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Nanomaterials for Energy Applications: From Photovoltaics to Plasmonic Catalysis

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Nanomaterials for Energy Applications: From Photovoltaics to Plasmonic Catalysis

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Mechanical Engineering

by

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June 2019

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A mis papás.
ABSTRACT OF THE DISSERTATION

Nanomaterials for Energy Applications: From Photovoltaics to Plasmonic Catalysis

by

Alejandro J. Alvarez Barragan

Doctor of Philosophy, Graduate Program in Mechanical Engineering
University of California, Riverside, June 2019
Dr. Lorenzo Mangolini, Chairperson

Energy applications are essential for the development of technologies capable of confronting the challenges inherent to a growing global population. Among the different renewable energies, the solar resource has advanced as the most promising due to its omnipresence in Earth life. This work investigates the synthesis and properties of three materials with the potential to contribute to the utilization and storage of solar energy. In detail, this dissertation addresses the feasibility of Cu$_2$ZnSnS$_4$ (CZTS) as a novel thin film photovoltaic material by studying the role of process parameters on the phase segregation and grain-to-grain homogeneity of CZTS thin films. It also studies the stability of silicon-carbon heterostructures for lithium-ion batteries and introduces a non-thermal plasma/chemical vapor deposition (CVD) process that offers good control on particle size and composition. Finally, this work presents a comprehensive investigation of plasmonic titanium nitride nanoparticles synthesized with a non-thermal plasma method. It demonstrates their potential as photocatalysts and photothermal absorbers with good thermal stability as compared to conventional plasmonic materials based on costly noble metals.
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Chapter 1: Background

1.1: Introduction

The world population broke the barrier of 7 billion people in 2011 and is projected to reach 8 billion by the end of 2023.\(^1\) This exponential increase results in a higher demand for several services and products. The energy required to meet this demand is naturally rising as well. Given the already-evident strains to which the Earth has been subjected due to human expansion, some economic policies are starting to look for a long-term solution to the damage humans are causing to the planet while, at the same time, preventing future humanitarian catastrophes driven by geopolitical conflict over depleting resources.\(^2,3\)

One key objective relies on transferring our main energy sources from natural gas, coal, and other combustible hydrocarbons towards renewable energies that do not contribute to the emission of greenhouse gases into the atmosphere. Consequently, this would limit human-caused climate change, which has been well-documented throughout several decades.\(^4-6\) Figure 1.1 shows the various energy sources currently used worldwide. Although non-renewable energies remain the most utilized, a considerable increase in the last few years reflects a recent push towards renewable energies. However promising, this increase is far from the ideal, and further efforts have to be made in order to curb greenhouse gas emissions.
Among the various available energy sources, several studies point to solar energy as the most promising. A study from the Department of Energy in 2006, for example, established that the energy the Sun provides to Earth in 1.5 hours is the same amount of energy humans consume in a whole year. This conclusion underscores the great potential of solar energy and the challenges associated to efficiently harnessing it for human consumption.

Among the challenges associated with solar energy utilization are increasing the efficiency of solar cells, decreasing the cost of solar energy relative to other sources, and developing energy storage technologies to account for the intermittency of solar energy caused by uncontrollable phenomena such as day and night and unpredictable weather patterns. A unifying factor related to these and other problems is the development of Figure 1.1. Energy consumption by resource. Figure obtained from reference.
alternative materials that can result in better technologies towards a more sustainable future.

1.2: The Importance of Materials Research

Every technology change throughout human history resides on mastering the use of new materials towards certain applications. Throughout the last 10,000 years, human civilization has gone from the stone age, in which our species differentiated from others by using stone tools for grinding, hunting, and building, to a complex era were a variety of materials are the backbone of every technology that sustain our intricate global civilization. Materials research is therefore a crucial part of the physical sciences and remains key to the implementation of newer technologies in the future. For the specific case of solar energy applications, materials research is a key component on the development of better devices that allow us to harness light efficiently and economically. With this in mind, this dissertation aims to evaluate three material systems that have been proposed as possible alternatives to various solar energy-related applications. First, in the field of thin film photovoltaics, the feasibility of Cu$_2$ZnSnS$_4$ (CZTS) is investigated in terms of grain-to-grain homogeneity and composition control. Second, in the field of energy storage, silicon-carbon-based anodes are investigated as an alternative to the graphite anodes currently used in most lithium-ion battery technologies. Third, plasmonic titanium nitride is investigated as an alternative to gold and silver for visible light driven chemistry. In the remainder of this chapter, a basic background on these materials will be
provided to contextualize the results and discussions presented throughout the dissertation.

1.3: CZTS for Thin Film Photovoltaics

1.3.1: Crystalline Silicon

Current photovoltaic (PV) technologies are dominated by crystalline silicon. The production cost of crystalline silicon solar cells has consistently decreased in recent years. However, there are some disadvantages that limit the growth of this material. Crystalline silicon is an indirect bandgap semiconductor. Therefore, to promote an electron to the conduction band, it is necessary for the electron not just to reach the band gap energy, but also to acquire momentum via lattice vibrations in the material — known as phonons — in order to generate electron hole pairs (Figure 1.2). Since three entities — photons, electrons, phonons — are required to promote electrons to the conduction band, the rate of electron hole pair generation is much slower than in other semiconductors. Consequently, the thickness of the solar cell material has to be hundreds of micrometers in size in order to fully absorb light at visible-near infrared (NIR) wavelengths. In addition, the brittle nature of crystalline silicon requires that solar technology manufacturers develop sturdy panels to prevent the fracture of silicon solar cells. This directly increases the cost of the final product due to sturdy structural components that are not actively converting photons to electricity.
Figure 1.2. a) Direct bandgap semiconductors do not require a phonon transition to promote excited electrons from the valence band to the conduction band. b) Indirect bandgap semiconductors, such as crystalline silicon, do require the contribution of lattice vibration to promote valence electrons to the conduction band, making the transformation of photons to electrons inefficient.

1.3.2: CZTS: The Alternative in Thin Film PV

Thin film solar cells have been proposed as a good alternative to crystalline silicon.\textsuperscript{10,11} Thin film PV materials are made of direct band gap semiconductors, which do not require the contribution of lattice vibrations to promote an electron to the conduction band (Figure 1.2). In this case, just two entities—photons and electrons—are involved in the electron-hole generation process, consequently increasing the rate at which this phenomenon occurs. The absorption coefficient of thin film semiconductors can be over an order of magnitude higher than silicon-based solar cells.\textsuperscript{11} This in turn decreases the thickness necessary to absorb photons at specific wavelengths to just a few hundreds of nanometers. This advantage allows thin film PV to be used on flexible substrates, potentially facilitating the installation of the solar cells and reducing the associated costs.\textsuperscript{10,11} However, there are still important disadvantages regarding thin film PV. The most important relies on the material efficiency.\textsuperscript{9,12,13} There are still various
technologies that do not get close enough to the crystalline and polycrystalline silicon numbers in order to be competitive. Another disadvantage is related to the availability and toxicity of the materials. Most thin film solar cell technologies are based on cadmium telluride (CdTe) and copper indium gallium selenide (CIGS), in which cadmium is a carcinogen element, and indium and gallium are costly and scarce.\textsuperscript{12,13}

In recent years, research interests have focused towards Cu\textsubscript{2}ZnSnS\textsubscript{4}, a quaternary material analogous to CIGS that is composed of earth abundant elements.\textsuperscript{14–17} Instead of using the inaccessible elements indium and gallium, CZTS contains zinc and tin, which are relatively abundant and non-toxic (Figure 1.3). Despite having the same crystalline kesterite structure as CIGS and having a theoretical maximum efficiency of 30\%, previous work on CZTS has resulted in cells with efficiencies close to 13\%.\textsuperscript{18} This is still too far from crystalline silicon and CIGS, which is an analogous material that should perform in a similar way based in all their structural similarities.

A lot of work has been done in order to identify the causes to the low efficiency of CZTS. Some groups have pointed to the formation of grain boundaries that prevent the effective transport of electrons along the film.\textsuperscript{18,19} Others point to problems associated with atomic-level defects that contribute to inefficient charge generation.\textsuperscript{14,18} One key problem related to CZTS lies on the very narrow window of synthesis conditions at which the formation of CZTS is stable and not dominated by undesirable secondary phases such as SnS\textsubscript{2}, Cu\textsubscript{2}S, or ZnS (Figure 1.4).\textsuperscript{20} This works addresses this issue by investigating the formation of secondary phases at various synthesis parameters and by identifying phase segregation at a localized level. The findings presented in Chapter 2
highlight the challenges in developing this material as an alternative to other thin-film technologies.

Figure 1.3. CIGS and CZTS have the same kesterite structure. Earth-abundant elements Zn and Sn are used as replacements of the scarce In and Ga.
Figure 1.4. Ternary phase diagram of Cu$_2$S, ZnS, and SnS$_2$ shows a very narrow window at which pure CZTS can be synthesized at 670 K. Figure obtained from reference.  

1.4: Silicon-Carbon Nanostructures for Lithium-ion Batteries

1.4.1: Graphite

Lithium-ion batteries (LIB) have been a quintessential part of everyday life since their introduction into commercial markets in the early 1990’s. In order to accommodate lithium ions in the anode and cathode, layered materials have been utilized to sustain a redox reaction for longer periods without material decay (Figure 1.5). This architecture has remained relatively unaffected since the birth of LIBs.
Figure 1.5. Components of a standard LIB. Oxidation reaction occurs between the electrolyte and the graphite anode. Li-ions are then transported to the CoO$_2$ cathode, where the reduction reaction takes place.

Graphite is the preferred anode material in LIBs. It is a cheap, available carbon allotrope that allocates lithium ions in an intercalated fashion between the 2-dimensional carbon layers. This allows for an effective ion transport and a relatively low volume expansion upon lithiation/delithiation. Graphite has a specific capacity of 372 mAh$^{-1}$. Although highly effective when powering portable electronic devices such as lap tops and smartphones, the specific capacity of graphite is not ideal for powering locomotive devices with higher energy requirements. For such cases, different alternatives have been considered.

1.4.2: Silicon as an Alternative to Graphite

In recent years, the world has seen a rising demand of lithium-ion batteries in the automotive industry. Therefore, the need for higher specific capacity and durability of the batteries has increased significantly. Although several engineering innovations have been implemented to pack a higher energy density in LIB, the need for a fundamental change of materials on the LIB is now inescapable. Silicon is among the most promising
anode materials; and has been heavily investigated in recent years as an alternative to graphite. Silicon is the second most abundant element in the Earth’s crust. It is also the backbone of a multibillion-dollar semiconductor industry. The diamond structure of silicon (Figure 1.6) can retain a high number of lithium ions in its lithiated state (SiLi$_{4.4}$). This results on a specific capacity that, theoretically, is 10 times larger than that of the commercial graphite-based anodes (4200 mAhg$^{-1}$).

There are still, however, several considerations that have to be addressed with silicon-based technologies. Given the non-layered structure of silicon, the volume changes associated to lithiation and delithiation are close to 300 %. The high-volume change results in the fracture of the material, leading to the early decay of battery performance. In addition, this volume change also leads to a very unstable solid electrolyte interface (SEI), which is a layer created between the active material and the electrolyte during the redox process. If stable, this layer can protect the active material from the harsh chemical conditions in the electrolyte. However, for the case of pure silicon anodes, the SEI is constantly fractured and reformed with every cycle. This effect causes a sharp decrease in the performance of the battery.
11

Figure 1.6. Silicon diamond crystalline structure. Its non-layered structure causes considerable volume change and strain in the lattice upon the lithiation/delithiation cycle.

1.4.3: Silicon-Carbon-Based Nanomaterials

Alternatives to the problems stated above can be found at the nanoscale.

Nanometer-size samples such as nanoparticles or nanorods have helped with the stability of silicon-based battery anodes.\textsuperscript{29} In addition, carbon-protected silicon batteries aid with additional protection of the active material from the interface. The promise of these novel architectures has reinvigorated the field to the point where several Si-C compound synthesis methods have been reported.\textsuperscript{27,30,31} This has led to a contradictory consensus regarding which methods should be favored over others in terms of material quality, control, and reproducibility.\textsuperscript{32} The information in Chapter 3 offers a comparative study of different carbon deposition approaches, and highlights the introduction of a new non-thermal plasma synthesis method of branched silicon nanoparticles and a chemical vapor deposition method of carbon that results in highly uniform carbonaceous layers around
the silicon nanostructures that recorded a higher specific capacity and better cyclability than other methods commonly used.

1.5: Plasmonic TiN Nanoparticles

1.5.1: The Localized Surface Plasmon Resonance

When interacting with electromagnetic radiation at length scales smaller than the wavelength of the incident light, negative free electrons in metallic nanoparticles oscillate against positive heavy nuclei, generating what is known as a localized surface plasmon resonance (LSPR, Figure 1.7.). This light-matter interaction leads to a series of phenomena that are of interest in several applications. First, the oscillation of electrons back and forth from the atomic nuclei create strong and localized electric fields. This has been utilized for sensing applications, where the atomic vibrations of molecules adsorbed to plasmonic particles can be amplified and detected via their Raman signal. Second, the subsequent decay of the excited electrons results in the generation of electron-hole pairs at high energy levels that, on the absence of light excitation, would not be available at ambient temperatures. This has been of interest in the field of photocatalysis, which has observed the rise of a burgeoning body of research regarding hot electron transfer from plasmonic catalysts towards adsorbates to drive chemistry with visible light. Third, the inelastic interaction of the LSPR with lattice vibration cause a localized increase in temperature on the nanoparticle surface. Localized heating has been proposed for solar-induced steam generators, photothermal therapy, and other thermal applications.
Figure 1.7. Localized surface plasmon resonance (LSPR). When the nanoparticle size is smaller than the wavelength of the impinging radiation, the collective oscillation of free electrons takes place and leads to the generation of strong localized electric fields, highly energetic “hot” electrons, and localized heating at the nanoparticle surface.

Given that the solar spectrum is composed of 45% and 53% of visible and IR radiation respectively, an ideal characteristic for any plasmonic material, regardless the application, is to have a LSPR in the visible-NIR spectrum. Per Mie Theory’s dipole approximation, the intensity of the wavelength dependent LSPR is defined by the extinction cross section of the nanoparticle:

\[
\sigma_{\text{ext}}(\omega) \sim \frac{\varepsilon_2}{[\varepsilon_1(\omega) + 2\varepsilon_m(\omega)]^2 + \varepsilon_2(\omega)^2} \quad (1)
\]

Where \(\varepsilon_m\) is the relative permittivity of the surrounding medium and \(\omega\) is the light frequency. The material constants \(\varepsilon_1\) and \(\varepsilon_2\) represent the polarizability and the optical losses due to interband and intraband transitions, respectively. Two conditions have to
take place in order to maximize $\sigma_{\text{ext}}$ \textit{(i.e.} the LSPR\textit{)}. First, $\varepsilon_1$ has to be equal to $-2\varepsilon_m$. Second, $\varepsilon_2$ has to be minimized. Figure 1.8 shows the values of $\varepsilon_1$ as a function of wavelength for various materials. The LSPR takes place when $\varepsilon_1$ intersects the dashed horizontal line ($-2\varepsilon_{m,\text{air}}$).

**Figure 1.8.** Polarizability of various metals as a function of wavelength. Figure obtained from reference.\cite{ref41}
1.5.2: Gold and Silver

From Figure 1.8, one can identify that only silver and gold intersect the horizontal line represented by $-2\varepsilon_m,\text{air}$ at visible wavelengths and, at the same time, have low optical losses in such wavelengths (Figure 1.9). In fact, the favorable properties of both metals have been already used for several applications in sensing, photothermal therapy, photocatalysis, and photovoltaics. In addition, for the case of gold, it has a good chemical stability, which makes it stable in nanoparticle form in harsh chemical environments. However, there are obvious cost-related factors that hinder the development of gold and silver technologies at a massive scale. In addition, both metals
have a relatively low bulk melting point, which acquires an even lower value when the materials are in the nanoscale.\textsuperscript{44}

1.5.3: Titanium Nitride (TiN) as an alternative plasmonic material

The search for alternative plasmonic materials has increased in recent years. Some groups have pointed towards highly doped semiconductor nanocrystals. Although interesting results have been observed,\textsuperscript{45} there are fundamental problems associated to the successful homogeneous doping of semiconductor in nanoparticles at nanometer scales.\textsuperscript{46} Titanium nitride is another material that has shown promise from several reports.\textsuperscript{47–49} Similar to gold and silver, this material has a theoretical LSPR located in visible wavelengths and relatively low optical losses at such wavelengths. Moreover, TiN has a high melting point in its bulk form, which presumably makes it a good candidates for high temperature applications.\textsuperscript{50} It is also a chemically stable ceramic. This rises its prospects in the field of photocatalysis, where stability over time in harsh chemical conditions is a valuable property. Although plenty theoretical work has been done on TiN nanoparticles, and some experimental work shows promising results,\textsuperscript{51–54} there are still some issues associated to the synthesis methods of the material and to the in-depth analysis of their optical properties.\textsuperscript{55–57} In Chapters 4, a non-thermal plasma synthesis method, which provides outstanding control in particle size and tunability of the LSPR position, is introduced. In Chapter 5, the first direct demonstration of plasmon-induced chemistry with TiN nanocrystals is presented. Chapter 6 depicts a comprehensive investigation of the thermal stability of TiN and presents a novel TiN-SiO\textsubscript{x}N\textsubscript{y} core-shell heterostructure that enhances the LSPR response of TiN by limiting its oxidation.
1.6: References


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3370–3374.


Chapter 2: Phase Segregation and Grain-to-Grain Homogeneity of CZTS Thin Films

2.1: Introduction

As mentioned in Chapter 1, Cu$_2$ZnSnS$_4$ has been considered a promising material for thin film photovoltaics. CZTS is composed of earth abundant, non-toxic elements, making it an ideal candidate for the scalable and economically feasible production of thin film solar cells.$^{1-3}$ The efficiency of various devices has already been reported.$^{4-8}$ Champion CZTS/CZTSSe cells have achieved efficiencies of 7.6% and 12.6% for sputtered metallic stacks and solution-based devices, respectively.$^{4,9}$ Although remarkable improvements have been made, these efficiency values are considerably lower than the theoretical limit of a ~1.4 eV bandgap material, which is close to 30%.$^{10}$

In addition, despite having a similar crystal structure to the commercially available CIGS technology, the efficiency of CZTS remains below feasible values for its use at industrial levels.$^{11,12}$ This dissertation identifies potential issues that have hindered the further development of CZTS-based solar cells. First, there are a multitude of synthesis processes yielding contradictory data in the CZTS literature. This makes it difficult to reach a consensus on the effect different process parameters have on the final composition and properties of the material. More specifically, although the influence of several parameters such as annealing temperature, annealing time, utilized substrate, preheating, and precursor stoichiometry have been thoroughly studied,$^{13-18}$ there are only a few studies on the effects sulfurization pressure. The lack of information addressing this topic leads to inconsistencies associated to the role of pressure in grain size and post-annealing
stoichiometry. Second, as stated in Chapter 1, the narrow composition window where the formation of stable CZTS is obtained requires very fine tuning of the process parameters. The appearance of secondary phases could therefore be overlooked due to limitations associated to the characterization procedures. Energy-dispersive spectroscopy (EDS) and Raman scattering are two of the most utilized techniques for CZTS characterization. Such measurements are usually conducted on larger areas of the sample rather than individual grains. This procedure assumes that the film stoichiometry and structure is the same for every grain present on it. However, experimental results have shown that different Raman modes may be detected among CZTS microcrystals within the same sample. Although this investigation in focused on the sintering dynamics in films obtained from CZTS nanoparticle coatings, it suggests that structural inhomogeneity may be prevalent in this material system. In summary, to address the aforementioned issues, this chapter presents two experiments that look to 1) Unequivocally define the effect of sulfurization pressure on the composition of CZTS films, and 2) perform grain-to-grain Raman and EDS measurements to test the homogeneity of the CZTS in localized regions of the film to identify the presence of secondary phases previously overlooked in recent studies.

2.2: Role of sulfurization pressure in CZTS films

2.2.1: Materials and Methods

50nm of Zn were initially deposited on a quartz substrate by RF magnetron sputtering, followed by the deposition of 80nm of Cu and 110nm of Sn by electron beam
evaporation. This combination of techniques facilitates the deposition of a smooth-
surface film for each metallic precursor. Five samples were independently annealed in a
sealed quartz ampule (203mm long, 7mm in diameter) at 500°C for 8h. A base pressure
of 1x10^{-5} Torr was achieved with an Oerlikon Leybold TURBOVAC SL 80 turbo pump.
The ampules were heated in a tube furnace at a rate of 7 °C/min. After annealing, the
films were let to cool down naturally for 120 minutes. One end of the ampule was gently
pushed out of the heating zone in order to induce constant sulfur condensation in that
region and away from the sample. The sulfurization pressure was controlled by
modifying the amount of sulfur introduced into the closed system. Pressure calculations
were based on the application of the ideal gas law. In accordance to previous reports, the
mole fractions of the various molecular species present in sulfur vapor (S_8 to monoatomic
sulfur) were considered for these estimations. The corresponding pressure data for each
mass value, listed in increasing order, is approximately 32 (1mg), 95 (3mg), 191 (6mg),
287 (9mg), and 383 (12mg) Torr. SEM/EDS analysis was performed on a FEI Nova
NanoSEM 450 system equipped with an Oxford Instruments Aztec Synergy software.
EDS data was obtained from diverse areas of each sample. The average stoichiometry
and standard deviation were recorded. XRD characterization was held on a PANalytical
Empyrean X-ray system using CuKα radiation with a wavelength of 1.74nm. A Horiba
LabRam HR instrument, equipped with a 532nm laser source, was used for Raman
analysis.
2.2.2: Results and Discussion

Figure 2.1 shows low and high magnification SEM images of the CZTS films sulfurized at different pressures. There are no obvious morphological differences among the samples synthesized at lower pressure (Figure 2a-f). On the other hand, three-dimensional structures are visible in the films sulfurized at 287 and 383 Torr (Figure 2g-j). These features are randomly dispersed over the surface of the films. The regions in between the 3D structures are very similar to those shown in the previous samples.

Figure 2.1. Low and high magnification SEM images showing the surface morphology of the CZTS samples sulfurized at various pressures.
Table 2.1. Summary of EDS analysis performed in all samples reported in the present manuscript.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Zn</th>
<th>%Cu</th>
<th>%Sn</th>
<th>Pressure (Torr)</th>
<th>%Zn</th>
<th>%Cu</th>
<th>%Sn</th>
<th>%S</th>
<th>Cu/Sn</th>
<th>Zn/Sn</th>
<th>Cu/Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.4±0.4</td>
<td>46.5±0.5</td>
<td>29.1±0.5</td>
<td>-</td>
<td>16.7±1.5</td>
<td>22.7±0.8</td>
<td>14.4±1.2</td>
<td>46.2±0.7</td>
<td>1.58</td>
<td>1.16</td>
<td>1.36</td>
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<tr>
<td>2</td>
<td>23.8±0.4</td>
<td>47.0±0.5</td>
<td>29.1±0.1</td>
<td>95</td>
<td>15.4±1.5</td>
<td>24.0±1.0</td>
<td>14.5±1.0</td>
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</tr>
<tr>
<td>3</td>
<td>24.4±0.3</td>
<td>46.6±0.2</td>
<td>29.0±0.3</td>
<td>191</td>
<td>16.2±1.9</td>
<td>23.9±0.8</td>
<td>14.1±1.4</td>
<td>45.8±1.4</td>
<td>1.70</td>
<td>1.15</td>
<td>1.48</td>
</tr>
<tr>
<td>4-SA1</td>
<td>25.2±0.9</td>
<td>46.1±1.0</td>
<td>28.6±0.6</td>
<td>287</td>
<td>18.1±0.9</td>
<td>24.4±0.8</td>
<td>12.8±0.6</td>
<td>44.6±1.2</td>
<td>1.90</td>
<td>1.41</td>
<td>1.35</td>
</tr>
<tr>
<td>4-SA2</td>
<td>25.2±0.9</td>
<td>46.1±1.0</td>
<td>28.6±0.6</td>
<td>287</td>
<td>16.0±0.4</td>
<td>23.7±0.6</td>
<td>14.4±0.5</td>
<td>45.8±0.5</td>
<td>1.64</td>
<td>1.11</td>
<td>1.48</td>
</tr>
<tr>
<td>5-SA1</td>
<td>23.7±0.6</td>
<td>46.6±0.3</td>
<td>29.6±0.6</td>
<td>383</td>
<td>17.8±0.3</td>
<td>25.2±0.4</td>
<td>12.7±0.4</td>
<td>44.3±0.5</td>
<td>1.99</td>
<td>1.41</td>
<td>1.41</td>
</tr>
<tr>
<td>5-SA2</td>
<td>23.7±0.6</td>
<td>46.6±0.3</td>
<td>29.6±0.6</td>
<td>383</td>
<td>15.1±0.3</td>
<td>23.2±0.4</td>
<td>15.3±1.1</td>
<td>45.5±0.8</td>
<td>1.54</td>
<td>0.99</td>
<td>1.54</td>
</tr>
</tbody>
</table>

EDS analysis is broken down in Table 2.1. Due to film inhomogeneity, data for samples 4 and 5 is reported under Scanning Areas 1 and 2 (SA1, SA2). SA2 includes every relevant feature in the sample, whereas SA1 does not comprise the characteristic 3D morphologies solely present in the films synthesized at higher pressures. Figure 2.2 shows a graphic representation of the stoichiometry values reported in Table 2.1 while only considering data from SA1. Cu/Sn and Zn/Sn ratios (Figure 2.2a, b, respectively) are considerably larger at 287 and 383 Torr. The Cu/Zn ratio (Figure 2.2c), however, does not show a clear dependence on the sulfurization pressure. This information suggests that there is major Sn loss in SA1 as the pressure is raised. When including the 3D structures into these measurements (i.e., reporting values from SA2) the Cu/Sn, and Zn/Sn ratios (Figure 2.2d, e, respectively) are remarkably similar. There is therefore no material loss at higher pressures, but rather a displacement of Sn into clearly defined regions of the film. Additional EDS mapping of these 3D features is displayed in Figure 2g-k. Strong S
and Sn signals are detected in the region of interest (Figure 2.2j, k, respectively). In contrast, Cu and Zn signals at Figure 2.2h, i are much weaker in that particular sector.

![Figure 2.2](image)

**Figure 2.2.** Cu/Sn (a, d), Zn/Sn (b, e), and Cu/Zn (c, f) stoichiometry ratios of samples sulfurized at various pressures. Data from both SA1 and SA2 is included for the samples synthesized at higher pressures. (h-k) EDS mapping of the framed region in (g). S (j) and Sn (k) comprise most of the elemental stoichiometry of that specific feature.

XRD data from the as-synthesized films is shown in Figure 2.3a. Peaks associated to CZTS, Cu$_2$SnS$_3$, and ZnS are present at 28.5°, 33.1°, 47.5°, and 56.2°. Additional weak peaks at 34.6°, 50.0°, and 52.1° indicate there is minor segregation of secondary phases in all films. These reflections may be related to the Cu$_{39}$S$_{28}$ alloy (JCPD 036 0380). Peaks from SnS$_2$ at 15.0° and 32.1° become visible at 287 and 383 Torr, adding up to the evidence of SnS$_2$ segregation at high pressures. The remarkable similarity among the CZTS, ZnS, and Cu$_2$SnS$_3$ XRD peaks makes it impossible to fully confirm the presence of CZTS by solely employing this characterization technique. Raman analysis

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is a useful complimentary tool for CZTS detection. Fig. 2.3b shows the Raman spectrum for each of the five samples synthesized at various sulfurization pressures. Strong CZTS peaks at 337cm\(^{-1}\) and 289cm\(^{-1}\) are readily detected in all the films. As pressure increases, a hexagonal SnS\(_2\) peak at 314cm\(^{-1}\) becomes stronger. This trend is consistent with the EDS and XRD data presented above.
Figure 2.3. (a) XRD data showing characteristic CZTS peaks and weak Cu$_{39}$S$_{28}$ reflections in all films. Hexagonal SnS$_2$ reflections are observed at 287 and 383 Torr. (b) Raman analysis of samples sulfurized under various pressure conditions. A strong CZTS signal is observed in all films. A hexagonal SnS$_2$ peak becomes more visible as pressure increases.
Previous investigations on CZTS sulfurization in closed systems emphasize the importance solid-gas phase reactions have in the chemical pathways that lead to the formation of CZTS crystals.\textsuperscript{27} At low sulfurization pressure, the proposed mechanism consists in the formation of gaseous SnS as a result of the interaction between solid Sn with the S atmosphere. Further incorporation of SnS into the film leads to a solid-state interaction with CuS phases to form Cu$_2$SnS$_3$. Finally, ZnS diffuses into Cu$_2$SnS$_3$ to yield CZTS. The presence of SnS$_2$ at high pressure suggests that the chemical route explained above is partially altered under these anomalous conditions. Instead of forming SnS (g), interaction between Sn (s) and S (g) favors the growth of solid SnS$_2$ three-dimensional structures. Since these features appear in the final film morphology, it is evident that there is no further reaction between SnS$_2$ and other phases during the sulfurization process. Higher stability of SnS$_2$ (s) over SnS (g) may readily explain this phenomenon.

An additional experiment was designed in order to discard the effects that the cooling rate may have over the film morphology. Two extra samples, sulfurized at 32 and 287 Torr, underwent a slower cooling process. The overall cooling time was increased from 120 to 240 minutes. Stoichiometry values as obtained from EDS measurements are reported in Table 2.1 (samples 6 and 7). A larger amount of Sn and S is detected. Zn and Cu losses are also evident. Nonetheless, despite the stoichiometric variations there were no morphological changes associated to the cooling rate. Film features are very similar to those shown in Fig. 2.1a-2.1b and 1g-1h, suggesting that there is no influence of the cooling rate in the formation of SnS$_2$ 3D structures. It is apparent that the cooling rate is a relevant and often overlooked factor in the final stoichiometry of the film. Gaseous sulfur
left in the ampule keeps reacting with the sample while cooling. These notable stoichiometric variations shed light on the great complexity related to the formation mechanisms of CZTS, in which subtle changes in any parameter play a substantial role on the final film properties.

2.2.3: Conclusion

The effects of pressure during CZTS sulfurization in a closed system was investigated. Higher pressure yields samples with evident segregation of 3D SnS$_2$ structures randomly dispersed along the film. Collected data suggests that the formation of these structures follows different reaction pathways to those reported for lower pressure processes. A greater chemical stability of solid SnS$_2$ compared to that of gaseous SnS explains the fact that the formation of SnS$_2$ does not lead to further interaction with other phases in the film. Additionally, the cooling rate has a substantial influence on the sample final stoichiometry. However, the surface morphology is unaffected by changes in this parameter.

2.3: Grain-to-Grain Characterization of CZTS Films

2.3.1: Materials and Methods

CZTS films were synthesized by sputtering a 250 nm film of Cu, Zn, and Sn stacked layers on a bare soda lime glass (SLG) substrate. The thickness of each layer was 80 nm (Cu), 60 nm (Zn), and 110 nm (Sn). The samples were then inserted in a quartz ampule together with a small charge (~1mg) of elemental Sulphur. The ampule was subsequently evacuated using a turbo pump and sealed at 10$^{-5}$ Torr. The sample was heated up to
600°C for 8 hours and let to cool down naturally. This synthesis approach is very similar to those adopted by several other research groups.\textsuperscript{7,28,29} SEM/EDS analysis was performed on a FEI Nova NanoSEM450 system equipped with an Oxford Instruments Aztec Synergy software and a X-Max 50mm$^2$ SDD detector with resolution of 127 nm at MnKα. For EDS characterization, the accelerating voltage was kept at 20 kV and the working distance at 5 mm. Raman characterization was conducted with two different instruments in order to compare individual grain versus standard measurement results. A Renishaw micro-Raman spectrometer with a 488 nm excitation laser and a ~0.4 µm spot size was used for individual grain characterization. A Horiba LabRam HR instrument equipped with a 532 nm laser source and a ~5 µm spot size was used to obtain the spectra of larger areas of the sample containing several grains. The spectra in both instruments were recorded with a 1800 lines/mm grating. The laser power was kept below 0.2 mW to avoid any local heating and damage to the sample. In order to improve the signal-to-noise ratio for such a small power, the exposure time was increased to 100 seconds. XRD characterization was held on a PANalytical Empyrean X-ray system using CuKα radiation with a wavelength of 1.54 Å.

2.3.2: Results and Discussion

The elemental composition of the sample before sulfurization is presented in Table 2.2. SEM images of the film before and after annealing are shown in Figure 2.4 and Figure 2.5a,b, respectively. There is no clear trace of either ZnS or SnS$_2$ phases, which have been reported elsewhere as having very specific features that could be easily detectable with the aid of SEM microscopy.\textsuperscript{30,31} The grain size ranges between 1-5 microns. This is
not unexpected since impurities from the SLG substrate, more specifically Na and K, have shown to enhance grain growth, most likely by diffusing into the grain boundaries and facilitating cation diffusion through several proposed mechanisms.\textsuperscript{32-34} There is a substantial amount of voids along the sample. This is most likely due to a high material loss during the annealing process.\textsuperscript{30} The Cu/Sn ratio before and after annealing went from 1 to \~1.8, indicating a large Sn loss. This phenomenon has been reported elsewhere.\textsuperscript{50} EDS scans were performed over large areas of approximately 150 \( \mu \text{m}^2 \) that included several grains. The average composition and elemental ratios are displayed in Table 2.3. The recorded measurements show a stoichiometry very close to that of CZTS. In fact, there is a slightly Zn rich composition that has proven beneficial for higher performance CZTS devices.\textsuperscript{35-37} XRD and Raman characterization are shown in Figure 2.5c and 2.5d, respectively. The XRD data shows reflections at 28.5°, 32.9°, 47.2°, and 56.1°. These peaks are assignable to CZTS, but also to secondary phases such as Cu\textsubscript{2}SnS\textsubscript{3} and ZnS. However, smaller peaks previously associated only to CZTS appear at 37.0° and 37.9°, suggesting that the analyzed film is mainly composed of CZTS. The peak at 50.4°, however, is unequivocally neither CZTS, Cu\textsubscript{2}SnS\textsubscript{3} nor ZnS. The study in\textsuperscript{29} provides a broad perspective on the major peaks from several binary and ternary sulfide phases that have been reported in the CZTS literature. Together with SnS\textsubscript{2}, Cu\textsubscript{4}SnS\textsubscript{4} is the only phase with a peak assigned at 50.4°. Raman analysis (Figure 2.5d) discards the presence of SnS\textsubscript{2} since its signature at 314 cm\textsuperscript{-1} is not present and could not be found in any of our scans. It is also worth noting anomalous intensities from the (2 0 0) and (4 0 0) CZTS planes. This is an indication of preferential grain orientation. For randomly oriented
crystals, there is not known Cu-Sn-S (CTS) phase with only one main peak at 50.4°. The overlap between the CZTS peaks and those associated with secondary phases (Cu$_2$SnS$_3$ and ZnS) is an intensively-discussed topic and calls for more conclusive CZTS characterization techniques.\textsuperscript{38} A combination of Raman spectroscopy and EDS have been used as a more definitive approach for the identification of phase pure CZTS. For this investigation, we applied a standard Raman spectra acquisition that uses a 532 nm laser with a ~5 µm spot size and compared it with a more thorough individual-grain characterization procedure explained below. For the standard method (large area), Raman spectra were obtained at random locations of the sample. There were no major differences between one another. Figure 1d is a representative measurement of all the spectra acquired under these conditions. There is a strong and narrow peak at 336 cm$^{-1}$ and a weaker signal at 287 cm$^{-1}$. Both peaks correspond to the well-known CZTS Raman signature.\textsuperscript{39,40} A weak shoulder is also visible at 376 cm$^{-1}$ and may be associated with a CTS ternary phase. Cu$_4$SnS$_4$ has been previously assigned to this shift position.\textsuperscript{29}

**Table 2.2.** Elemental analysis of Zn/Cu/Sn stack before annealing

<table>
<thead>
<tr>
<th>Element</th>
<th>at %</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>38.56</td>
<td>0.4</td>
</tr>
<tr>
<td>Zn</td>
<td>23.07</td>
<td>0.45</td>
</tr>
<tr>
<td>Sn</td>
<td>38.36</td>
<td>0.17</td>
</tr>
<tr>
<td>Cu/Zn</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>Cu/Sn</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>Zn/Sn</td>
<td>0.60</td>
<td></td>
</tr>
</tbody>
</table>
Figure 2.4. SEM image of Zn/Cu/Sn stack before annealing.
Figure 2.5. Standard characterization of seemingly phase pure CZTS on a bare SLG substrate. (a), (b) SEM images at low and high magnification do not show obvious phase segregation of secondary phases such as ZnS or Sn$_2$S. (c) XRD reflections of the sample. Most reflections are in accordance with CZTS. Anomalous intensities detected at the (2 0 0) and (4 0 0) planes indicate preferential grain orientation on the film. The peak at 50.4° is definitely not CZTS, Cu$_2$SnS$_3$, nor ZnS and could be assigned to the Cu$_4$SnS$_4$ phase. (d) Representative Raman spectrum performed on a large area including several grains.
Table 2.3. Average stoichiometry, standard deviation, and elemental ratios obtained from EDS characterization on large-areas of the sample.

<table>
<thead>
<tr>
<th>Element</th>
<th>at %</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>24.67</td>
<td>±1.5</td>
</tr>
<tr>
<td>Zn</td>
<td>13.39</td>
<td>±0.6</td>
</tr>
<tr>
<td>Sn</td>
<td>14.14</td>
<td>±0.6</td>
</tr>
<tr>
<td>S</td>
<td>47.8</td>
<td>±1.2</td>
</tr>
<tr>
<td>Cu/(Zn+Sn)</td>
<td>Zn/Sn</td>
<td>S/metal</td>
</tr>
<tr>
<td>0.90</td>
<td>0.95</td>
<td>0.92</td>
</tr>
</tbody>
</table>

The analysis above is usually part of a standard set of characterization procedures used to identify CZTS films suitable for high efficiency devices. From these results, it is tempting to conclude that the CZTS films have optimal composition and are phase pure. A statistical analysis of the sample was carefully conducted by measuring the stoichiometry of individual CZTS grains by EDS. The scanned areas varied between 10 and 20 µm² depending on the grain size. Data was acquired from 20 individual grains picked at random. Figure 2.6 shows the distribution of Zn/Sn and Cu/(Zn+Sn) ratios (Figure 2.6a and 2.6b, respectively) obtained from the 20 scans. There are significant changes in the grain-to-grain stoichiometry. The Zn/Sn ratio fluctuates between 1.04 and 0.84. The Cu/(Zn+Sn) ratio varies even more, ranging between 0.78 to 1.06, which indicates a more significant variation in copper concentration than in Zn and Sn. Raw values from this elemental analysis can be found in Table 2.4. Figure 2.6c and 2.6d
display the corresponding elemental ratio distribution from several acquisitions performed over the same grain. The resulting narrow spreads indicate that the EDS measurement reproducibility is sufficiently high to conclude that the variation in composition is not an instrument artifact. Moreover, we also found that the Cu stoichiometry appears to be closely related to that of sulphur. Figure 2.7 shows how the Cu/(Zn+Sn) ratio increases as the sulphur/metal ratio decreases. On the other hand, there does not seem to be any relation between the Zn/Sn ratio and the sulphur/metal ratio. EDS analysis may be influenced not only by grain composition but also by grain orientation when dealing with very anisotropic crystal structures. However, previous measurements on CZTS microfibers with different crystal orientations did not yield any significant variations on the EDS data. In general, from EDS characterization we can conclude that there are evident changes in grain-to-grain stoichiometry, proving that the seemingly homogeneous CZTS film assumption is not valid.
Figure 2.6. (a) Zn/Sn ratio and (b) Cu/(Zn+Sn) ratio distribution from an individual-grain EDS statistical analysis. (c) Zn/Sn ratio and (d) Cu/(Zn+Sn) ratio distribution from several acquisitions performed over the same grain.
Table 2.4. At% of individual grains resulting from elemental EDS analysis

<table>
<thead>
<tr>
<th>Grain#</th>
<th>Zn (%)</th>
<th>Cu (%)</th>
<th>Sn (%)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
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<td>22.81</td>
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<td>49.83</td>
</tr>
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<td>13.84</td>
<td>49.31</td>
</tr>
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<td>13.78</td>
<td>23.76</td>
<td>14.45</td>
<td>48.01</td>
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</table>
Figure 2.7. Scatter plot summarizing the correlation between copper and sulphur concentrations. Copper-rich regions tend to be sulphur-poor.

In similar fashion to the EDS analysis, additional Raman spectra were obtained for individual grains. A more precise Raman tool (details in experimental section) was used for capturing the Raman signature of grains large enough to be independently scanned. Figure 2.8 shows two representative spectra from two different grains. In general, the 337 and 289 cm\(^{-1}\) intensity peaks are constant along various grains. However, peaks at 376 and 265 cm\(^{-1}\), and a shoulder that extends from 351 to 362 cm\(^{-1}\) are detected sporadically at every other grain. This finding suggests that major differences between individual CZTS grains are not detected with standard characterization procedures. The 376 cm\(^{-1}\) peak has previously been assigned to the Cu\(_4\)SnS\(_4\) phase.\(^{29}\) This strengthens the argument made for the XRD reflection at 50.4°, which does not correspond to neither CZTS, ZnS, nor Cu\(_2\)SnS\(_3\). The shoulder at 351 cm\(^{-1}\) and the weak signal at 265 cm\(^{-1}\) can
be associated to cubic ZnS.\textsuperscript{39,42} In this case, XRD data cannot confirm this statement since the ZnS XRD signature overlaps with that of CZTS.

![Representative Raman spectra from two distinct grains. A peak at (a) 376 cm\textsuperscript{-1} and a shoulder beginning at (b) 351 cm\textsuperscript{-1} appear sporadically, while the main CZTS peaks at 337 and 289 cm\textsuperscript{-1} are present in every grain.](image)

**Figure 2.8.** Representative Raman spectra from two distinct grains. A peak at (a) 376 cm\textsuperscript{-1} and a shoulder beginning at (b) 351 cm\textsuperscript{-1} appear sporadically, while the main CZTS peaks at 337 and 289 cm\textsuperscript{-1} are present in every grain.
Additional to the individual grain study, the intensities of the peaks at 337, 351, and 376 cm\(^{-1}\) were analyzed with the high-resolution spectrometer by mapping an area of 200 µm\(^2\). Figure 2.9b-d show maps that reveal the intensity variations of peaks at 337 (CZTS), 376 (Cu\(_4\)SnS\(_4\)), and 351 (ZnS) cm\(^{-1}\) over the scanned area. Except for the evident low signal coming from voids in the sample, the CZTS peak intensity remains steady. In contrast, there are notable intensity variations in the other two peaks, which account for signals from the secondary phases. Similar to EDS characterization, Raman intensity is also influenced by grain orientation. It could then be argued that these intensity variations are a result of scanning grains with different orientations rather than differences in composition. In order to refute this argument, Figure 2.10 shows the correlation between Raman spectra and EDS characterization obtained from two individual grains. The major ZnS Raman peak in Figure 2.10a is consistent with the excess Zn stoichiometry measured on this grain. On the other hand, there is no major hint of secondary phases in Figure 2.10b. Consequently, the resulting Zn/Cu ratio is close to that of stoichiometric CZTS, confirming that the acquired Raman data is dependent on grain stoichiometry and not on grain orientation. Data from Figure 2.9 and Figure 2.10, together with that of Figure 2.6 and Figure 2.8, strongly suggest that CZTS is the main phase in the system. However, there are still significant variations that involve the segregation of secondary phases that are likely to be detrimental in the performance of a CZTS device.
Figure 2.9. Intensity mapping of peaks at (b) 337 cm\(^{-1}\) (CZTS), (c) 376 cm\(^{-1}\) (Cu\(_4\)SnS\(_4\)), and (d) 351 cm\(^{-1}\) (ZnS). CZTS intensity peak remains relatively unchanged while the signal from the secondary phases fluctuates considerably. The scanned area in (a) is 200 \(\mu m^2\).

Figure 2.10. Correlation between Raman and EDS analysis. ZnS signal (350 cm\(^{-1}\)) in (a) is in good agreement with the Zn-rich stoichiometry measured for that grain. Low signal from secondary phases in (b) matches with a nearly-stoichiometric CZTS grain.
The results presented herein are consistent with theoretical predictions regarding the phase stability of CZTS and the influence of structural inhomogeneity on device performance. The narrow range of stability of CZTS, i.e. its tendency to segregate other binary and ternary phases, is a well-known issue. Our findings suggest that such segregation is likely to occur at short length scales, so that careful microscopic characterization is needed to monitor the quality of CZTS films. With respect of device performance, previous theoretical studies attribute a low $V_{OC}$ to compositional dissimilarities caused by point defects and the formation of secondary phases. The fact that we unequivocally observe the presence of low bandgap secondary phases like Cu$_4$SnS$_4$ (~1.2 eV) is consistent with these studies. The presence of a wide band gap secondary phase such as ZnS (~3.7 eV) is expected to reduce the light absorption of the film, decreasing photocurrent.

2.3.3: Conclusion

We have performed an in-depth Raman and EDS analysis of individual CZTS grains. The results show a considerable variation in stoichiometry and Raman signal intensity that indicates the presence of secondary phases. Furthermore, the same sample also went through a standard characterization analysis that is commonly employed to report seemingly phase-pure homogeneous CZTS films. Contrary to the more-rigorous individual grain analysis, the results for the standard characterization did not yield evidence of compositional inhomogeneity. The contrasting data from both approaches suggests that the standard characterization procedures are not precise enough to detect grain-to-grain disparities. This issue should not be overlooked, given that the low-
performance of CZTS-based devices is often attributed to compositional dissimilarities in the active layer. This work suggests that the routine use of microstructural characterization is necessary to advance this material system.
2.4: References


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(33) Prabhakar, T.; Jampana, N. Effect of sodium diffusion on the structural and


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Chapter 3: Silicon-Carbon Composites for Lithium-ion Batteries

3.1: Introduction

The outstanding specific capacity of silicon is limited by the high-volume changes associated to lithiation and delithiation of the material.\(^1,2\) This results in rapid decay of the device. It is well-known that silicon needs to be used in nanostructure form to avoid pulverization upon cycling and rapid capacity fading.\(^3-5\) This introduces additional complications. The high specific surface area of nanoparticle-based coatings leads to significant solid electrolyte interface (SEI) formation, resulting in low first cycle coulombic efficiency,\(^6\) although the use of a modified electrolyte formulation (for instance by adding FEC) can alleviate this issue.\(^7\) In addition, silicon has poor electrical conductivity and the use of active layers which are composed of an assembly of nanoparticles further exacerbates this problem. Silicon-carbon nanostructures have been proposed as a viable solution to some of the problems mentioned above.\(^7,8\) A carbon shell can provide additional protection to the active material by buffering the mechanical stresses resulting from the lithiation/delithiation process.\(^9\) The higher conductivity of carbon can enhance charge transport from the active material to the metal collector. Several groups are seeking to disperse silicon particles in a carbon matrix with the dual goal of reducing specific surface area and increasing the conductivity of the assembly.\(^3,10-12\) Xu et al. dispersed nano sized silicon in a polyvinylidene fluoride (PVF) solution and performed a 700°C pyrolysis step to obtain a silicon-amorphous carbon core-shell structure.\(^3\) Zhou et al. synthesized hollow silicon-carbon heterostructures by pyrolyzing a mixture of sucrose powder.\(^13\) Yin et al. used an electrospray synthesis of
silicon microspheres with sodium alginate as a carbon source followed by an additional pyrolysis step to coat the particles using polyvinyl chloride (PVC) as a secondary carbon source.\textsuperscript{14} Ren et al. reacted silicon with methyl chloride gas at 400°C to subsequently grow silicon-carbon nanobranches after a low-temperature nitric acid post treatment.\textsuperscript{15} Greco et al. proved that the use of few-layered graphene flakes outperform graphene oxide and amorphous carbon additives due to a superior electrochemical performance of the graphene flakes.\textsuperscript{8} Our own group has also previously used carbon nanotubes and polyvinyl pyrrolidone (PVP) to make a silicon quantum dot-polymer matrix anode.\textsuperscript{16} The synthesis of carbon nanoshells has also been achieved by flowing hydrocarbon compounds into high-temperature reactors. Su et al. decomposed benzene precursor at 1000°C to deposit a carbon layer around spherical silica spheres by a chemical vapor deposition (CVD) method.\textsuperscript{17} Evanoff et al. used chemical vapor deposition of ethylene at 700°C to apply an outer carbon coating to core-shell carbon nanotube-silicon structures.\textsuperscript{18} Sourice et al. have developed a 1-step laser pyrolysis technique that uses silane and ethylene as precursor gases for the formation of a core-shell Si-C structure.\textsuperscript{10,19}

This literature overview suggests that there is a large number of options when it comes to realizing a core-shell silicon-carbon structure. This raises the question of how different carbon sources and different coating methodologies can influence the performance of a finished battery. To the best of our knowledge, and despite the copious silicon-carbon studies for lithium-ion batteries, there is no comprehensive work that explores this issue. The present manuscript addresses this question by analyzing the composition and morphology of silicon-carbon heterostructures produced either by high-
temperature carbonization of a polymer precursor or by chemical vapor deposition of a
gaseous precursor. The results of the materials characterization (TEM, EDS, Raman) are
correlated with the electrochemical performance of anodes based on these structures.
These samples, produced using different approaches to the synthesis of the carbon shell,
contain silicon particles produced with the same protocol, thus ensuring that the results
are directly comparable. Our main finding is that a CVD coating is preferable under
many points of view. This gas-phase approach allows an easy control of the silicon-to-
carbon ratio and, under the right processing conditions, leads to the deposition of a highly
conformal coating of the silicon nanoparticles. The polymer carbonization route on the
other hand inevitably leads to an increase in the oxidation level of the particles, and
results in a lower quality carbon coating. As a result, the anodes based on the CVD-
coated particles show the best stability upon electrochemical cycling. This chapter is
organized as follows: the sample preparations techniques are described first. The results
of the materials characterization with respect of composition, morphology and structure
of the carbon coatings are then described in detail. The electrochemical performance of
the structures is then discussed.

3.2: Materials and Methods

3.2.1: Silicon nanoparticle synthesis

The in-house synthesis of silicon nanoparticles was performed by a non-thermal
plasma process that has been thoroughly studied and described elsewhere.\textsuperscript{20-22} Silane
(SiH\textsubscript{4}) gas was continuously fed to a 50-mm diameter, 375-mm long quartz plasma
reactor operated at a pressure of 3.5 Torr. A 13.56 MHz (RF) power supply was used to initiate the discharge. The high energy and reactivity of the plasma reactor ionizes the gas and leads to the nucleation and growth of ~10 nm nanoparticles. The aerosol was transported into a second in-flight quartz reactor heated by a 50-mm long tube furnace to a temperature of 1100°C. During the high-temperature stage, the nanoparticles coalesce and grow into branched structures composed of particles with a primary size around 50 nm. A schematic of the system is shown in Figure 3.1. We have found that the in-flight annealing step is highly beneficial to the anode performance, likely because of a reduction in specific surface area (from ~250 m²/g for the non-annealed nanoparticle to 35 m²/g for the in-flight annealed particles). Surface area measurements were obtained by a Brunauer-Emmet-Teller (BET) theory Quantachrome analyzer. The details of the in-flight nanoparticle growth process go beyond the scope of this manuscript, which focuses on how the carbon shell affects the device performance, and will be summarized in another report. In addition, we should stress that the same batch of powder was used to fabricate all the batteries reported in this manuscript.
3.2.2: Acetylene-based samples

100 mg of Si powder were introduced in a borosilicate glass test tube and placed into the tube furnace. C₂H₂ gas was transported into a 25-mm quartz reactor heated at 650°C by a tube furnace. A needle valve was installed at the furnace exhaust to control the reactor pressure and tune the growth rate. The pressure was set constant at 380 Torr. These process parameters were selected, after careful trials, to achieve a conformal coating of carbon onto the silicon particles. Temperature higher than 650°C leads to non-uniform carbon coatings and to the undesired nucleation and growth of carbon nanoparticles. The coating thickness was adjusted by varying the coating time (5, 15, and 30 minutes).
3.2.3: PVP-based Samples

100 mg of Si particles and 250 mg of PVP (Sigma Aldrich) were diluted in 15 mL of ethanol. The solution was poured into a test tube and vacuum-dried at 50°C to absorb the polymer onto the nanoparticles surface. The test tube was then placed inside a 25-mm tube furnace system. The Si particles-PVP powder was heated up under a 70 sccm Ar flow at 700°C for 1 hour. The pressure was kept at 0.23 Torr during the carbonization process. The same process was repeated for a second sample with 500 mg of PVP in order to investigate variations in carbon composition.

3.2.4: Sucrose-based Samples

Similar to PVP, 100 mg of Si particles and 250 mg of sucrose were diluted in 15 mL of water. The remaining steps were identical to those described above for PVP. A second sample with 500 mg of sucrose was also made.

3.2.5: Battery Fabrication and Testing

The carbonized powder was mixed with carboxymethyl cellulose (CMC, Sigma Aldrich) diluted in water (1% solution, by weight), and with carbon black Super P (Alfa Aesar). The slurry composition was such that after drying, the weight percentage of the coating was 0.7:0.15:0.15 Si-C powder: carbon black: CMC. The slurry was applied on top of a 50-by-50 mm copper foil and spread evenly with a Meyer rod. The anode was dried under vacuum for 12 hours at 90°C. The weight loading for the samples described in this contribution is between 0.5 and 1 mg/cm². Individual 12.5-mm anodes for coin cell batteries were punched from the 2-by-2 coatings and subsequently used for battery fabrication. Polymer separators were used for the battery assembly. Lithium foil was used
as counter electrode. A solution of lithium hexafluorophosphate (LiPF$_6$) in 1:1 v/v ethylene carbonate/diethyl carbonate was used as electrolyte. Fluoroethylene carbonate (FEC) was added to the electrolyte at 10% volume fraction. Coin cells were cycled between 0.01 V and 1.5 V with an Arbin Instruments Co. multi-channel potentiostat. Electrochemical impedance spectroscopy (EIS) is performed on a Gamry potentiostat with frequency range from 10 KHz to 1 mHz.

3.2.6: Materials Characterization

TEM analysis was performed on a Tecnai T12 transmission electron microscope. STEM imaging was performed on a FEI Titan Themis 300 instrument with EDS capability. TEM samples were prepared by drop casting the Si-C powder onto lacey carbon grids. A Horiba LabRam HR instrument equipped with a 532 nm laser was used to characterize the carbon coating in every sample. The spectra were recorded with a grating of 1800 lines/mm and a laser power of 0.151 mW. EDS characterization was obtained with a FEI Nova NanoSEM450 system equipped with an Oxford Instruments Aztec Synergy software and a X-max 50 mm$^2$ detector with resolution of 127 nm at Mn Kα. The accelerating voltage was kept at 5 kV with a working distance of 5 mm. For the acquisition of the IR spectra, we use a modular FTIR system from Newport-Oriel equipped with a deuterated triglycine sulfate detector. Samples were diluted in chloroform and drop casted onto an attenuated total reflection (ATR) crystal mounted along the path of the IR beam.
3.3: Results and Discussion

3.3.1: TEM/STEM

The as-produced particles without a secondary in-flight annealing step are around 10 nm in size. However, upon heating at 1100°C, particle morphology changes considerably. Figure 3.2a shows branch-like structures formed by 50-100 nm particles clustered together. The plasma environment within the first reactor leads to the negative charging of nanoparticles,\textsuperscript{23} and as a result it is difficult to increase the particle size above 10-15 nm using this process. On the other hand, non-thermal plasma processes provide a highly reactive environment that leads to the rapid and efficient conversion of the precursor into nanoparticles.\textsuperscript{24} We have found that the addition of an in-flight thermal annealing step is a convenient way to increase particle size while still taking advantage of the high reactivity of the plasma for the nanoparticle nucleation. During the in-flight high temperature annealing stage the particles agglomerate and sinter to form dendritic nanostructures. Figure 3.2b shows the TEM micrograph for the silicon-carbon particles produced via carbonization of PVP. The carbon appears as a thin and non-uniform coating surrounding the silicon cores. TEM micrographs of sucrose samples, not shown here for brevity, show similar features. Figure 3.2c and 3.2d shows high magnification micrographs of the particles after the 30 minutes C\textsubscript{2}H\textsubscript{2} CVD process, with the difference that now a 4 nm layer of carbon is surrounding the particles. There is a uniform coating that provides evidence of the high conformality intrinsic to this method. Lattice fringes from the 111 planes of silicon are distinguishable in Figure 3.2d, suggesting that there is a sharp interface between the silicon core and the carbon shell. The quality of the C\textsubscript{2}H\textsubscript{2}-
based coating is confirmed with STEM mapping presented in Figure 3.3a-c. The
distribution of carbon (green) is mainly limited to the surface of the silicon
nanostructures (red). For comparison, the same analysis was performed for PVP and
sucrose-treated samples (Figure 3.3d-f and Figure 3.3g-i, respectively). The
superimposed map images (Figures 3.3c,f,i) unequivocally show that a more uniform
coating is achieved with the CVD method. High uniformity is an important characteristic
on silicon-carbon core-shell structures for a few reasons: first, it limits the volume change
associated with the lithiation-delithiation process (clamping effect), thus improving
cycling stability. A uniform coating will not lead to an increase in specific surface area,
which would be detrimental with respect of first cycle coulombic efficiency. Second, a
uniform coating is expected to be highly beneficial with respect of charge transport
through the film.
Figure 3.2. (a) TEM micrographs of bare Si nanobranches. (b) After annealing of PVP coated particles. (c,d) After C$_2$H$_2$ deposition.
Figure 3.3. (a,d,g) STEM/EDS silicon mapping of nanobranches. The uniformity of the carbon coating after CVD of C$_2$H$_2$ (b) is substantially better than that of the PVP and sucrose-treated samples (e,h). The superimposed maps are shown in (c,f,i) for clarity.

3.3.2: EDS

The approximate composition of all the samples was measured by EDS. Samples were prepared by diluting the particles in chloroform and drop casting them on a copper foil. Special care was taken on ensuring the coatings were thick enough to avoid the detection of signal from the substrate. Table 3.1 summarizes the results. The C$_2$H$_2$ CVD
process appears to provide good control on carbon deposition since there is a linear increment in atomic percentage as the deposition time is increased from 5 minutes to 30 minutes. The oxygen content in these samples is low (~5%). We attribute the presence of oxygen to the growth of a native oxide layer at the particle surface. No special step was taken to prevent air exposure after the silicon nanoparticle synthesis and before the carbon coating process. The scans corresponding to both PVP and sucrose samples do not show a strong correlation between atomic percentage and the amount of carbon precursor added to the silicon particles, i.e. it is not possible to control the composition when using such polymeric precursors. Doubling the mass of either PVP or sucrose does not change the amount of carbon-to-silicon ratio significantly. On the other hand, the higher oxide level in the PVP and sucrose samples strongly suggests that the oxygen from both precursors is contributing to further oxidation of the active material. This is generally considered detrimental with respect of both the specific capacity of the anode and with respect of first cycle coulombic efficiency. It is well known that silicon oxide can be reduced to silicon during the first lithiation cycle at the cost of the irreversible formation of a lithium oxide phase.\textsuperscript{25} It is important to highlight that PVP and sucrose have previously been used as carbon sources on the synthesis of Si-C nanostructures for lithium-ion batteries.\textsuperscript{26–28}
Table 3.1. Summary of EDS compositional analysis of all samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>at% C</th>
<th>at% Si</th>
<th>at% O</th>
<th>C/Si</th>
<th>O/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 min C₂H₂ CVD</td>
<td>17.9 ± 1</td>
<td>77.88 ± 1.13</td>
<td>4.23 ± 0.15</td>
<td>0.23</td>
<td>0.05</td>
</tr>
<tr>
<td>15 min C₂H₂ CVD</td>
<td>28.89 ± 1.97</td>
<td>67.69 ± 2.06</td>
<td>3.42 ± 0.09</td>
<td>0.43</td>
<td>0.05</td>
</tr>
<tr>
<td>30 min C₂H₂ CVD</td>
<td>44.14 ± 5.54</td>
<td>52.67 ± 5.81</td>
<td>3.19 ± 0.29</td>
<td>0.84</td>
<td>0.06</td>
</tr>
<tr>
<td>250 mg PVP</td>
<td>6.85 ± 3.33</td>
<td>85.36 ± 5.61</td>
<td>7.79 ± 2.28</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>500 mg PVP</td>
<td>10.61 ± 0.44</td>
<td>79.66 ± 0.64</td>
<td>9.73 ± 0.31</td>
<td>0.13</td>
<td>0.12</td>
</tr>
<tr>
<td>250 mg Sucrose</td>
<td>21.14 ± 0.67</td>
<td>64.02 ± 0.71</td>
<td>14.84 ± 0.4</td>
<td>0.33</td>
<td>0.23</td>
</tr>
<tr>
<td>500 mg Sucrose</td>
<td>19.06 ± 10.9</td>
<td>71.38 ± 10.47</td>
<td>9.55 ± 0.91</td>
<td>0.27</td>
<td>0.13</td>
</tr>
</tbody>
</table>

3.3.3: Raman Spectroscopy

Figure 3.4 shows the Raman spectra of samples synthesized by CVD of C₂H₂. The well-known silicon peak appears at ~520 cm⁻¹ in all the samples, indicating the presence of Si nanocrystals. The interpretation of the carbon component of the spectra requires a deeper analysis. The great flexibility natural to the C-C bond leads to a variety of vibrational modes due to changes in bond orientation. Moreover, defects and bond disorder in the material also contribute to the Raman signal. It is therefore not trivial to identify the nature of the material given all its potential orientations and structures.

Ferrari and Robertson propose a three-stage model for a better understanding of disordered and amorphous carbon. The G peak position and the I_d/I_g band ratio are indicators of the degree of disorder in the material. More importantly, second order vibrations around ~2400 cm⁻¹ are also associated to the presence of graphitic carbon.
Nanocrystalline graphite has a G peak position located at \(~1600\ \text{cm}^{-1}\) and an \(I_d/I_g\) ratio close to 2.0, whereas those values are \(~1510\ \text{cm}^{-1}\) and 0.20 for amorphous carbon, respectively. In the case of the \(\text{C}_2\text{H}_2\)-CVD particles, the G peak appears around \(~1590\ \text{cm}^{-1}\), pointing to the presence of nanocrystalline graphite in the sample. The \(I_d/I_g\) ratio of the three samples is close to 1.0. Particles synthesized after 15 and 30 minutes of CVD clearly show a shoulder at \(~2400\ \text{cm}^{-1}\), suggesting that the carbon coating is at least partially graphitic. The G peak positions and \(I_d/I_g\) ratios of all samples are summarized in Table 3.2.

**Table 3.2. Summary of Raman analysis performed on all samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>G peak position (cm(^{-1}))</th>
<th>(I_d/I_g)</th>
<th>Second order</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 min (\text{C}_2\text{H}_2) CVD</td>
<td>1597</td>
<td>0.96</td>
<td>No</td>
</tr>
<tr>
<td>15 min (\text{C}_2\text{H}_2) CVD</td>
<td>1596</td>
<td>0.89</td>
<td>Yes</td>
</tr>
<tr>
<td>30 min (\text{C}_2\text{H}_2) CVD</td>
<td>1593</td>
<td>0.93</td>
<td>Yes</td>
</tr>
<tr>
<td>250 mg PVP</td>
<td>-</td>
<td>-</td>
<td>No</td>
</tr>
<tr>
<td>500 mg PVP</td>
<td>1576</td>
<td>0.93</td>
<td>No</td>
</tr>
<tr>
<td>250 mg Sucrose</td>
<td>1590</td>
<td>0.94</td>
<td>No</td>
</tr>
<tr>
<td>500 mg Sucrose</td>
<td>1592</td>
<td>0.95</td>
<td>No</td>
</tr>
</tbody>
</table>
Figure 3.4. Raman spectra of C$_2$H$_2$ CVD samples after 5 (a), 15 (b), and 30 (c) minutes of high-temperature treatment.

Figure 3.5 shows the Raman spectra of the PVP and sucrose samples. There are no remarkable variations on the G peak position or the I$_d$/I$_g$ ratio with respect to the C$_2$H$_2$
samples. However, the carbon signal appears to be weaker judging from the higher intensity of the silicon peak relative to the carbon contribution. In fact, the 250 mg PVP sample does not show any evident carbon signal. This correlates well with the low carbon content obtained in the EDS analysis. There were no second order vibrations in any of these samples. It is important to note that several Raman spectra were acquired from different spots within the same samples. The data from Figure 3.5 are representative scans of what appeared to be the most consistent measurements. However, there were important variations on the carbon signature. This finding is in good agreement with the inhomogeneous distribution of carbon observed on the TEM micrographs.
3.3.4: **FTIR**

The EDS data above indicates that the oxygen content of the PVP and sucrose samples is considerably higher than that of the C$_2$H$_2$ CVD powder. This was also corroborated by FTIR spectroscopy (Figure 3.6). Signal around ~1050 cm$^{-1}$ and ~1250 cm$^{-1}$ is assigned to asymmetric stretching of SiO$_2$ and O-Si-C bonds. Stronger peaks are present on the PVP and sucrose-based powder, suggesting that an important fraction of the oxygen original from the precursors remains in the material after the 700 °C annealing step. For the case of the C$_2$H$_2$ sample, the aforementioned vibrational modes
are mostly absent. This is consistent with the low oxygen content detected in the three samples prepared by this method. Moreover, the peak at ~850 cm\(^{-1}\), previously associated to Si-N vibrations, also appears stronger for PVP and sucrose.\(^{36,37}\) This suggests that even more of the nitrogen present in the polymer precursor reacts with silicon in the thermal annealing step.

![FTIR spectra](image)

**Figure 3.6.** FTIR spectra of C\(_2\)H\(_2\), PVP, and sucrose samples.

### 3.3.5: Battery Performance

The cycling performance of the batteries with the C\(_2\)H\(_2\) CVD anodes is shown in Figure 3.7. The three samples have a first-cycle coulombic efficiency (CE) of ~82%. This initial value is generally below 100% because of the irreversible decomposition of the electrolyte during SEI formation and because of the occurrence of irreversible reactions that take place during the first lithiation cycle, such as the electrochemical reduction of the silicon oxide layer.\(^{25}\) Irreversible binding of lithium to defects and residual hydrogen
within the carbon matrix has also been proposed a mechanism that may be detrimental to first cycle performance.\textsuperscript{11} The CE value should be as high as possible, as this is particularly critical with respect of integration in a full cell, i.e. a cell that does not use lithium foil as counter electrode (i.e. a large reservoir of lithium ions). Graphite-based anodes typically have a first cycle CE of 93%. The 82% value reported here, while comparing favorably with many other reports in the literature, clearly needs further improvement. Upon further cycling, the CE of the three batteries stabilizes around 98%. The sample with the thinner coating (5 minutes CVD treatment) requires a higher number of cycles to reach that number (Figure 3.7b). On the other hand, the 15 and 30 minutes samples reach a 97.5% CE within the first 10 cycles. Moreover, the sample with the thicker carbon coating clearly shows both the highest capacity and capacity retention over almost 100 cycles (Figure 3.7a). It should be stressed that these anodes have been cycled at a 0.1C rate, and that a slow cycling rate is actually more demanding with respect of stability compared to faster cycling (such as 1C) since the material goes through the full charge-discharge cycle, i.e. it experiences the maximum volume change. In addition, the capacity values reported in this contribution are calculated over the total mass of the material. Therefore, the sample with the thicker carbon coating (smaller silicon weight fraction) shows even higher charge-discharge capacity compared to the samples with the lower carbon content. In fact, just by taking into account the weight fraction of the active material, the specific capacities of the 5, 15, and 30 minutes samples are \(\sim 1500\ \text{mAh}\ \text{g}^{-1}\), \(\sim 1800\ \text{mAh}\ \text{g}^{-1}\), and \(\sim 2400\ \text{mAhg}^{-1}\) after 80 cycles, respectively. Raman data (Figures 3.4
and 3.5, Table 3.2) show that only the 15 and 30 minutes samples have second order vibrations associated to graphitic carbon.

Figure 3.7. (a) Cycling performance of C$_2$H$_2$ CVD. Longer deposition times lead to higher discharge capacity and improved stability. (b) Coulombic efficiency of C$_2$H$_2$ CVD samples after first 10 cycles.

The samples treated using PVP and sucrose as carbon sources show markedly lower performance. With respect of first cycle CE (Figure 3.8b), only one sample has a value approaching 82%, while the other are well below 80%. A variety of factors
contribute to this, such as an increase in the degree of oxidation and a lower quality of the carbon coating, as shown by the Raman data especially for the PVP samples. This last consideration is particularly important, since the low quality of the carbon can affect adversely both the charge transport properties and the density of defects in the carbon layer. Moreover, all these samples show rapid capacity fading, with the capacity dropping below 1000 mAhg\(^{-1}\) within few cycles (Figure 3.8a).

Overall, from the analysis presented above, we reach the following conclusions. First, the quality of the carbon layer, both in terms of uniformity and degree of ordering in the carbon structure, is essential to achieve a good performance in terms of both first cycle coulombic efficiency and overall cycling stability. This is clearly shown by the reasonably good coulombic efficiency (~82%) of the CVD C\(_2\)H\(_2\) samples over that of the PVP and sucrose-based anodes (~72%), which did not have a uniform carbon coating. Despite this, we reproducibly observe a reasonably good first cycle coulombic efficiency for the sample produce by carbonizing sucrose with a 2.5/1 sucrose-to-silicon ratio (the 250 mg sample, see Figure 3.8). This samples shows a relatively high value of both carbon-to-silicon and oxygen-to-silicon ratio after carbonization at 700\(^{\circ}\)C (33% and 23% respectively, as shown in Table 3.1). This result may challenge the commonly accepted understanding that oxygen should be avoided at all cost in silicon-based anode materials. Previous studies have also questioned how large of a negative impact the presence of a surface oxide layer may have on the battery stability.

A chemical vapor deposition process seems to be clearly preferable to the polymer carbonization route for the realization of a carbon shell. The main advantages of
this process are the facts that a conformal coating can be easily achieved, once the correct
growth temperature is identified, and that the process is highly controllable. The carbon
coating thickness can be easily adjusted by simply varying the coating time. On the other
hand, varying the ratio of silicon to the polymeric carbon precursor does not seem to
affect the silicon-to-carbon ratio (see Table 3.1), and it seems to introduce unpredictable
amount of oxygen in the material.

Figure 3.8. (a) Cycling performance of PVP and sucrose. (b) Coulombic efficiency of PVP
and sucrose samples after first 10 cycles.
EIS measurements were performed on C$_2$H$_2$ CVD (30 min), PVP (500 mg), and sucrose (250 mg) batteries in order to analyze the stability of the SEI upon cycling (Figure 3.9). The high-frequency semicircle of the Nyquist plot in lithium-ion batteries is usually attributed to the contribution of the SEI resistance represented by a Warburg diffusion element.$^{38,39}$ The EIS spectra were fitted with a model previously used to analyze the effect of tin nanoparticles as conductive additives in silicon anodes. The resulting SEI resistances ($R_{SEI}$) for the three samples are shown in Table 3.3. There is an evident increase of $R_{SEI}$ in the three batteries after extended cycling. As opposed to the linear growth of $R_{SEI}$ in the C$_2$H$_2$ sample, the abrupt increase of $R_{SEI}$ in both the PVP and —more noticeably— the sucrose anode provides evidence of an unstable SEI that is constantly fractured and restored with every cycle. These spectra provides an explanation to the poor coulombic efficiency and cycling performance of the PVP and sucrose-based anodes.

**Table 3.3.** $R_{SEI}$ calculated for the C$_2$H$_2$ CVD, PVP, and sucrose anodes after 1, 2, and 5 charge/discharge cycles.

<table>
<thead>
<tr>
<th></th>
<th>$R_{SEI}$ C$_2$H$_2$ (Ohm)</th>
<th>$R_{SEI}$ PVP (Ohm)</th>
<th>$R_{SEI}$ Sucrose (Ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Cycle</td>
<td>137.6</td>
<td>148</td>
<td>41.4</td>
</tr>
<tr>
<td>2 Cycle</td>
<td>141.3</td>
<td>164.3</td>
<td>76.2</td>
</tr>
<tr>
<td>5 Cycle</td>
<td>159.3</td>
<td>192.7</td>
<td>191.6</td>
</tr>
</tbody>
</table>
Figure 3.9. EIS data of (a) C$_2$H$_2$, (b) PVP, and (c) sucrose batteries after 1, 2, and 5 cycles.
3.4: Conclusion

We have used a two-steps plasma-hot wall reactor process to synthesize silicon nanoparticles in the 50-100 nm size range. The resulting powder was coated with carbon using two categories of techniques: a chemical vapor deposition process using acetylene as a precursor, and the carbonization of common polymers such as PVP and sucrose which have been absorbed onto the particles surface. We have performed extensive materials characterization and we have fabricated anodes for lithium ion batteries using these materials. We have found the CVD process is highly preferable since it allows coating the silicon particles with a high-quality conformal carbon coating, it enables the direct control of the coating thickness, and it can prevent further oxidation of the particles during the coating step. On the other, the carbon coatings obtained by carbonization of the polymer are highly non-uniform, generally yield lower quality carbon, and the process is accompanied by uncontrolled growth of an oxide layer. These differences translate in a clearly superior performance for batteries realized using the CVD-coated silicon nanoparticles, with respect of both cycle stability and first cycle coulombic efficiency. This study also suggests the presence of an oxide layer may not be entirely detrimental to the battery performance. Future efforts should be devoted towards clearly elucidating the role of the oxide layer and the electrochemical performance of the material.
3.5: References


Chapter 4: A Non-Thermal Plasma Route to Plasmonic TiN Nanoparticles

4.1: Introduction

The development of novel plasmonic structures and materials is highly relevant for fields such as biophotonics, photovoltaics, photocatalysis, sensing, and waveguiding. Gold is well-known for having a localized surface plasmon resonance (LSPR) in the visible. Its biocompatibility and high chemical stability make it a great candidate for several applications, but its high cost and poor thermal stability, a problem exacerbated by the reduction in melting point observed in nanostructures, limit its utilization. In addition, the design and realization of more complex structures such as gold nanoshells is needed to red-shift the LSPR peak towards the so-called biological transparency window, a region in the near-infrared regime where light is mostly transmitted through biological tissue. TiN has become a promising alternative to gold because of its high melting point and good chemical stability. TiN shows active LSPR in the NIR region. TiN nanoparticles outperform gold in local heating enhancement in the biological transparency window. A well-documented growth of a native oxide layer on TiN films motivates the use of TiN-TiO$_2$ nanostructures for photocatalytic applications in high-temperature environments. Moreover, TiN may offer an additional degree of freedom in the tuning of its optical properties compared to silver and gold-based plasmonics, whose response is typically controlled by engineering nanoparticle size and shape. Careful characterization of the optical properties of sputtered TiN films reveals that changes in titanium-to-nitrogen ratio affect both plasma frequency and
relaxation time of conduction electrons,\textsuperscript{19} opening the possibility of controlling the position of the plasmonic response by compositional tuning.

Considering that the position of the plasmon peak is highly dependent on particle size and composition, an adequate control of these parameters is crucially important to advance the field. Scalability of the process is equally important to break into mass-production markets. TiN nanoparticles have been prepared by nitridation of precursor powders,\textsuperscript{20} laser ablation in solution,\textsuperscript{21} microwave and thermal plasma,\textsuperscript{22,23} and other chemical routes.\textsuperscript{24} These methods have limitations such as the need for high temperature environments and low processing rate (nitridation of precursor powders at 800 °C for 5 h), use of specialized laser equipment and production of non-free-standing particles (laser ablation in solution), and broad particle size distribution (microwave and thermal plasmas). The non-thermal plasma synthesis of nanoparticles can overcome these limitations. This approach is characterized by high chemical reactivity,\textsuperscript{25} by the unipolar charging of particles suspended in the plasma,\textsuperscript{26} and by a high rate of nanoparticle heating induced by the interaction between the particles and the plasma-produced radicals.\textsuperscript{25,27,28} These translate into the capability of producing powders composed of a wide range of materials (Si,\textsuperscript{29} Si-Ge,\textsuperscript{30} ZnO,\textsuperscript{31} and SiC\textsuperscript{32}), with small size and narrow size distribution, and with high-quality crystalline structure. In this manuscript, we report for the first time the utilization of a similar procedure for the production of TiN nanoparticles, highlighting the possibility to tune their optical properties by modifying controllable process parameters such as NH\textsubscript{3} flow rate. An in-depth study of the nanoparticles structure, as well as the effects of oxidation in their optical properties is
also presented. To complement our experimental results, we investigated the effect a surface oxide layer has on the optical properties of TiN nanoparticles by using large-scale, real-time quantum dynamics calculations.

4.2: Experimental Methods

The synthesis of TiN nanoparticles is based on the continuous flow non-thermal plasma reactor design described by Mangolini et. al.,\textsuperscript{29} and consists in supplying the appropriate titanium and nitrogen precursors to a plasma sustained by a 13.56 MHz (RF) power supply. A simplified schematic of this system is shown in Figure 4.1. Titanium tetrachloride (TiCl\textsubscript{4}) and ammonia (NH\textsubscript{3}) are used as precursors. The reactor is composed of a 25.4 mm outer diameter quartz tube with a thin copper plate wrapped around it as powered electrode. The width of the copper plate is also 25.4 mm. The vacuum flange upstream of the powered electrode serves as electrical ground. The distance between the flange and the powered electrode is 50 mm. The RF power supplied to the reactor is 180 W. This power is the minimum necessary to consistently produce crystalline nanoparticles. TiCl\textsubscript{4} is delivered using a bubbler kept at atmospheric pressure and in a water bath at 22°C. Argon (70 sccm) is used as carrier gas. Based on the vapor pressure of TiCl\textsubscript{4},\textsuperscript{30,33} we estimated the TiCl\textsubscript{4} flow rate to be 1 sccm. The pressure in the reactor is set at 3 Torr. TiN nanoparticles are collected downstream from the reactor on a stainless steel mesh filter. After collection, we have found that it is necessary to heat up the sample in a tube furnace at 200°C under argon atmosphere in order to evaporate ammonium salts, which are a by-product of the TiCl\textsubscript{4}-NH\textsubscript{3} reaction.\textsuperscript{34} XRD characterization is
performed on a PANalytical Empyrean X-ray system using CuKα radiation with a wavelength of 1.54 Å. TEM and STEM imaging are performed with a FEI Titan Themis 300 instrument with energy dispersive X-ray Spectroscopy (EDS) capability. EDS spectra were processed using a Bruker Instruments Esprit 1.9 software. Quantification is based on the Cliff-Lorimer approach using calculated k-factors and correcting for thickness by estimating the size of the aggregated particles. Extinction measurements are performed on a Varian Carry 500 UV-vis-NIR spectrophotometer. Samples were prepared by diluting 1 mg of powder in 5 mL of 99.9% methanol to form a clear solution. X-ray photoelectron spectroscopy (XPS) characterization is carried out by using a Kratos AXIS ULTRA DLD XPS system equipped with an Al K(alpha) monochromated X-ray source and a 165-mm mean radius electron energy hemispherical analyzer. Vacuum pressure was kept below $3 \times 10^{-9}$ Torr during acquisition. A 3 kV Ar-ion beam was used to sputter the particles’ surface.
Figure 4.1. Simplified schematic of nonthermal plasma system. Ar gas carries precursor gas (TiCl₄) and is mixed with NH₃ at the entrance of the reactor.

4.3: Theoretical Methods

We carried out our electronic calculations using the self-consistent density functional tight-binding (SCC-DFTB) formalism. For probing the optical properties (such as the absorbance spectrum) of our nanoparticles, we implemented and utilized a locally modified real-time, time-dependent DFTB (RT-TDDFTB) code, which is based on the real-time quantum mechanical propagation of the one electron density matrix. This formalism has been previously used to probe the nonequilibrium electron dynamics in several large chemical systems, including photoinjection dynamics in dye-sensitized TiO₂ solar cells and many-body interactions in solvated nanodroplets. Based on our XRD structure analyses, we optimized the rock-salt arrangement of bulk TiN using the DFTB+ code. Next, a spherical cluster of 2.8-nm diameter was cut out of this bulk TiN and used for the subsequent absorbance spectrum calculations. Similarly, for generating
the TiO$_2$-coated TiN cluster, we optimized the anatase structure of bulk TiO$_2$, which is known to be the more stable phase, particularly in nanocrystalline clusters of TiO$_2$. A shell structure, cut out of the optimized TiO$_2$ bulk, and a core cut out of the previously optimized TiN bulk were conjoined to form a core-shell structure. The TiO$_2$ shell thickness was set to 2 Å and the TiN core diameter was set to 2.4 nm.

4.4: Results and Discussion

4.4.1: Structural Characterization

The production rate of the free-standing powder is ~50 mg/h, corresponding to a titanium precursor utilization of 30%. Particle size and composition are highly dependent on the amount of NH$_3$ introduced into the system. Figure 4.2a shows XRD data for samples synthesized under different NH$_3$ flow rate conditions. Reflections of cubic TiN are clearly identified in every sample with peaks at 36.6°, 42.6°, 61.8°, 74.1°, and 77.9° corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes of rock-salt TiN. Scherrer analysis indicates an increase in crystallite size from ~4 nm to ~8 nm when running the system with 6 sccm and 1.5 sccm of NH$_3$, respectively. In good agreement with the XRD findings, particle size distributions (Figure 4.2b,c) obtained by analyzing TEM micrographs confirm that particles produced with less NH$_3$ are bigger than those produced at higher NH$_3$ flow rates (Figure 4.3). This dependence of particle size as a function of the titanium-to-nitrogen precursor ratio becomes evident for NH$_3$ flow rates under 10 sccm, i.e. for a TiCl$_4$/NH$_3$ ratio higher than ~0.2 (Figure 4.2d). The biggest particles — produced at 1.5 sccm of NH$_3$— have a characteristic cubic morphology that
has been reported elsewhere (Figure 4.2e).\textsuperscript{16} Moreover, the selected area diffraction pattern shown at the inset is also consistent with the XRD reflections from Figure 4.2a. Additional high magnification TEM micrographs are shown in Figure 4.4.

**Figure 4.2.** (a) X-ray diffraction of TiN nanoparticles synthesized under different NH\textsubscript{3} flow rate conditions. (b), (c) Particle size distribution of samples produced at 6 sccm (b) and 1.5 sccm (c) of NH\textsubscript{3}. (d) Dependence of particle size determined by Scherrer’s formula on the ratio between titanium and nitrogen precursors. (e) TEM micrograph of particles synthesized with 1.5 sccm of NH\textsubscript{3}.
Figure 4.3. TEM micrographs of (a) small particles (~4nm) and (b) large particles (~8nm) under the same magnification.
4.4.2: Oxidation Stability and Optical Properties

The LSPR peak of plasmonic metallic nanoparticles is mainly dependent on their shape, size, and surrounding medium.\textsuperscript{17,42} However, composition-based control of optical properties is impossible with pure-metal nanoparticles. The nature of the TiN system enables the use of this additional degree of freedom. The extinction spectra of TiN
nanoparticles produced with different ammonia flow rates and dispersed in methanol are shown in Figure 4.5. The spectra are normalized at 350 nm. There is evidence of LSPR peaks in every curve. The peak position varies with processing parameters, ranging from 1000 nm for the particles produced with the higher ammonia flow rate (NH$_3$/TiCl$_4$ = 6) to 800 nm for those produced with the smaller ammonia flow rate (NH$_3$/TiCl$_4$ = 1.5). The plasmon peak is narrower and more intense when its position is at lower wavelength. Differences are obvious even by visual inspection (Figure 4.6), with particles with peak LSPR position at 1000 nm appearing yellow and particles with peak at 800 nm appearing blue under white light illumination.

Figure 4.5. Extinction spectra of TiN nanoparticles produced with different ammonia-to-titanium tetrachloride ratios.
The analysis summarized in Figure 4.2 suggests that an increase in NH$_3$/TiCl$_4$ ratio leads to a smaller nanoparticle size. Yet these particles have a red-shifted LSPR peak compared to larger particles produced with a smaller NH$_3$/TiCl$_4$ ratio. This trend is opposite to what the Mie theory predicts,$^{43,44}$ suggesting that there are additional factors affecting the optical response of the material. To address this issue, we have carefully investigated the degree of nanoparticle oxidation for materials produced with different processing parameters. The Ti2p XPS spectra shown in Figure 4.7 provide important insight on how oxygen is distributed in different-sized particles. The TiO$_2$ signal (~458.2 and ~463.7 eV)$^{45}$ is evident in both small and big particles (Figure 4.7a,b, respectively). However, shoulders at ~455.0 and ~461.3 eV clearly indicate the presence of TiN,$^{45}$ especially in the bigger particles. The substantial amount of oxygen detected may imply these are actually oxynitride nanoparticles. The formation of rock salt titanium oxynitride (TiON) microspheres with an absorbance band in the near infrared has been reported in the literature.$^{46}$ To discard this possibility, we performed additional XPS measurements after a two-steps sputtering process to gain some information on the oxygen distribution.

**Figure 4.6.** Solution with (a) small and (b) large particles under white light illumination. Change in color is evident and in good agreement with the absorbance spectra in Figure 2.
in the particle core. For the case of the smaller particles, the characteristic TiO\textsubscript{2} peaks are still present after a 150 s sputtering treatment (Figure 4.7c). However, the oxide-related signals are clearly much weaker than the nitride peaks for the bigger particles (Figure 4.7d). We estimate a sputter depth of \(~1.5\) nm and \(~3\) nm after 10 s and 150 s of treatment, respectively, based on the formula reported by McCafferty et. al. on their study on XPS sputter profiling of air-oxidized titanium films.\textsuperscript{47} From this data it is evident that oxidation is relevant in TiN nanoparticles, but that the extent of the oxidation is different for particles produced at a higher ammonia flow rate (smaller particles). Moreover, we have confirmed that for the case of the bigger particles most of the oxidation occurs at the surface, while the bulk is mainly composed of TiN. Table 1 summarizes the results of complementary STEM/EDS measurements for particles produced at high ammonia flow rate (small particles) and at low ammonia flow rate (big particles). The data summarized in Table 1 are obtained by sampling the signal over a large number of particles (we estimate few hundreds in the field of view). The EDS data show low oxygen levels and a very-close-to-stoichiometry N-to-Ti ratio for the bigger particles. On the other hand, smaller particles shows higher oxygen levels and a considerably lower N-to-Ti ratio. Overall, and in good agreement with XPS characterization, small particles appear to be nitrogen deficient and oxygen rich, whereas bigger particles are very close to stoichiometry and have a significantly lower oxygen level.
Figure 4.7. XPS spectra at the surface of small (a) and big (b) particles. XPS spectra after two sputtering steps (10 s and 150 s) on small (c) and big (d) particles. Decrease in oxidation is evident as a function of sputtering depth.
Table 1. Composition of samples before and after NH$_3$ compared to that of small and big particles.

<table>
<thead>
<tr>
<th>Element</th>
<th>small particles</th>
<th>big particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti at%</td>
<td>46.22 ± 4.4</td>
<td>42.1 ± 2.5</td>
</tr>
<tr>
<td>N at%</td>
<td>27.6 ± 7.5</td>
<td>42 ± 3.9</td>
</tr>
<tr>
<td>O at%</td>
<td>26.18 ± 5.3</td>
<td>15.9 ± 3.3</td>
</tr>
<tr>
<td>N/Ti</td>
<td>0.60</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Overall the combination of the XPS and the STEM/EDS data confirm that the bigger particles, produced with a lower NH$_3$/TiCl$_4$ ratio, are stoichiometric and have an oxide-rich surface. Smaller particles are nitrogen-poor and show clear sign of oxidation not only at the surface but at the core of the particle as well. The non-thermal plasma process utilized for the synthesis of these particles is effectively oxygen free, since the reactor has negligible leakage rate (2.06 x 10$^{-5}$ Pa·m$^3$·s$^{-1}$) and all the precursors are of ultra-high purity grade. Oxidation occurs when the particles are extracted from the system and exposed to air. It is reasonable to expect that the high density of vacancies in the nitrogen-deficient particles makes them more susceptible to oxidation, with oxygen clearly diffusing within the core of the particles. This vacancy-induced oxidation mechanism has been reported for other refractory materials such as ZrC.$^{48}$

4.4.3: Role of oxidation on the plasmonic response

We have investigated the role of oxidation on the plasmonic response of TiN particle by monitoring the changes in their optical properties after annealing in air. Figure
4.8 shows the results of an oxidation experiment were a sample of big particles was air-annealed first at 150 °C and then at 250 °C for 1 hour at each temperature. The plasmonic response of the particles is remarkably similar to that observed in Figure 4.5. This experiment provides conclusive evidence that the degree of oxidation clearly affects the LSPR peak position and width. The blue-shift in LSPR peak position detected for bigger particles (Figure 4.5) is not a consequence of size, but of composition. Nitrogen-deficient particles are more prone to oxidation due to the high degree of vacancy defects present in their structure. Finally, the plasmonic nature of the near-infrared peak observed in the extinction spectra is confirmed in Figure 4.9. We diluted the same batch of particles in two different solvents (methanol and toluene, n = 1.32 and n = 1.49, respectively). The toluene solution red-shifted relative to that with methanol. This effect is in good agreement with an in-depth study on solvent-dependence of the LSPR position on silver nanoparticles.49
Figure 4.8. ~8 nm TiN nanoparticles before and after air-annealing at 150 °C and 250 °C. Plasmonic response is remarkably similar to that observed in Figure 2.

Figure 4.9. Extinction measurements on ~8 nm TiN nanoparticles in solvents with different refractive indexes ($n_{\text{methanol}} = 1.33$, $n_{\text{toluene}} = 1.49$).
4.4.4: DFT Calculations

To complement and support our experimental results, we calculated the optical properties of TiN nanoparticles to understand how the plasmon peak absorbance band is modified by the surface layer properties. Figure 4.10 plots the RT-TDDFTB absorbance spectrum of a 2.8-nm TiN nanoparticle without a TiO$_2$ shell (Figure 4.10a) and a 2.4 nm TiN nanoparticle with a 2 Å thick TiO$_2$ layer (Figure 4.10b). A strong peak, corresponding to the plasmon energy, is observed at around 2 eV (615 nm) for the pure TiN particle. Previous computational studies on various titanium nitride nanostructures have reported plasmon energy values which match closely with these RT-TDDFTB results.\textsuperscript{15,50} The absorbance spectrum of the TiN/TiO$_2$ nanoparticle shows a clear reduction in the energy of the LSPR peak relative to that of the pure TiN nanoparticle. This observation directly supports our experimental results and strongly implies that the surface oxide layer (1) plays an important part in controlling the optical properties of the TiN nanoparticles and (2) even a thin oxide surface layer (2 Å) can significantly alter the optical properties of these nanoparticles. These calculations support our experimental findings that the LSPR peak position is strongly dependent on the degree of oxidation.
Figure 4.10. Absorbance spectra of the pure TiN (blue line) and the TiO2-coated TiN (red line) nanoparticles.

It is apparent that the non-thermal plasma process tends to produce nitrogen-poor and smaller particles when the NH$_3$ flow rate is increased with respect of the TiCl$_4$ flow rate. The exact mechanism leading to the nucleation and growth of TiN particles in this kind of reactive system is completely unexplored at this point and it will be the subject of future contributions. Nevertheless, based on our previous experience with the synthesis of nanoparticles using non-thermal plasma reactors,$^{28,51}$ we expect an increase in the vapor pressure of molecular species such as NH$_3$ to lead to a quenching of the discharge, in turn
leading to a decrease in the density of chemically reactive species (radicals such as atomic nitrogen) likely responsible for the nitridation of the particles.

4.5: Conclusions

We have successfully applied a continuous flow non-thermal plasma synthesis technique to the case of TiN nanoparticles. Plasma-produced TiN particles show a plasmonic peak in the near infrared part of the spectrum, and the position of the LSPR peak can be controlled by tuning process parameters such as the NH3/TiCl4 ratio. A combination of XPS and STEM/EDS analysis suggest that the red-shift in LSPR peak is observed in particles with a lower N/Ti ratio, i.e. nitrogen poor particles. Due to the high concentration of vacancies, these particles are particularly prone to oxidation after production, upon exposure to air. Particles produced at stoichiometric conditions still show an oxide-rich surface layer and are susceptible to oxidation after annealing in air at temperatures as low as 150°C. The annealing in air is accompanied by a red-shift in plasmon peak position, consistent with the explanation that the oxide layer reduces the energy of the plasmon resonance. Experimental results are in good agreement with time-dependent DFT simulations performed on pure TiN and TiO2-coated TiN nanoparticles. This contribution, while describing a novel approach to the production of novel plasmonic nanoparticles with narrow size distribution and controllable composition, highlights the need for more extensive studies on this complex material.
4.6: References


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Chapter 5: Plasmon-induced Photoplatinng with TiN nanocrystals

5.1: Introduction

The possibility of using plasmonic nanostructures to drive photochemical reactions has generated significant excitement in recent years.\textsuperscript{1,2} Plasmonic materials provide pathways for converting radiation into chemical energy which are novel and fundamentally different than in semiconductors. There are two approaches for harnessing such potential. In a first strategy, the decay of the localized surface-plasmon resonance (LSPR) leads to the formation of hot electrons or holes, which can then drive chemical changes in molecules adsorbed onto the surface of the nanostructure.\textsuperscript{3,4} A direct charge transfer from the plasmonic structure to the adsorbates can also occur, which has often been called chemical interface damping.\textsuperscript{5–7} Alternatively, the field enhancement at the surface of plasmonic nanostructures can increase the photo-activity of other structures (such as a catalyst particles) placed in their near-field.\textsuperscript{6,8–11} Both approaches leverage the very high extinction cross section of plasmonic structures and their potential for driving reactions at low temperature and with high selectivity.\textsuperscript{6,13} This field has been so far dominated by the use of silver and gold as plasmonic materials because they strongly resonate in the visible spectrum. This introduces a number of constraints. First, the thermal stability of gold and silver is limited by their relatively low bulk melting point. This is exacerbated by the melting point reduction at the nanoscale.\textsuperscript{14} Second, silver nanoparticles are chemically unstable at even mild environments,\textsuperscript{15} and therefore cannot perform appropriately over long time periods. Third, the inherent high cost of gold and silver may impact the viability of industrial application of plasmonic catalysis, among
other applications of plasmonic materials. These considerations motivate the search for alternative plasmonic materials. Metal nitrides are among these proposed materials because they are refractory ceramics with good chemical and thermal stability\textsuperscript{15–18} and they have a surface plasmon resonance in the vis-NIR region.\textsuperscript{16,19,20} The work on plasmonic titanium nitride, for example, has already been focused towards the development of plasmonic heat transducers,\textsuperscript{21} photothermal cancer treatment,\textsuperscript{22} and plasmonic waveguides.\textsuperscript{23}

With respect of the photochemistry of TiN, there are to our knowledge only two published reports discussing it. Successful injection of charge carriers generated by LSPR decay in TiN into a TiO\textsubscript{2} substrate has been confirmed in a photo-electrochemical cell by correlating photocurrent and optical extinction spectra.\textsuperscript{24} Also, the photoactivity of TiO\textsubscript{2} powders has been enhanced using TiN nanoparticles as additives,\textsuperscript{25} although no enhancement in the visible-only part of the spectrum was observed. Therefore, a direct demonstration of the capability of TiN to perform useful photochemical reactions under plasmonically-coupled, visible-only radiation is still missing.

This work addresses this issue by demonstrating the plasmon-mediated growth of platinum clusters on the surface of TiN nanoparticles. Platinum has been selected because it is ubiquitous in heterogeneous catalysis. Moreover, heterostructures composed of a plasmonically active components in close proximity to catalyst particles have been proposed by several groups,\textsuperscript{1,6,11,26} although many of such reports rely on silver, gold, and other thermally unstable metals as plasmonic material. Platinum clusters have been grown directly onto plasmonic TiN nanoparticles by utilizing hot carriers generated in
TiN to reduce Pt$^{4+}$ to Pt metal, all while simultaneously oxidizing methanol to balance charge. We synthesized TiN nanoparticles via a non-thermal plasma method previously used in the production of other metal nitrides, semiconductors, and metallic nanoparticles.$^{27-32}$ To summarize, ammonia (NH$_3$) and titanium tetrachloride (TiCl$_4$) precursors were transported independently into a non-thermal plasma reactor sustained with a 13.56 MHz (RF) power supply. The high reactivity inside the plasma,$^{33}$ the unipolar charging of particles,$^{34}$ and the nanoparticle heating due to interactions with plasma-produced species (radicals and ions)$^{33,35}$ lead to the nucleation and growth of refractory TiN nanocrystals. The resulting powder was diluted in an aqueous solution with methanol and chloroplatinic acid. Upon vis-NIR light illumination (600 nm to 900 nm) the platinum precursor was reduced. TEM, STEM-EDX, and XPS analyses conclusively show the presence of Pt$^0$ at the TiN surface. Measurements of CO$_2$ evolution as a function of time, which resulted from methanol oxidation by holes, show a substantial increase with respect to a sample that was not subjected to light excitation. Moreover, the molar ratio of Pt deposition-to-CO$_2$ production is 1.69±0.37, in good agreement with the theoretical value of 1.5 which is expected from the charge balance of the redox reaction under consideration. Pt deposition and CO$_2$ production plateaued after 6 hours because an increasing amount of Pt at the TiN surface induced interfacial damping of the plasmon that limited the reaction. This is demonstrated through the analysis of experimental spectra and DFT simulations. The work presented here provides strong evidence of the plasmonic capabilities of TiN in photochemistry and sets a
baseline for the development of more efficient TiN-based plasmonic heterostructures for cost-effective photocatalytic processes.

5.2: Materials and Methods

5.2.1: TiN Nanoparticle Synthesis

A well-documented non-thermal plasma method was used to synthesize ~10 nm TiN nanoparticles. Ammonia (NH\textsubscript{3}) and titanium tetrachloride (TiCl\textsubscript{4}) were used as precursor gases and transported independently into the upstream flange of a 25.4-cm long, 2.54-cm diameter quartz reactor, where a plasma discharge was initiated with a 5-cm long, 2.54-cm diameter cylindrical copper electrode wrapped around the reactor and connected to a 13.56 MHz (RF) power supply. The distance between the center of the electrode and the upstream flange was 4 cm. TiCl\textsubscript{4} was delivered using a bubbler kept at atmospheric pressure and in a water bath at 22 °C. Argon was used as a carrier gas and maintained at a flow rate of 70 sccm. Based on the vapor pressure of TiCl\textsubscript{4}, we estimate that the net TiCl\textsubscript{4} flow rate is 1 sccm under these conditions. The NH\textsubscript{3} flow rate was maintained at 2.0 sccm. The pressure in the reactor was set to 3 Torr. The TiN particles were collected downstream of the reactor on a stainless-steel mesh filter. The samples were subsequently annealed in a tube furnace under an Ar atmosphere at 250 °C to evaporate ammonium salts, which are a by-product of the TiCl\textsubscript{4}-NH\textsubscript{3} reaction.

5.2.2: Platinum Photodeposition

TiN was added to a 90:10 (v/v) water-methanol solution at a concentration of 160 µM. After sonication for 10 minutes, an 8 wt. % H\textsubscript{2}PtCl\textsubscript{6} aqueous solution (Sigma Aldrich)
was added at a concentration of 70 µM. The solution was then illuminated with a 500 W Hg-Xe Newport 67005 Arc Lamp Housing and kept under constant stirring. The distance between the reactor and the light source was 23 cm. Two optical filters (600 nm longpass and 900 nm shortpass, Edmund Optics Inc.) were used to limit the incident light in between 600 nm and 900 nm. The spectrum of the incident light was measured with an Avantes SensLine AvaSpec ULS-RS-TEC spectrometer. The light intensity was obtained by placing a Thor Labs PM400 optical power meter in the path of the incident light at precisely the same distance as the illuminated sample. Control samples (under no illumination) were maintained under stirring at 40 °C to match the maximum temperature reached by the illuminated samples due to heating by light absorption of the nanoparticles. Different samples were illuminated for 20 min, 30 min, 1 h, 2 h, 4 h, and 6 h. A pH of 4.0 was measured in the solution throughout all the experiments.

5.2.3: Characterization of TiN-Pt Heterostructure

After illumination, samples were centrifuged and rinsed with water twice to eliminate any additional reactant or Pt precursor. TEM samples were prepared by dropcasting a solution of TiN-Pt particles on a lacey carbon copper grid. The dry samples were characterized in a Tecnai T-12 TEM for lower resolution characterization. High resolution TEM (HR TEM) and STEM images were obtained with a FEI Titan Themis 300 instrument with energy dispersive X-ray spectroscopy (EDX) capability for elemental mapping. XPS characterization was performed at the UC Irvine Materials Research Institute (IMRI). Samples were prepared by dropcasting the TiN-Pt solution on a piece of prime-grade silicon previously cleaned with acetone, isopropanol, and DI water. Spectra were
acquired with an AXIS Supra by Kratos Analytical tool with a dual anode Al/Ag monochromatic X-ray source. EDX characterization was performed with a FEI Nova NanoSEM450 system equipped with an Oxford Instruments Aztec Synergy software and a X-max 50 mm$^2$ detector with resolution of 127 nm at Mn Kα. The accelerating voltage was kept at 20 kV with a working distance of 5 mm. Extinction measurements were performed on a Varian Carry 500 UV-vis-NIR spectrophotometer. Samples were collected from the reactor and thoroughly washed and centrifuged before obtaining the spectra. Samples were prepared by diluting in DI water and transferred to a 1 cm x 1 cm quartz cuvette.

5.2.4: DFT Calculations

All calculations were performed with Kohn-Sham density functional theory using the PBE exchange-correlation functional as implemented in the FHI-aims software package.\textsuperscript{36,37} To simulate the Pt-TiN interface, 6-layers of a Pt(111) surface were placed on top of a 6-layer TiN(111) surface, and the combined structure was optimized until the forces were less than 0.01 eV/Å. A vacuum of at least 15 Å was used to avoid any spurious interactions between the periodic images. The Brillouin zone was integrated using a 4x4x1 Monkhost-Pack k-grid.\textsuperscript{38} 6-layer thick slabs along with 15 Angstroms of vacuum and a 4x4x1 Monkhost-Pack k-grid were used for the work-function calculations for the (111) surfaces of TiN and Pt. Due to the large system sizes in all these calculations, the FHI-aims tier-1 basis was used.
5.2.5: CO$_2$ Evolution

The Pt photodeposition experiment was performed in a three-neck glass reactor with a 35 mm quartz window. Throughout the experiment, the reactor was wrapped in aluminum foil except for the quartz window to focus the incident light onto the reaction solution. The three reactor necks were sealed from the environment with a septa cap, a plastic cap with a thermometer and an O-ring adapter, and a three-way valve adapter connected to an Ar line and a vacuum output. A manometer was also attached to measure the pressure inside the reactor. The valve was opened to vacuum and, after 10 seconds, it was turned towards the Ar line to refill the reactor up to a pressure of 10 psi. This purging cycle was repeated 5 times. 1 mL gas samples were collected with a pressurized syringe injected into the septa cap. The sample was injected into a previously calibrated SRI MG #5 gas chromatograph (SRI Instruments) equipped with a flame ionization detector (FID) with a built-in methanizer for CO$_2$ detection and a thermal conductivity detector (TCD), both downstream of a molecular sieve column (6’ mol sieve 13x). Ar gas was used as the carrier gas. Samples were extracted after 20 min, 40 min, 1 h, 2 h, 4h, and 6 h of visible light illumination.

5.3: Results and Discussion

Figure 5.1a shows a schematic of the Pt photodeposition reaction. We used chloroplatinic acid as the metal precursor. Upon visible light excitation and subsequent plasmon decay, produced energetic electrons can drive the reduction of the Pt precursor
from Pt\(^{4+}\) to Pt\(^0\). Four electrons are necessary to fully reduce platinum to its metallic state, as shown in the reaction below:

\[
Pt\text{Cl}_6^{2-} + 4e^- \rightarrow Pt^0 + 6Cl^- \quad (5.1)
\]

The photogenerated holes initiate the oxidation reaction, which corresponds to the other half of the overall process. Organic compounds are commonly used as sacrificial electron donors to overcome the kinetic limitations associated to the oxidation of water.\(^{39,40}\) The oxidation of methanol has been studied previously for the production of hydrogen with platinized TiO\(_2\).\(^{40-43}\) The mechanism of methanol oxidation is a multistep process that involves the production of stable intermediates and protons that are later reduced by photogenerated electrons to form CO\(_2\) and H\(_2\). In this case, the electrons are scavenged by the hexachloroplatinate species to form Pt\(^0\) (Reaction 5.1) and the protons generated via hole injection (Reaction 5.2) are likely reduced by chlorine ions obtained from Reaction 1 to yield metallic Pt, CO\(_2\) and HCl as final products.

\[
CH_3OH + H_2O + 6h^+ \rightarrow CO_2 + 6H^+ \quad (5.2)
\]

Based on the number of charges needed to fully reduce Pt\(^{4+}\) (4 electrons) and oxidize methanol to CO\(_2\) (6 holes), one finds a 3:2 ratio of Pt\(^0\): CO\(_2\) product formation. Figure 5.1b shows the extinction spectrum of the TiN nanoparticles before photodeposition. The red rectangle indicates the wavelength range incident on the nanoparticle solution during the experiment. Figure 5.2 shows the optical spectrum of the
lamp after filtering the white light source with 600 nm longpass and 900 nm shortpass filters. By exciting the nanoparticles at these wavelengths, we discard any contribution from interband transitions that take place below 500 nm. It is important to note that the experiments were initiated at ambient conditions and that the maximum temperature measured was 38°C. Experiments on control samples not exposed to light were maintained at the same temperature to make up for the thermal contribution of the light source.

Figure 5.1. a) Schematic of the intended photocatalytic reaction. Platinum precursor anions adsorb to the surface of the TiN nanoparticles and are reduced by photogenerated electrons. Methanol is oxidized by photogenerated holes to form CO₂ and protons. b) Extinction spectrum of the TiN nanoparticles before the reaction. The red rectangle indicates the optical band that is incident on the sample. It coincides with the plasmon peak of the spectrum.
Figure 5.2. Optical spectrum of incident light on the reactor acquired with an optical power meter after filtering the white light from a 500 W Hg-Xe Newport 67005 Arc Lamp with 600 nm longpass and 900 nm shortpass filters.

5.3.1: Photodeposition of Pt Nanoparticles

The resulting samples were thoroughly characterized to confirm the deposition of metallic Pt. Figure 5.3 shows HR-TEM imaging of a sample produced after 6-hour illumination of TiN particles submerged in a 10 % methanol (v/v) aqueous solution containing chloroplatinic acid at a concentration of 70 µM. Well-defined lattice fringes from the TiN and Pt nanostructures are observed in Figure 5.3a. After FFT post-processing, we identified signal corresponding to the 111 Pt (yellow square) and 111 TiN (blue square) planes with a d spacing of 0.226 nm and 0.245 nm, respectively. The two signatures can be superimposed and identified upon analysis at the interface of both nanostructures (red square). A HAADF-STEM image and its corresponding EDX map are presented in Figure 5.3b,c. Since the signal obtained with a HAADF detector has a proportional dependence to the atomic number of the sample, the regions with a higher
intensity in Figure 5.3b are attributed to a heavier element. EDX mapping unequivocally confirms the deposition of Pt (green) on the TiN (red) nanoparticles (Figure 5.3c).

**Figure 5.3.** a) High resolution TEM imaging shows the lattice fringes of the TiN and the Pt nanostructures. The squares to the left show FFT signal of regions on the image marked with their corresponding colors. Pt 111 and TiN 111 were identified in this analysis. b) HAADF-STEM image of a TiN nanoparticle with Pt clusters. c) EDX mapping of HAADF-STEM image shows a clear signal from Pt atoms.
5.3.2: XPS Analysis of TiN-Pt Heterostructures

To complement the findings from TEM and EDX characterization we also performed XPS on the TiN-Pt samples after 6 hours of irradiation to identify the presence of fully reduced platinum (Figure 5.4). The Pt 4f spectrum in Figure 5.4a shows a strong signal from Pt$^0$ doublets at $\sim$71.0 eV and $\sim$74.3 eV.$^{44,45}$ Additional TEM images for experiments performed in presence of methanol are presented in Figure 5.5. Under illumination, there are $\sim$2 nm Pt clusters adsorbed to the TiN particles. In the dark, such clusters were not observed. Alternatively, Figure 5.4b shows the Pt 4f XPS spectrum of a sample exposed to light in an aqueous chloroplatinic acid solution, but without the addition of methanol as an electron donor. The Pt$^{4+}$ and Pt$^{2+}$ primary doublets are observed at $\sim$75 eV and $\sim$72.7 eV.$^{44,45}$ No signal from Pt$^0$ was identified. TEM images of this sample (Figure 5.6) show clusters below 1 nm in size adsorbed to the TiN surface for both the cases under illumination and in the dark. Based on the XPS data and the low pH of the solution throughout the reaction ($\sim$4.0), we conclude that these clusters are non-reduced aggregates resulting from the adsorption of the platinum precursor on the TiN surface. The higher concentration of protons in acidic environments translates into the positive charging of the particles. The negatively charged hexachloroplatinate anions (PtCl$_6^{2-}$) are therefore electrostatically adsorbed onto the TiN.$^{46,47}$ This highlights the importance of methanol as a sacrificial electron donor and its role in balancing the TiN charge therefore enabling the reduction of the platinum-containing adsorbates. In addition, the difference between the light and the dark experiments is clear. Under
illumination, visibly larger Pt clusters where deposited on the TiN surface, whereas in the dark such clusters were not observed.

**Figure 5.4.** a,b) Pt 4f spectra of TiN-Pt samples after 6 hours with and without methanol under illumination. c,d) Ti 2p spectra of TiN-Pt samples after 6 hours under illumination and in the dark. e,f) Cl 2p spectra of TiN-Pt samples after 6 hours under illumination and in the dark.
Figure 5.5: TiN-Pt samples in the dark and after illumination with the addition of methanol as a sacrificial electron donor. Low (a) and high (c) magnification images of the illuminated samples show that large clusters (~2 nm) have been deposited at the TiN surface. These clusters were not observed in the control sample (b, d) that remained unexposed to the light source. These data provide evidence on the role of methanol as a sacrificial electron donor upon excitation of TiN with visible light.
Figure 5.6: TiN-Pt samples in the dark and after illumination without the addition of methanol as a sacrificial electron donor. Low (a) and high (c) magnification images of TiN-Pt sample under illumination. Small sub ~1 nm clusters coat the surface of the TiN particles. Similar clusters appear even when the sample is not exposed to light (b, d). XPS data in Figure 5.4a reveals that these adsorbates correspond to non-reduced platinum species.

The Ti2p spectra of both illuminated and non-illuminated samples show two pairs of doublets with primary 2p$_{3/2}$ peaks at ~458.8 eV and ~456.2 eV (Figure 5.4c,d). We attribute these signals to Ti-O and Ti-N bonds, respectively. These results were expected based on previous work regarding the oxidation mechanism of TiN nanoparticles and thin
For this study, we did not observe a substantial difference between the Ti 2p signal of the experiment and control samples. This suggests that the composition of the TiN nanoparticles remains stable during light exposure. Moreover, EDX analysis of the Ti-to-N ratio shown in Figure 5.7 demonstrates that, over several hours of illumination, the Ti-to-N ratio remains close to 1.0 and relatively unchanged, providing further evidence of the stability of the TiN nanoparticles during the reaction. In contrast, the Cl 2p spectra of the illuminated and dark samples shown in Figure 5.4e,f differ considerably. While there is no chlorine signature in the spectrum of the illuminated sample (Figure 5.4e), doublets attributed to Pt-Cl bonds do appear in the control (Figure 5.4f). This result further strengthens the working hypothesis, which states that the TiN plasmon, excited with vis-NIR radiation, contributes with hot electrons towards the full reduction of \( \text{H}_2\text{PtCl}_6 \). To discard the possibility of direct photodecomposition of \( \text{H}_2\text{PtCl}_6 \), we acquired the absorbance spectrum of the precursor solution (Figure 5.8). There is negligible light absorbance of the precursor between 600 nm and 900 nm. Consequently, the photobleaching of \( \text{H}_2\text{PtCl}_6 \) cannot occur at those wavelengths.
5.3.3: Growth of Pt Nanoparticles

Some groups have reported difficulties in controlling the particle size of the reduced species in certain photodeposition experiments.\textsuperscript{49-51} For instance, in the case of Pt
photodeposition on TiO$_2$, particles and agglomerates with a broad size distribution were obtained when the pH of the solution was close to the isoelectric point of TiO$_2$ (pH = 6.25).$^{52}$ However, narrow particle size distributions, with an average size of $\sim$2 nm, have been observed when the photodeposition process takes place in acidic conditions (pH = [3.5 – 4.1]).$^{53}$ To analyze the growth and morphology of the Pt nanoparticles deposited on TiN, we performed HR TEM characterization on samples obtained at different photodeposition times (Figure 5.9). When there is no light exposure, a low-density distribution of sub nanometer spots is detected at high magnification (Figure 5.9a). It is worth noting that the visual appearance of these particles, which were immediately filtered after mixing with methanol and H$_2$PtCl$_6$, is very similar to that of the control sample that was filtered after 6 hours of mixing with methanol and H$_2$PtCl$_6$ without light exposure (Figure 5.5b,d). This suggests that the adsorption of the non-reduced platinum species on the TiN surface occurs within the first few minutes of interaction between TiN and the platinum precursor. After 30 minutes (Figure 5.9b) of illumination, slightly bigger features are observed. The density of such features on the surface of the TiN is also higher. A higher contrast between the small particles and the TiN is visible in Figure 5.9c, suggesting a change in density of the clusters, likely due to the formation of reduced Pt on its initial stages. After 120 minutes, lattice fringes become visible in some of the small Pt clusters (Figure 5.9d). After 360 minutes, bigger crystalline particles are observed (Figure 5.9e). The resulting particle size distribution of this sample is shown in Figure 5.9f. Most particles are within 1 and 3 nm in size. Lower magnification images are presented in Figure 5.10. Overall, the narrow distribution reported herein is in good
agreement, with references $^{52,53}$ where the authors obtained ~2 nm Pt particles photodeposited on TiO$_2$ under acidic conditions.

Figure 5.9. HR TEM micrographs of TiN nanoparticles after a) 0, b) 30, c) 60, d) 120, e) 360 minutes of Pt photodeposition. The particle size distribution of the image in e) is shown in f).
Figure 5.10: Low magnification TEM micrographs of TiN nanoparticles after a) 0, b) 30, c) 60, d) 120, e) 360 minutes of Pt photodeposition.

5.3.4: Oxidation of Methanol to CO₂

As stated in Reaction 5.2, H⁺ and CO₂ are the products of the methanol oxidation reaction and require 6 photogenerated holes to be formed. In order to ensure that methanol oxidation was coupled to Pt⁴⁺ reduction, we measured the CO₂ evolution — under illumination and in the dark — as a function of time by gas chromatography. There was a 4-fold increase in CO₂ evolution upon illumination (Figure 5.11a). The evolution of CO₂ corresponds solely to the oxidation half of the reaction. It is therefore necessary to investigate the reduction half — determined by the deposition of Pt⁰ — to get a complete perspective of the photodeposition process. To correlate the CO₂ evolution with the amount of Pt deposited, we obtained samples after 20 min, 1 h, 4 h, and 6 h of illumination and measured the Pt-to-Ti weight loading by EDX (Figure 5.11b). The
samples were carefully washed and filtered to remove excess Pt precursor. The molar Pt-to-CO\(_2\) ratio after 6 hours was 1.69±0.37. This number is in good agreement with the theoretical 3:2 ratio expected after from the charge balance of the redox reaction. To calculate this value, we used the Pt-to-Ti wt. ratio data presented in Figure 5.11b — obtained by EDX measurements— to obtain the Pt mass \(m_{Pt}\) deposited on the TiN particles with simple arithmetic based on the molecular weight of TiN and Ti. The final equation used to calculate \(m_{Pt}\) deposited after 6 hours is:

\[
m_{Pt} = f_{Pt-Ti}m_{Ti} \quad (5.3)
\]

\[
m_{Pt} = f_{Pt-Ti}m_{TiN} \left(\frac{MW_{Ti}}{MW_{TiN}}\right) \quad (5.4)
\]

Where \(f_{Pt-Ti}\), \(m_{Ti}\), \(m_{TiN}\), \(MW_{Ti}\), and \(MW_{TiN}\) are the Pt-to-Ti ratio as measured from EDX, the TiN mass, the Ti mass, the molecular weight of Ti, and the molecular weight of TiN, respectively. For the TiN loading used in all the experiments (1.7 mg), \(m_{Pt}\) after 6 hours is 0.55 mg, which corresponds to 2.85 µmol of Pt. This value was later adjusted by the optical length of the reactor to be 7.09 µmol. As stated in section 5.2.5, the CO\(_2\) evolution was initially measured by injecting 1 mL of gas extracted from the reactor. This amount is normalized by the volume of the syringe (1 mL) and therefore has to be multiplied by the volume of the reactor that remains in the gas phase (\(V_g = 31.7 \text{ cm}^3\)) to obtain the total CO\(_2\) evolution. The photo-induced CO\(_2\) evolution was then obtained by subtracting the value from the control measurement to that of the experiment. After 6
hours, the photo-induced CO\textsubscript{2} evolution was 4.18 \(\mu\text{mol}\). The resulting Pt-to-CO\textsubscript{2} ratio is 1.69. Based on the EDX error data, we estimate an error of \(\pm 0.37\).

**Figure 5.11.** a) CO\textsubscript{2} evolution is significantly higher under illumination. The production declines at increasing times. b) The Pt-Ti wt. ratio has a similar behavior to the CO\textsubscript{2} evolution rate, demonstrating the interrelation of both processes linked by the electron-hole pair generation from the plasmon decay at the TiN surface. c) Vis-NIR spectra of TiN particles before and after the Pt photodeposition experiment. Increasing deposition of Pt results in the damping of the TiN plasmon. d) Plasmon broadening of the spectra at longer reaction times.

At longer reaction times, both the CO\textsubscript{2} and Pt production rates diminished considerably. We hypothesize that this is a result of the interfacial damping of the plasmon caused by the increasing Pt deposited at the TiN surface. The high optical losses
of Pt at the illumination wavelengths, defined by the imaginary part of the dielectric function $\varepsilon(\text{Im})$ (Figure 5.12), cause a decrease of the plasmon dephasing time $t$, which is inversely proportional to the plasmon bandwidth $\Gamma$ through the relation $t = \hbar/\pi\Gamma$, where $\hbar$ is the Planck constant.$^{2,54-56}$ An evident quenching of the TiN plasmonic band is observed after Pt photodeposition (Figure 11c). Additional spectra obtained at different reaction times (shown in Figure 5.13 and normalized to the intensity at 400 nm for clarity) were analyzed by fitting them to a bi-gaussian model to make up for their asymmetric nature (Figure 5.14). Figure 5.11d shows the change in peak width of the TiN plasmon peak during the photoplating reaction. An increase of $\Gamma$ at longer reaction times provides evidence of the shortening of the dephasing time. As more Pt is deposited at the TiN surface, interfacial damping becomes more predominant and impedes the effective reduction of the platinum precursor and the oxidation of methanol. We should also mention that we have performed finite-difference time-domain (FDTD) calculation for TiN nanoparticles using standard and widely utilized software (Lumerical) and have found that, in agreement with previous studies,$^{18}$ the extinction spectra are dominated by absorption, with negligible contribution from scattering (Figure 5.15).
Figure 5.12: Imaginary part of dielectric function of TiN and Pt as a function of wavelength. Red rectangle indicates the illumination band used during the experiment. Optical losses of Pt shorten the dephasing time of the TiN plasmon, resulting in the gradual decrease of photoactivity with increasing Pt deposition at the TiN surface.

Figure 5.13: Normalized extinction spectra of TiN nanoparticles as a function of Pt photodeposition time. The plasmon resonance of TiN nanoparticles with higher Pt photodeposition show a quenching of the LSPR. The spectra were normalized to the extinction at the transition from visible to UV light.
Figure 5.14: FWHM of extinction spectra as a function of Pt photodeposition time. Normalized TiN spectra from Figure 5.13 before (0 min) and after 20 min, 60 min, 240 min, and 360 min of Pt photoplating. A bi-gaussian model was used to fit the asymmetric TiN plasmon, which is a result of certain degree of variation in size and additional interparticle-related effects within the ensemble of particles. The FWHM values obtained from the model were used to show a qualitative analysis of the plasmon damping due to increasing Pt at the TiN surface.

Figure 5.15: Absorption and scattering cross section of TiN nanoparticles obtained by FDTD simulations. FDTD simulations of 10 nm TiN nanoparticles show that most of the extinction spectrum is dominated by absorption, while light scattering remains negligible at vis-NIR wavelengths.
We have calculated the quantum yield of the reaction by obtaining both the photon flux of the incident light and the photodeposition rate as per the work of Li et. al.:

\[
\text{quantum yield } \left( \frac{\text{molecules}}{\text{photon}} \right) = \frac{\text{photodeposition rate } \left( \frac{\text{molecules}}{s} \right)}{\text{absorbed photon flux } \left( \frac{\text{photons}}{s} \right)} \tag{5.5}
\]

The resulting quantum yield of the reaction was 0.0024%. To calculate this value, we measured the light intensity \( I_L \) at the reactor position with an optical power meter (~335 mW/cm\(^2\)). However, due to the relatively low concentration of the solution, not all the power is absorbed and is instead reflected back outside of the reactor window. To estimate the power absorbed by the TiN nanoparticles, we first calculated the wavelength-dependent molar extinction coefficient \( \varepsilon(\lambda) \) based on the Beer-Lambert law for a sample in a 1 cm cuvette.

\[
\varepsilon(\lambda) = \frac{A_1(\lambda)}{bc} \tag{5.6}
\]

Where \( c \) is the sample concentration and \( A_1(\lambda) \) is the wavelength-dependent absorbance for a path length of \( b = 1 \) cm. We then used \( \varepsilon(\lambda) \), a property intrinsic of the sample, and calculated a new value of absorbance \( A_2(\lambda) \) for a path length of 12.4 cm, given by \( 2d \) — where \( d \) is the diameter of the reactor — and defined as the distance travelled by the light inside the reactor.
Finally, we again invoked the Beer-Lambert law to calculate the percentage of power reflected ($I_R$):

$$T\% = \frac{I_R}{I_L} = 10^{-A_2(\lambda)} \times 100 \quad (5.8)$$

Where $T\%$ is the percentage of light transmitted (14.8 %). The approximate absorbed light intensity $I_A = I_L - I_R$ is therefore 285 mW/cm$^2$.

To obtain the power input $P$, we multiplied $I_A$ by the area of the quartz window of the reactor (35 mm diameter). We then calculated the photon flux with:

$$P = f\hbar\nu \quad (5.9)$$

Where $P$ is the total power provided into the reactor, $f$ is the photon flux, $\hbar$ is the Planck’s constant, and $\nu$ is the average frequency of the incident photons (4.16e5 GHz). The latter value was obtained from integrating the spectrum of the lamp after filtering (Figure 5.2). The photon flux was $1.918 \times 10^{19}$ photons/s. The initial photo-induced CO$_2$ evolution rate was calculated based on the first 3 data points of the CO$_2$ evolution curves (Figure 5.16). The rate in the dark was subtracted from the rate under illumination. The photoinduced
rate was $2.406 \times 10^{14}$ CO$_2$ molecules/s. We finally obtained a QY of 0.0024 % by applying Equation 5.5.

![Graph showing photodeposition rate of CO$_2$.](image)

**Figure 5.16**: Initial photodeposition rate of the reaction. To calculate the photodeposition rate of CO$_2$ we obtained the slopes of the red (under illumination) and black (in the dark) lines and subtracted the rate of the control sample to the rate of the sample exposed to the visible light.

While low quantum yields have also been reported for similar structures, such as in the case of hydrogen evolution from plasmonically excited gold nanorods,$^{58}$ such low QY underscores the need for a better understanding of plasmon-driven photochemistry in alternative plasmonic materials. The reduction potential of Pt$^{4+}$ is around 0.75 V with respect of the Standard Hydrogen Electron (SHE), corresponding to 5.2 V to vacuum. The low efficiency of the photo-reduction process suggests that only a small fraction of hot electrons generated in TiN may be sufficiently energetic to drive the reaction. Atomistic simulations have been performed to provide additional insights with that respect.
5.3.5: DFT Calculations

DFT calculations have been performed on a 6-layer thick slab of TiN(111) with another 6-layer thick slab of Pt(111) on top of it. Figure 5.17a shows the atomic structure of the simulated interface. Figure 5.17b depicts charge-density difference maps between the Pt and the TiN surfaces. Specifically, the purple-colored surfaces denote areas that have gained electrons, and the green-colored surfaces represent areas with depletion of electron density. Upon convergence, we find that electron density is depleted from the Pt interface, which is concomitantly gained by the TiN interface. Thus, we conclude that at the interface there is a charge transfer from the Pt to the TiN. We have also calculated the work-functions for the 111 faces of the TiN and Pt and found them to be 5.86 and 5.23 eV, respectively. These calculations suggest that hot electron transfer from TiN to Pt is possible for sufficiently energetic carriers, but an energy barrier nevertheless exists. In addition, as the photodeposition proceeds, the enhanced dephasing rate (see Figure 5.11d) is likely going to result in less energetic carriers. This is consistent with an increasingly reduced rate of electron transfer to Pt and the experimental observation of a self-limiting process. We stress that the calculated work function for Pt(111) is close to experimentally reported values.\textsuperscript{59,60} There is substantially less experimental data on the work function of TiN(111), with one study on a sputtered sample reporting values between 4.5 eV and 5 eV,\textsuperscript{61} and another reporting values even lower than 4 eV.\textsuperscript{62} These are significantly lower than what we find via DFT. A more careful investigation of the electronic structure of TiN is necessary to engineer effective interfaces with other catalysts and fully exploit its potential as a photoactive material.
Figure 5.17. a) Resulting Ti(111)-Pt(111) interface after DFT simulations. b) Charge transfer from Pt to N (of TiN) at the interface. Green lobes represent a loss in electron density, and purple lobes represent a gain in electron density. An iso-value of 0.01 eÅ^{-3} was used.

5.4: Conclusion

In summary, we have used TiN nanoparticles to drive the photoplating of Pt via plasmon excitation with vis-NIR (600-900 nm) radiation. TEM, HAADF-STEM, EDX, and XPS analyses conclusively show that, after illumination, metallic platinum nanoparticles are deposited at the TiN surface. CO$_2$ evolution measurements associated with hole-mediated methanol oxidation show a significant increase upon light excitation. The molar Pt-to-CO$_2$ ratio after 6 hours of illumination is in excellent agreement with the charge balance of both the Pt reduction and methanol oxidation reactions. The Pt$^0$ and
CO₂ production declines at longer reaction times. The high optical losses of Pt at vis-NIR wavelengths cause an interfacial plasmon damping effect. In addition, DFT calculations suggest the presence of a significant energy barrier at the TiN-Pt interface. This results in an overall low quantum yield and in a self-limiting photo-reduction reaction. To conclude, this work expands the prospects of TiN as viable alternative to gold and silver but also highlights areas that require further consideration for this system. Access to alternative plasmonic materials with higher energy plasmon, such as zirconium nitride, and a deeper understanding of the electronic structure of these materials are necessary for advancements in this area.
5.5: References


Chapter 6: Enhanced Optical Properties of TiN Achieved with a SiO$_x$N$_y$ Protective Coating

6.1: Introduction

In Chapter 4, a non-thermal plasma method was introduced as a means to synthesize crystalline TiN nanoparticles. It was observed that the oxidation content in the material is influential on the LSPR peak position and intensity. Chapter 5 demonstrates a photochemical reaction directly induced by the plasmonic effect of TiN nanocrystals. However, it was also observed that the reduction of platinum is a self-terminating reaction resulting from unfavorable energetics at the TiN-Pt interface. This chapter culminates the body of work on TiN by addressing the oxidation issues presented in Chapter 4 and complementing the study of the optical properties of TiN under high temperature conditions.

Given the oxidation mechanisms reported in Chapter 4, where the oxygen in the ambient diffuses from the surface to the core of the nanoparticles, it was hypothesized that a layer of a different material around the nanoparticles would act as a diffusive barrier against the oxidation of plasmonic TiN. To achieve this, a secondary reactor was added to the non-thermal plasma system presented in Chapter 4 (Figure 4.1). SiH$_4$ gas was introduced through an independent line into the new module to coat the TiN particles synthesized in the first reactor with a silicon nitride (Si$_3$N$_4$) layer. Upon exposure to air, the silicon nitride reacts with oxygen to form a SiO$_x$N$_y$. Characterization of the resulting powder showed that the oxidation degree of TiN decreased, and that the optical properties of the particles were enhanced. Extinction measurements show a 60% increase of the
absorption and scattering capabilities of TiN-SiO$_x$N$_y$ over TiN. High temperature measurements in air show that, after a 300 °C annealing step, the ~10 nm TiN-SiO$_x$N$_y$ particles still conserve a fraction of their plasmonic properties, whereas the plasmon peak of the uncoated particles fades completely. Emissivity measurements of the TiN-SiO$_x$N$_y$ particles under vacuum show a higher temperature resistance over the bare TiN. The optical properties of the powder remain stable at 700 °C. Interestingly, the emissivity of the material increases with temperature. These results may represent an advance in the field of thermophotovoltaics, where selective emitters of visible light are used with the goal of increasing the efficiency of regular solar cells, which are naturally limited by the black body spectrum of the Sun.$^{1,2}$ The experimental data was corroborated by finite-difference time-domain (FDTD) simulations, demonstrated a strong dependence between the plasmon peak position and the degree of oxidation of the active material. Overall, this chapter addresses two important issues of oxidation of TiN depicted in Chapter 4 by introducing a SiO$_x$N$_y$ diffusion barrier. In addition, high temperature extinction and emissivity measurements show a substantial improvement in thermal stability of the core-shell heterostructures as compared with the bare TiN particles. The results are promising for various high-temperature applications such as solar thermophotovoltaics and thermoplasmonics.$^{1-3}$
6.2: Materials and Methods

6.2.1: Synthesis of TiN-SiO$_x$N$_y$ core-shell heterostructures

A simple schematic of the apparatus is shown in Figure 6.1. The synthesis of TiN nanoparticles takes place in the first reactor, where TiCl$_4$ and NH$_3$ are used as precursor gases. The power is maintained at 180 W with a 13.56 MHz RF power supply. The resulting TiN nanoparticles are then transported to a secondary reactor, where SiH$_4$ gas is introduced as a new precursor. SiH$_4$ and the remaining NH$_3$ that was left out from the first stage react to form a Si$_3$N$_4$ layer around the TiN. The power in the secondary reactor is 20 W and is also sustained with a RF power supply. The rationale for such low power is to prevent the nucleation and growth of isolated silicon nanoparticles. The powder is collected downstream of the second reactor on a stainless-steel mesh filter.

Figure 6.1. Schematic of the modular non-thermal plasma reactor. TiN nanoparticles nucleate and grow in the first stage. A Si$_3$N$_4$ layer is added in the second stage. The Si$_3$N$_4$ eventually converts to SiO$_x$N$_y$ after the powder is exposed to air.
6.2.2: Characterization of TiN-SiO$_x$N$_y$ heterostructures

High resolution TEM (HR TEM) and STEM images were obtained with a FEI Titan Themis 300 instrument with energy dispersive X-ray spectroscopy (EDX) capability for elemental mapping. Lower magnification images were obtained on a Tecnai 12 TEM. XPS characterization was carried out on a Kratos AXIS ULTRA$^{\text{DLG}}$ XPS system equipped with an Al K(\alpha) monochromated X-ray source and a 165-mm mean radius electron energy hemispherical analyzer. Vacuum pressure was kept below $3 \times 10^{-9}$ Torr during acquisition. A 3 kV Ar-ion beam was used to sputter the particles’ surface. Extinction measurements were performed on a Varian Carry 500 UV-vis-NIR spectrophotometer. Samples were prepared by diluting in DI water and transferred to a 1 cm x 1 cm quartz cuvette.

6.2.3: Finite-Difference Time-Domain (FDTD) simulations

Optical spectra of the bare TiN, Pt, and TiN-Pt samples were obtained with the FDTD method for solving the Maxwell’s equations. The software FDTD Solutions (v8.20), from Lumerical, Inc. was employed. The TiN particles were simulated as 10 nm x 10 nm x 10 nm cubes given the appearance of such shapes in the experimental data of this and other reports on TiN nanoparticles. To simulate various oxide compositions, the Maxwell-Garnett model was used to introduce a homogeneous mixture of TiO$_2$ inclusions into a TiN matrix.$^4$ It has previously been demonstrated that oxidation is an influential factor in the plasmonic response of TiN nanoparticles. To simulate the effects of Si$_3$N$_4$ thickness on the optical properties of TiN, rectangular slabs of Si$_3$N$_4$ were added around the TiN cubes. The optical constants of TiO$_2$, TiN, and Si$_3$N$_4$ were obtained from
the materials database of Palik. Total-field/scatter-field light source conditions were used in all simulations. The illumination wavelengths ranged from 1350 nm to 300 nm. The incident light was injected towards the y+ direction. The mesh step was 0.25 nm and remained uniform for all simulations.

6.2.4: Emissivity Measurements

An apparatus depicted in Figure 6.2 was used to measure the emissivity of the TiN and TiN-SiOₓNᵧ nanoparticles. The samples were introduced in a high temperature chamber with three KBr windows within a Praying Mantis (Harrick Scientific) diffuse reflectance accessory. The system remained under vacuum with a 70 sccm flow of ultra-high purity argon gas. A Thor Labs white light source was directed through one of the windows of the temperature chamber and focused onto the sample with the planar and ellipsoidal mirrors of the Praying Mantis accessory. The light was reflected outside of the chamber and directed from the Praying Mantis into an Ocean Optics USB4000 spectrometer. A background reflectivity measurement of a stainless-steel substrate with a polished face was acquired first. Afterwards, the reflectivity of the stainless-steel substrate, coated with the sample powder, was obtained. The ratios at various temperatures of both signals—the coated substrate and the bare substrate—were calculated to account for the reflectivity of the nanoparticles. Assuming a uniform nanoparticle coating, it is then possible to obtain the emissivity of the material according to Kirchoff’s Law:

\[ \epsilon(\lambda) = \alpha(\lambda) = 1 - \rho(\lambda) - \tau(\lambda) \ldots (6.1) \]
Where \( \varepsilon \) is the emissivity, \( \alpha \) is the absorptivity, \( \rho \) is the reflectivity, and \( \tau \) is the transmittivity of the coating.

**Figure 6.2.** Schematic of emissivity measurement apparatus.

### 6.3: Results and Discussion

#### 6.3.1: TEM/STEM of bare TiN and TiN-SiO\(_x\)N\(_y\) nanoparticles

Figure 6.3 shows low and high magnification TEM images of bare (Figure 6.3a and b) and coated (Figure 6.3c and d) nanoparticles. There are no major changes other than the appearance of a ~2 nm layer around the TiN. Lattice fringes are visible in the core material in Figure 6.3d, whereas the coating at the absence of any ordered structure at the peripheral layer suggests that the coating is amorphous. HAADF mapping images of TiN particles with and without the coating are shown in Figure 6.4. The TiN signal
(red) appears to be homogenously mixed with the oxygen signal (green) for the case of bare TiN samples (Figure 6.4b). However, for the TiN-SiO$_x$N$_y$ samples, there is evidence of higher oxygen concentrations at the periphery of the heterostructures (Figure 6.4d). This suggests that the protective layer is indeed preventing further diffusion of oxygen into the center of the nanostructure, where the active material resides.

Figure 6.3. TEM images of bare (a,b) and SiO$_x$N$_y$-coated (c,d) TiN nanoparticles.
6.3.2: Extinction spectra of bare TiN and TiN-SiO$_x$N$_y$ nanoparticles

As stated previously, it is hypothesized that, if oxygen is absent from the active material, the plasmonic performance of the coated particles will see an improvement compared to that of bare TiN. To demonstrate this, the extinction spectra of TiN and TiN-
SiO$_x$N$_y$ samples is presented in Figure 6.5. The processing conditions in the first reactor remained unaffected, and the only difference was the addition of the protective SiO$_x$N$_y$ layer. The plasmon peak on the extinction spectrum of the TiN sample is less pronounced, whereas the plasmon peak intensity of the coated material experiences 60% increase in intensity and a blue-shift from ~800 nm to ~680 nm. To test the thermal stability of the samples, they were subjected to an annealing process in air. Their extinction spectra were measured after 1 hour annealing at various temperatures. Despite observing a decrease in the plasmon peak intensity, the TiN-SiO$_x$N$_y$ still maintains a LSPR band after annealing at 300 °C, whereas the TiN sample loses its peak completely at 250 °C. These measurements show that the protective coating raises the prospects of the material’s performance at higher temperatures, and therefore opens the door to a variety of applications in harsh environments.
Figure 6.5. a) Normalized extinction of bare and coated nanoparticles. b) Normalized extinction of TiN-SiOₓNᵧ nanoparticles after an air annealing process at increasing temperatures. c) Normalized extinction of bare TiN nanoparticles after an air annealing process at increasing temperatures.
6.3.3: XPS characterization of TiN and TiN-SiO$_x$N$_y$ nanoparticles

Further surface analysis of the TiN and TiN-SiO$_x$N$_y$ samples was realized by XPS characterization (Figure 6.6). Figure 6.6a shows the Ti 2p spectrum of TiN bare samples. A strong signal from oxidize TiO$_2$ can be easily identified. This is in agreement with previous measurements presented in Chapter 4. On the other hand, coated TiN-SiO$_x$N$_y$ particles have more pronounced doublets corresponding to TiN (Figure 6.6b). There are still peaks from TiO$_2$, which provides evidence that the TiN is not fully oxide free, offering further room for improvement in protection of the nanoparticles. The Si 2p spectrum of the coated particles, shows signal from a peak at ~102.5 eV. This peak can be fitted with the signature peaks from SiO$_2$ and Si$_3$N$_4$, which is in good agreement with the identification of the protective layer as an oxynitride.
Figure 6.6. Ti 2p and Si 2p XPS spectra of bare TiN (a,b) and TiN-SiO$_x$N$_y$ (c,d) nanoparticles.

6.3.4: FDTD Simulations

FDTD simulations were performed to demonstrate that the increase in extinction spectrum of the coated TiN particles occurred due to reduced oxidation (Figure 6.7). Figure 6.7a shows the absorption efficiency of bare TiN particles with different oxygen contents. Since the experimental extinction measurements are acquired from aqueous nanoparticle solutions, the dielectric constant of the surrounding medium was set to that of water. The wavelength-dependent real and imaginary dielectric constants of the oxidized TiN were calculated according to the Maxwell-Garnett model, which defines
new optical constants for a homogeneous mixture of materials with known dielectric functions:\textsuperscript{11}

\[
\epsilon_{\text{eff}} = \epsilon_h + 2f \epsilon_h \frac{\epsilon_i - \epsilon_h}{\epsilon_i + \epsilon_h - f(\epsilon_i - \epsilon_h)} \quad (6.2)
\]

Where \(\epsilon_{\text{eff}}\) is the new effective optical constant, \(\epsilon_h\) is the optical constant of a known “host” medium, \(\epsilon_i\) is the known optical constant of known “inclusions”, and \(f\) is the volume fraction taken by the inclusions in the host medium. For this case, a TiN host medium was used and different volume fractions of TiO\textsubscript{2} inclusions were added to the model. It is evident that, in good agreement with the experimental data on Chapter 4, an increase in oxidation of TiN results in a red shift and a decrease of the plasmon peak intensity. Figure 6.7b depicts the absorption efficiency of pure TiN particles with no oxygen content, but with a layer of Si\textsubscript{3}N\textsubscript{4} with various thicknesses. An increase in thickness also leads to a red shift in the plasmon peak because, from the Mie Theory’s dipole approximation, the absorption cross section of the plasmonic material is dependent on the dielectric constant of the surrounding medium,\textsuperscript{12} as depicted in Equation 1.1. Since the refractive index of Si\textsubscript{3}N\textsubscript{4} is higher than that of water, a red shift is expected.\textsuperscript{5} It is important to note, however, that the shift observed in Figure 6.7b, which occurs due to the protective coating, is less pronounced than the shift observed in Figure 6.7a, which takes place due to the oxidation of the material. Therefore, the dominating phenomenon that dictates the larger changes in optical properties is the oxidation of TiN. Since
oxidation is limited by the protective silicon nitride layer, there will be an overall blue shift as observed in the experimental data in Figure 6.6.

![Figure 6.7. FDTD simulations. a) Absorption efficiency of a 10 nm TiN nanoparticle with different degrees of oxidation. b) Absorption efficiency of pure TiN with a Si$_3$N$_4$ coating with different thicknesses.](image)

6.3.5: Emissivity measurements of TiN and TiN-SiO$_x$N$_y$ nanoparticles

To further investigate the optical properties of TiN nanoparticles at high temperature conditions, we measured the emissivity of the material. Figure 6.8 shows the emissivity of a thin coating of bare TiN particles. The emissivity of the coating decreases with increasing temperature (Figure 6.8a). At 900 °C, the emissivity takes a negative value. Given that we are directly measuring the reflectivity of the sample, i.e. the ratio of the substrate with the coating to the substrate without the coating, the interpretation of this result is that the particle coating is reflecting more light than the background itself. After going down from 900 °C to room temperature (Figure 6.8b), the feature obtained after 900 °C remains unchanged. The final visual appearance of the substrate with the coated
particles is gold-like in color. Given that the color of TiN films is gold, this suggests that the particle coating partially sintered together to form a consolidated film, which then contributed to the reflection of the light source.

Figure 6.8. Emissivity measurements of bare TiN nanoparticles at a) increasing and b) decreasing temperature.

A very different behavior was observed for the TiN-SiO$_x$N$_y$ samples (Figure 6.9). The emissivity of the material increased with increasing temperature until reaching a maximum at 700 °C (Figure 6.9a). When going down in temperature (Figure 6.9b), the emissivity goes down almost to the initial spectrum observed at room temperature. The visual appearance of the particles after the high temperature process is black. This suggests that, unlike the bare TiN samples, the TiN-SiO$_x$N$_y$ sample remains in its nanoparticle form, consequently conserving its plasmonic qualities. The increase in emissivity of visible light at high temperatures is a promising feature of TiN as a plasmonic material. Solar thermophotovoltaic applications look for materials that can selectively emit more light at energies above the bandgap of a given semiconductor and
less light at energies below it. This aims to enhance the overall efficiency of regular solar cells, which are dependent on solar spectrum governed by Planck’s black body equation.

![Graph](image)

**Figure 6.9.** Emissivity measurements of bare TiN-SiO<sub>x</sub>N<sub>y</sub> at a) increasing and b) decreasing temperature.

6.4: Conclusion

In summary, this chapter introduces a modular non-thermal plasma system with two stages. The first stage nucleates and grows TiN nanoparticles. The second stage coats the particles with a Si<sub>3</sub>N<sub>4</sub> layer that, upon exposure to air, is oxidized into SiO<sub>x</sub>N<sub>y</sub>. The role of this layer is to work as a diffusion barrier against oxidation of TiN, which acts as the active plasmonic material. Extinction measurements show an important increase in intensity and a blue shift of the plasmon peak of the TiN-SiO<sub>x</sub>N<sub>y</sub> particles. XPS and HAADF-STEM data show a decrease in oxygen content at the TiN core compared to the bare TiN. The optical properties observed experimentally were corroborated by FDTD simulations. Finally, emissivity measurements show an increase in emissivity with increasing temperatures on the TiN-SiO<sub>x</sub>N<sub>y</sub> particles. These results show the promising
outlook of this modular method for other material systems and highlight an enhancement of the optical properties and improved thermal stability of the TiN-SiO$_x$N$_y$ over the bare TiN, expanding the potential of this alternative plasmonic material towards more demanding applications.
6.5: References


(12) Link, S.; El-Sayed, M. A. Shape and Size Dependence of Radiative, Non-
Chapter 7: General Conclusions and Outlook

The work presented in this dissertation is a comprehensive investigation of the properties of three material systems that have been previously proposed as potential alternatives to consolidated technologies for energy applications. CZTS is a potential replacement of CdTe and CIGS in thin film PV. Silicon-Carbon composites have been mentioned as possible alternative to graphite anodes in lithium ion batteries. The plasmonic properties of titanium nitride nanoparticles make this material a strong candidate that could replace the costly and thermally unstable gold and silver in various applications.

Chapter 2 shows an in-depth study of the role of sulfurization pressure in the final composition of CZTS films as well as a new EDS and Raman characterization procedure that reveals grain-to-grain phase segregation and differences in composition. The results presented here provide important answers to why CZTS films have been underperforming against CIGS, which has the same crystal structure but has reported higher efficiencies. One assessment derived from this work is that there are major complications controlling the final composition of the film. This may be due to the narrow window at which pure CZTS can be synthesized without also generating undesired secondary phases. Another issue is related to the way the community has been characterizing CZTS films. The lack of localized characterization methods results in imprecise results and erroneous conclusions. To address this problem, it is necessary for researchers in the field to reach a consensus on the most promising synthesis methods and develop precise techniques with quality control over the final composition of the films. In
addition, it is crucial to improve characterization methods in order to better understand the underlying causes of the low efficiency of this material.

Chapter 3 presents a novel non-thermal plasma method and CVD technique to synthesize Si-C core-shell structures as base material for lithium ion battery anodes. The results show that this synthesis process is superior to other approaches that previously used different carbon precursor. There is good control in carbon deposition and in the size of the silicon nanoparticles. Results on the nanoparticle performance highlight the potential of this architecture and synthesis method. Further work is encouraged towards a better understanding of the carbon shell structure and thickness role on the battery performance. How much better is it to have a graphitized carbon shell over one with amorphous carbon? What is the optimal thickness of the coating that lead to the best specific capacity and stability of the battery? Does graphitized carbon also contribute as an active material in the lithiation/delithiation process?

Chapters 4, 5, and 6 are an in-depth exploration of plasmonic TiN nanoparticles. Chapter 4 introduces a non-thermal plasma synthesis method that yields crystalline TiN. It is also observed that the oxidation of the material is very influential in the optical properties of the nanoparticles. Chapter 5 explores the potential of TiN in the field of plasmonic catalysis. It shows the first direct demonstration of a light-induced reaction with TiN as an alternative to gold. Although successful in introducing a proof-of-concept, this work still underperforms in terms of efficiency and durability of the Pt reduction reaction. Chapter 6 introduces a modification on the non-thermal plasma method by adding a secondary module in the reactor to coat the TiN with a protective SiO$_x$N$_y$
barrier. This coating protects TiN from further oxidation and enhances its optical properties. The TiN-SiO$_x$N$_y$ core-shell structure also shows a better temperature resistance than bare TiN and raises the potential of this heterostructure in the field of thermophotovoltaics and thermoplasmonics. Overall the work on TiN opens the door to a variety of opportunities and challenges. Future work should be focused on acquiring better control in the particle size of TiN. A larger particle size would likely increase the absorption efficiency of the nanoparticles and also limit the oxidation of the material due to a decrease on the surface area-to-volume ratio. The introduction of an in-flight annealing reactor, similar to the one shown in Chapter 3 for the synthesis of silicon nanoparticles, could be an interesting area to explore this challenge. Given the interesting results with TiN, it is only logical to pursue similar work with other metal nitrides. Preliminary work with ZrN has already shown promise, as the optical properties of this material appear to be more favorable than those of TiN. The development of a controllable and reproducible synthesis method is a crucial and sometimes underestimated factor that could result in a faster growth of the technology. In addition, given the plethora of potential applications, collaborative research with experts in various fields is essential for the successful implementation of metal nitrides in energy-related technologies.