %f\n', SDA_results{3,:});
fprintf(fid, '%s, %s, %s, %s, %s, %s, %s,\n', EDA_results{1,:});
fprintf(fid, '%s, %f, %f, %f, %f, %f, %f\n', EDA_results{2,:});
fprintf(fid, '%s, %f, %f, %f, %s, %s, %s\n', EDA_results{3,:});
fclose(fid);

```

Plot results and save plot

```
figure
```

```

set(gcf, 'units', 'points', 'position', [300 100 500 500/1.618])
clf
h=[0 0 0];
% Plot data, SDA fit, and EDA fit on one figure
hold on
h(1)=plot(wavenumbers, absorption, 'k', 'linewidth', 3);
h(2)=plot([max(wavenumbers):-2:min(wavenumbers)]', ...
          absorptionSDA, 'b-', 'linewidth', 2);
h(3)=plot([max(wavenumbers):-2:min(wavenumbers)]', ...
          absorptionEDA, 'y-', 'linewidth', 2);
hold off

% Set figure properties
set(gca, 'box', 'on')
set(gca, 'fontsize', 16, 'fontname', 'Myriad', 'linewidth', 1.5)
axis([300 8000 0 (max(reducedAbsorption)+0.2)])
xlabel('Wavenumber (cm-1)')
ylabel('Absorbance')
text(3000, (max(reducedAbsorption)+0.1), sampleName, ...
     'fontsize', 12, 'fontweight', 'bold')
set(gcf, 'color', 'w')
Lh=legend(h, 'Data', 'Simple Drude', 'Extended Drude', ...
         'Location', 'NorthWest');
set(gca, 'Xdir', 'reverse')

% annotate plot with fitting coefficient results (3 sig figs)
teststring=[SDA_results{1,2} ': ' ...
            num2str(SDA_results{2,2},3) ' ,...
            [SDA_results{1,3} ': ' num2str(SDA_results{2,3},3) ' ,...
            [SDA_results{1,4} ': ' num2str(SDA_results{2,4},6) ' ,...

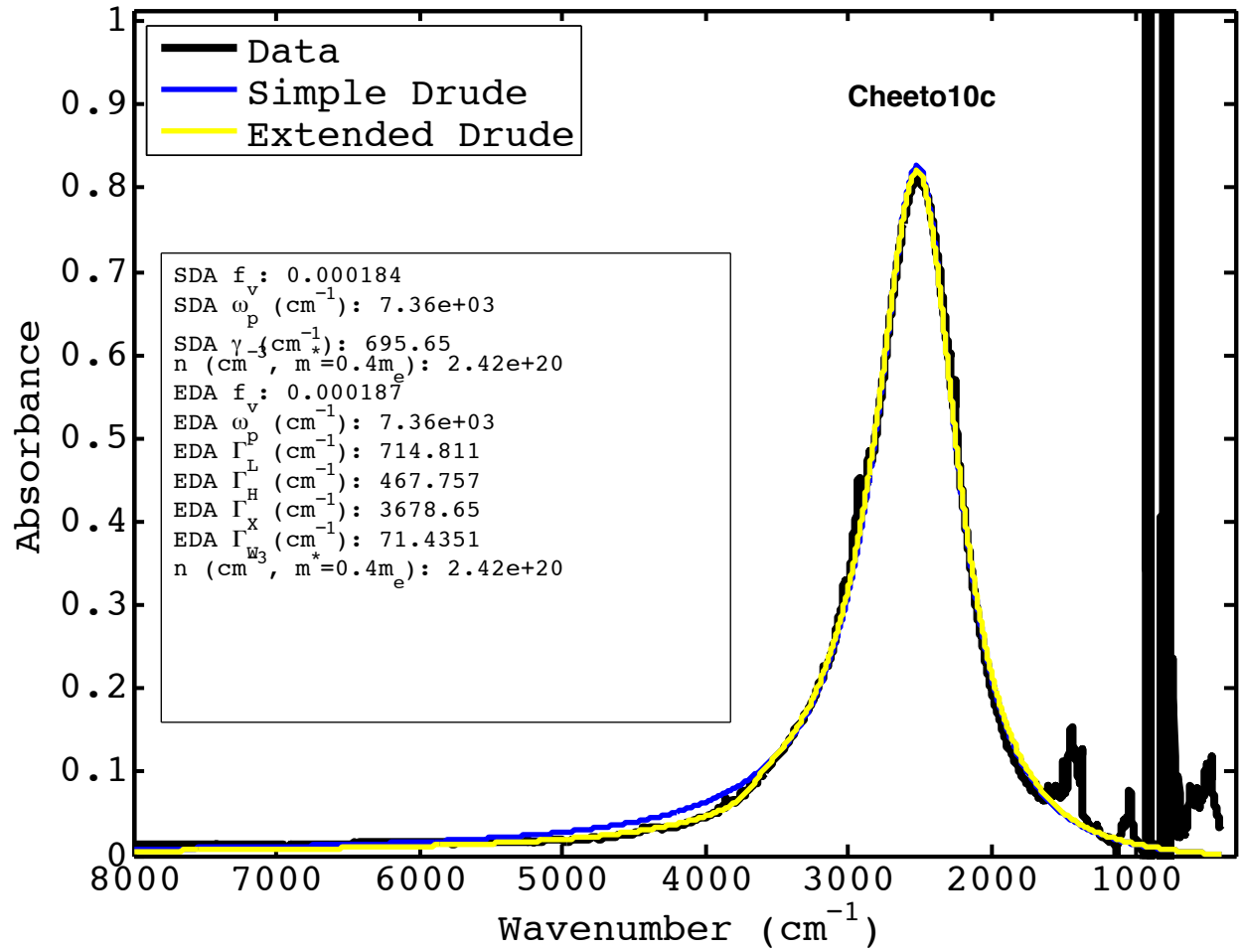
```

```

['n (cm-3, m*=0.4me): ' num2str(nSDA(2),3)],...
[EDA_results{1,2} ': ' num2str(EDA_results{2,2},3)] ,...
[EDA_results{1,3} ': ' num2str(EDA_results{2,3},3)] ,...
[EDA_results{1,4} ': ' num2str(EDA_results{2,4},6)] ,...
[EDA_results{1,5} ': ' num2str(EDA_results{2,5},6)] ,...
[EDA_results{1,6} ': ' num2str(EDA_results{2,6},6)] ,...
[EDA_results{1,7} ': ' num2str(EDA_results{2,7},6)] ,...
['n (cm-3, m*=0.4me): ' num2str(nEDA(2),3)]];
annotation('textbox', [.15 .24 .4 .45], 'String',teststring,...
'fontname' , 'Myriad')

saveas(gcf,['results/' sampleName '.png']);

```

B.2 SDA.m documentation

B.2.1 Matlab code

```
function A=SDA(a,omega)

%This function is used to calculate the Absorbance using only
%the simple Drude theory with the Maxwell Garnett Effective
%Medium Approximation
%
% Input variables
%   xm -- frequency variable in cm^-1           (omega)
%   a -- parameters:
%       a(1) -- volume fraction                  (volFraction)
```

```

%      a(2) -- plasma frequency cm-1      (omega_p)
%      a(3) -- damping constant cm-1      (gamma)
%
% Output variable
%  A -- absorbance of the solution

global epsilonNC epsilonSolvent pathLength diameter
volFraction=a(1);
omega_p=a(2);
gamma=a(3);

%Dielectric function of an isolated particle with a simple
  damping constant
epsilonParticle=epsilonNC-omega_p^2./...
  (omega.^2+1i*omega.*gamma);

% Effective dielectric function
C=volFraction*(epsilonParticle-epsilonSolvent)./...
  (epsilonParticle+2*epsilonSolvent)*1e-6;
% note the 1e-6 which is intended to help the solver in
% extended_drude_fit.m converge. This lets the initial guesses
% be of similar order of magnitude, so the initial guess for
  volume
% fraction is 106 times higher, the 1e-6 term here accounts
  for that

ep_eff=epsilonSolvent*(1+2*C)/(1-C);
% Calculate Absorbance
A=(4*pi*omega.*imag(sqrt(ep_eff)))*pathLength/log(10);

```

B.2.2 Explanation of math/model

This function is a basic or simple Drude Approximation based on frequency-independent scattering and an effective medium approximation. It takes in four arguments: the volume fraction of nanocrystals in the solvent ('volFraction', unitless), the plasma frequency ('omega.P', in wave numbers), a scattering or damping parameter ('gamma', in wave numbers), and a vector of frequencies ('omega', wave numbers) as the independent variable. Using these inputs it generates a dielectric function and in turn calculates the absorption. There are also global variables: the dielectric constant of the nanocrystal material ('epsilonNC'), the dielectric constant of the solvent ('epsilonSolvent'), and the path length of light in the measurement cell in cm ('pathLength'). First, the dielectric function of a single,

isolated nanocrystal is calculated using the expression:

$$\varepsilon_{\text{particle}} = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma}$$

If the nanocrystals are at an appreciable concentration in the solvent (this may be the case if doing FTIR liquid cell measurements with short path lengths) then it is necessary have to use the effective medium approximation (EMA) to account for far-field effects between nanocrystals. EMA also accounts for dielectric interactions between the nanocrystals and the solvent. The EMA is:

$$\frac{\varepsilon_{\text{eff}} - \varepsilon_{\text{solvent}}}{\varepsilon_{\text{eff}} + 2\varepsilon_{\text{solvent}}} = f_v \left(\frac{\varepsilon_{\text{particle}} - \varepsilon_{\text{solvent}}}{\varepsilon_{\text{particle}} + 2\varepsilon_{\text{solvent}}} \right)$$

If we set the term in parentheses equal to 'C' and solve for the effective dielectric function, we have:

$$\varepsilon_{\text{eff}} = \varepsilon_{\text{solvent}} \left(\frac{1 + 2C}{1 - C} \right)$$

Finally the absorption is calculated as:

$$A = 4\pi\omega \frac{\ell}{\ln(10)} \text{Im}[\sqrt{\varepsilon_{\text{eff}}}]$$

sectionEDA.m documentation

B.2.3 Matlab code

```
function A=EDA_sol(a,omega)
% This function is used to calculate the absorbance using the
% extended Drude theory with an empirical frequency-
% dependent scattering function and an effective medium
% approximation theory taking into account the volume
% fraction of nanocrystals dispersed in a solvent
%
%       Input variables
%       omega -- frequency variable in cm^-1
%       a -- a vector of parameters:
```

```

%      a(1) -- volume fraction
%              (volFraction)
%      a(2) -- plasma frequency cm-1
%              (omega_p)
%      a(3) -- low frequency damping constant cm-1
%              (Gamma_L)
%      a(4) -- high frequency damping constant cm-1
%              (Gamma_H)
%      a(5) -- crossover frequency cm-1
%              (Gamma_X)
%      a(6) -- width cm{-1}
%              (Gamma_W)
%
% Output variable
% A -- absorbance of the layer

global epsilonNC epsilonSolvent pathLength
volFraction=a(1);
omega_P=a(2);
Gamma_L=a(3);
Gamma_H=a(4);
Gamma_X=a(5);
Gamma_W=a(6);

%Calculate damping function for frequency dependent
%scattering based on the empirical formula
GAMMA=Gamma_L-((Gamma_L-Gamma_H)/pi)*
        (atan((omega-Gamma_X)/Gamma_W)+pi/2);

%Dielectric function of an isolated particle with frequency-
%dependent scattering
epsilonParticle=epsilonNC-omega_P^2./
        (omega.^2+1i*omega.*GAMMA);

%Calculate the effective dielectric function based on the
%effective medium approximation

%Right hand side of effective medium equation
emaRHS=volFraction*(epsilonParticle-epsilonSolvent)./(
        (epsilonParticle+2*epsilonSolvent)*1e-6;
% note the 1e-6 which is intended to help the solver in
% extended_drude_fit.m converge. This lets the initial guesses

```

```

% be of similar order of magnitude, so the initial guess for
  volume
% fraction is 10^6 times higher, the 1e-6 term here accounts
  for that

%rearranged EMA equation solved for
%effective dielectric function
epsilonEffective=epsilonSolvent.*(1+2*emaRHS)./(1-emaRHS);

%Calculate Absorbance
A=(4*pi*omega.*imag(sqrt(epsilonEffective)))*
    pathLength/log(10);
%Dividing by ln(10) converts the absorption coefficient
%to absorbance because A=-log_10(T), and T=exp(-a*l)

```

B.2.4 Explanation of math/model

This function is an extended Drude Approximation based on frequency-dependent scattering and an effective medium approximation. It takes in six arguments: the volume fraction of nanocrystals in the solvent ('volFraction', unitless), the plasma frequency ('omega_P', in wave numbers), four scattering or damping parameters: a low-frequency damping constant ('Gamma_L', wave numbers), a high frequency damping constant ('Gamma_H', wave numbers), a cross-over frequency ('Gamma_X', wave numbers), and a cross-over width ('Gamma_W', wave numbers); and, finally, a vector of frequencies in wave numbers as the independent variable ('omega', wave numbers). Using these inputs it generates a dielectric function and in turn calculates the absorption.

There are also global variables: the dielectric constant of the nanocrystal material ('epsilon_NC'), the dielectric constant of the solvent ('epsilonSolvent'), and the path length of light in the measurement cell in cm ('pathLength'). First, the dielectric function of a single, isolated nanocrystal is calculated using the expression:

$$\varepsilon_{\text{particle}} = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma(\omega)}$$

where $\Gamma(\omega)$ is a frequency-dependent damping function given by the expression:

$$\Gamma(\omega) = \Gamma_L - \frac{\Gamma_L - \Gamma_H}{\pi} \left[\tan^{-1} \left(\frac{\omega - \Gamma_X}{\Gamma_W} \right) + \frac{\pi}{2} \right]$$

If the nanocrystals are at an appreciable concentration in the solvent (this may be the case if doing FTIR liquid cell measurements with short path lengths) then it is necessary have to use the effective medium approximation (EMA) to account for far-field effects between

nanocrystals. EMA also accounts for dielectric interactions between the nanocrystals and the solvent. The EMA is:

$$\frac{\varepsilon_{\text{eff}} - \varepsilon_{\text{solvent}}}{\varepsilon_{\text{eff}} + 2\varepsilon_{\text{solvent}}} = f_v \left(\frac{\varepsilon_{\text{particle}} - \varepsilon_{\text{solvent}}}{\varepsilon_{\text{particle}} + 2\varepsilon_{\text{solvent}}} \right)$$

If we set the term in parentheses equal to C and solve for the effective dielectric function, we have:

$$\varepsilon_{\text{eff}} = \varepsilon_{\text{solvent}} \left(\frac{1 + 2C}{1 - C} \right)$$

Finally the absorption is calculated as:

$$A = 4\pi\omega \frac{\ell}{\ln(10)} \text{Im} [\sqrt{\varepsilon_{\text{eff}}}]$$