

Nanoparticle microstructures templated by liquid crystal phase-transition dynamics

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ABSTRACT

Liquid crystal (LC) phase transition dynamics can be used as a powerful tool to control the assembly of dispersed nanoparticles. Tailored mesogenic ligands can both enhance and tune particle dispersion in the liquid crystal phase to create liquid crystal nano-composites - a novel type of material. Soft nanocomposites have recently risen to prominence for their potential usage in a variety of industrial applications such as photovoltaics, photonic materials, and the liquid crystal laser. Our group has developed a novel phase-transition-templating process for the generation of micron-scale, vesicle-like nanoparticle shells stabilized by mesogenic ligand-ligand interactions. The mesogenic ligand's flexible arm structure enhances ligand alignment with the local LC director, providing control over the dispersion and stabilization of nanoparticles in liquid crystal phases. In this paper we explore the capsule formation process in detail, generating QD-based capsules over a surprisingly wide range of radii. We demonstrate that the initial nanoparticle concentration and cooling rate are important parameters influencing capsule size. By increasing particle concentration of nanoparticles and reducing the cooling rate we developed large shells up to 96 ± 19 μm in diameter whereas decreasing concentration and increasing the cooling rate produces shells as small as 4 ± 1 μm .

Keywords: Liquid crystals, nanocomposites, nanoparticles, quantum dots, phase transition, nematic

1. INTRODUCTION

Quantum dots, luminescent semiconductor nanocrystals, have proven useful as building blocks for numerous applications including optoelectronic devices, drug-delivery systems, and biochemical sensors¹⁻⁵. These nanocrystalline semiconductors are considered to be zero-dimensional materials and are commonly grown in an approximately spherical shape, 1-12 nm in diameter. These nanoscale dimensions give quantum dots unique size-tunable photonic properties when compared to the characteristics of the same material in bulk. Quantum dots absorb a fairly broad band of optical wavelengths, and will emit longer wavelengths in a lower energy but more defined emission band. The emitted wavelength range depends on the size of the quantum dot. This conversion efficiency in the visible spectrum arises from quantum confinement effects, a decrease in the size of nanocrystal results in an increase in the spacing between energy levels.

Closely packed assemblies of NPs can exhibit differing electronic, magnetic, and photonic properties^{6,7} when compared to those of isolated single particles. However controlling particle spacing well requires a strategy. Van der Waals attractions between bare nanoparticles can make it very difficult to control dispersion and so ligands are commonly used to both enhance dispersion in different solvents and to tune assembly with a defined inter-particle spacing.

Liquid crystal materials are ordered fluids characterized by their anisotropic properties and in this paper we focus on a strategy for particle assembly using the nematic liquid crystal phase. Molecules in the nematic phase have short-range orientational order, defined by a local director, \mathbf{c} , and no positional order. Many nematic liquid crystal materials have the ability to respond to an applied electric field and switchable electronic displays represent their primary application. However, liquid crystal science intersects the boundaries between several fundamental scientific disciplines, and has already made some very important contributions to nanoscience and nanotechnology, in particular in field of nanocomposites. Surface functionalized nanoparticles can be dispersed in liquid crystal media, creating a hybrid material that uses self-assembly to control dispersion^{8,9}. Stable dispersion over long timescales is an important goal for soft tunable photonic devices such as the liquid crystal laser. Recently, significant efforts have been devoted to developing hybrid

liquid crystal nano-composites¹⁰; materials that incorporate nanoparticles into a liquid crystal phase in a controlled fashion. By combining the switchable, fluid capabilities of liquid crystal materials with the added functionality of nanoparticles there is huge potential to create exciting multifunctional new systems. Recent studies have looked at creating stable dispersions of magnetic, metallic, and semiconductor particles in the smectic^{11,12}, nematic^{13,14}, columnar^{15,16} thermotropic phases¹⁷. The most promising of these studies include modification of surface ligands on the nanoparticle to achieve increased particle stability against precipitation¹⁸. In other work the goal has been not to produce a uniform dispersion of isolated particles in liquid crystal, but to design a system in which the particles assemble in defined clusters or three-dimensional structures.

A fundamental challenge for nanoscience is to find a way to organize different type of nanoparticles into defined distributions such as well dispersed distributions of particles in a fluid phase, closed-packed assemblies, and dynamic clusters of different particles. In a recent study, our lab developed a unique assembly method for mesogen-functionalized quantum dots using nematic liquid crystal as a host phase¹⁹. Mesogenic ligands can be used to control clustering¹⁹, dispersion stability²¹ and particle assembly at the liquid crystal transition²². In this system a liquid-crystal like ligand was attached to the QD surface and these modified particles were dispersed in the isotropic phase of a nematic liquid crystal. The resulting composite system produced remarkable vesicle-like microcapsules (micro-shells) when the liquid crystal was cooled into the nematic phase. The shells are robust and can tolerate temperatures up to 110 °C, and extraction from the liquid crystal medium¹⁹.

In this paper we explore the idea that the dynamic growth of the nematic phase can be used as a lengthscale - tunable template for the formation of defined nanoparticle-based structures such as the micro-shells. Typically a particle exhibiting homeotropic anchoring conditions (i.e. radially distributed ligands) will induce a local topological defect in the nematic phase with some elastic free energy cost. This means that nanoparticles preferentially locate in the isotropic phase under biphasic conditions (i.e. at the nematic/isotropic transition point). In this study, we take advantage of this effect to look at the effects of the nematic/isotropic phase transition dynamics on assembled microstructure size.

2. METHODS & MATERIALS

We first synthesized a rod-like mesogenic ligand (Fig. 1c) with flexible attachment arm as previously reported¹⁸ and exchanged it onto the surface of CdSe/ZnS core/shell Quantum dots (QDs) (NN Labs, 6.2 nm diameter, abs. peak 620 nm). The mesogenic ligand is expected to exhibit some alignment with the local liquid crystal director, acting as a surfactant between liquid crystal host and included nanoparticles and was previously shown to improve particle dispersion in the nematic phase at low concentrations¹⁸. The aim is to disperse these particles into the nematic liquid crystal (4-cyano-4'-pentylbiphenyl, 5CB, Sigma Aldrich) (Fig. 1b) at varying concentrations (0.075 to 0.3 wt %).

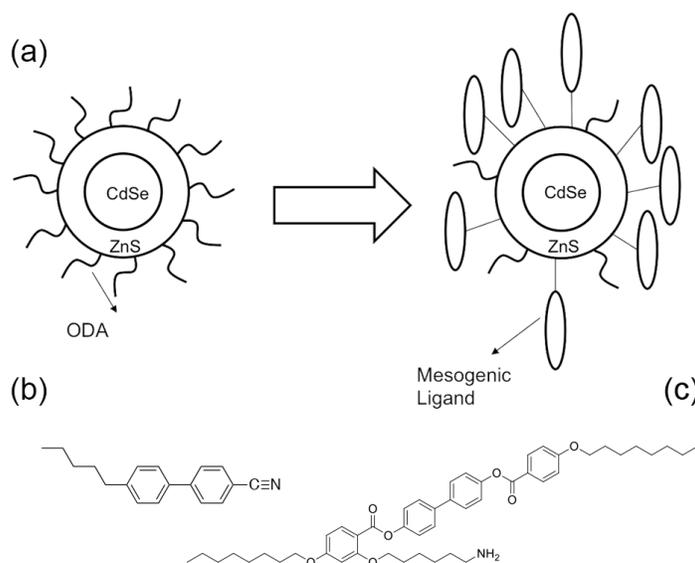


Figure 1. a) Schematic representation of non-mesogenic ODA ligands and modified surface of QDs with mesogenic and ODA ligands (LC-QDs), b) Molecular structure of 5CB (4-cyano-4'-pentylbiphenyl) and c) Molecular structure of the mesogenic ligand.

2.1 Ligand exchange

For surface modification of Octadecylamine (ODA) quantum dots, we exchanged the ODA ligand with a mesogenic ligand (to produce LC-QDs). To carry out the exchange we start with 1ml ODA quantum dot (CdSe/ZnS nanocrystal) solution in toluene (5mg/ml) and add 1ml of acetone. After mixing free unreacted ligands are removed in a washing step by centrifugation at 7000 rpm for 10 mins. The supernatant is discarded and the centrifuge step repeated to precipitate twice, each time resuspending the pellet in 1 mL acetone. After washing, the final precipitate is dissolved in 1ml chloroform and mixed with 1ml chloroform solution of mesogenic ligand for the ligand exchange. The mixture is heated to 40°C and stirred at 200 rpm for 5 hours. The mixture is then removed from the heating stage and left to cool to room temperature. Again we need to remove any free ligand so the washing process is repeated with ethyl acetate. We add 1ml ethyl acetate to the exchanged solution, centrifuge for 10min at 7000 rpm, and then wash twice by adding 1ml ethyl acetate. Finally, the precipitate is dissolved in 1ml toluene. We used ¹H NMR to quantify the ligand exchange process. ¹H NMR was recorded for the purified nanocrystals using the method described in the following section. Data is collected before and after ligand exchange to verify the completion of the reaction. Then NMR results for the ODA-QD, and the newly ligand-exchanged LC-QDs are used to calculate the ratio of mesogenic ligand to the remaining ODA ligand on the particle surface.

2.2 Liquid crystal/quantum dot mixtures

After completing and quantifying the surface modification, we proceeded to prepare the nanocomposite by mix the hard material (LC-QDs) with the soft liquid crystal host. To achieve a good initial dispersion, we take a small quantity of LC-QD in toluene and add this to 4'-pentyl'4-biphenylcarbonitrile (5CB) to produce mixtures at different LC-QD weight percentages (0.075 - 0.3 wt %). The LC/toluene/QD mixture is placed into a water bath sonicator and heated to 43°C (above the clearing point for 5CB). The mixture is sonicated for 3-8 hours to achieve a homogeneous dispersion of QDs in the isotropic LC phase and to evaporate excess toluene from the system. For low QD concentrations, below 0.1 wt %, the amount of added toluene will evaporate within 2 hours of sonication. If any toluene remains, it will lower the isotropic to nematic transition temperature, and if there is excess of toluene present, the nematic phase will no longer be present at room temperature. In general, it is important to test the transition temperature of the LC to ensure the solvent has been completely removed. Once dispersion is complete the mixture is removed from the sonicator and briefly stored in a 50°C oven.

To prepare microscope slides for observation, glass slides and cover slips are first washed with soap and water then sonicated in a progression of acetone, methanol and ethanol for 20 minutes each. Finally, the glass is blown dry with ultra high purity nitrogen. Clean glass can be prepared with an alignment layer depending on the desired orientation of the LC. For planar alignment (in which LC molecules orient parallel to the glass surface), the glass is coated with a 1wt % aqueous PVA solution for 20 minutes, dried under a nitrogen stream and subsequently rubbed uni-directionally with velvet to induce an alignment direction for the LC molecules. The material is sandwiched between a standard glass slide and we tuned the thickness of cover slip by using a polymer spacer film.

The composite material is transferred to a microscope slide at 50°C to maintain the isotropic phase then these slides are moved to a heated stage, to control the cooling rate of the slide. At 34.3°C, the transition from isotropic to nematic in the composites is present, similar to that for pure 5CB. QD dynamics can be observed using a Leica DM2500P upright microscope in epi-fluorescence mode, equipped with a Q-image Retiga camera. Luminescence of the QDs enables us to follow the movement and distribution of nanoparticles as a function of time. To provide controlled cooling in these experiments, we used a Linkham LTS350 hot stage with custom liquid nitrogen cooled-air attachment. This apparatus allowed us to observe the phase transition at 7°C/min, 15°C/min, 20°C/min, and 30°C/min.

2.3 Nuclear magnetic resonance (NMR) spectroscopy

Nuclear magnetic resonance spectroscopy (NMR) has emerged as an important tool for determining the chemical structure of organic molecules. NMR can quantitatively analyze a mixture of known compounds. There are varieties of NMR techniques that can be used for quantification of samples. For example; ¹H NMR is the most common NMR experiment that provides information about the number of protons in a sample. We performed ¹H NMR studies to quantify the ligand exchange process. Data was collected before and after ligand exchange to verify the completion of the reaction. NMR spectra for the ODA, the isolated mesogenic ligand, and the newly ligand-exchanged LC-QD were also

used to calculate the average ratio of mesogenic ligand to remaining ODA ligand on the particle surface. The mesogenic ligand was synthesized following our previous procedure¹⁹. NMR spectra were obtained in CDCl₃ solution on Agilent spectrometers, with ¹H NMR spectra obtained at 500 MHz and referenced to the residual CDCl₃ singlet at 7.26 ppm. ¹³C NMR spectra were obtained at 125 MHz and referenced to the centerline of the residual CDCl₃ triplet at 77.1 ppm. Selected spectral data were also collected for commercial ODA–QD: ¹H NMR (CDCl₃, 500 MHz) δ ; ¹³C NMR (CDCl₃, 500 MHz) δ.

As shown in figure 2: we used the triplet (CH₂ next to the amine) to obtain the ratio of mesogen:ODA on the particle surface. The CH₂ next to the amine of the free ligand has a chemical shift at 2.69 ppm in deuterated chloroform (we use deuterated solvents to prevent unwanted solvent signals). However, this chemical shift changes to 3.26 ppm when the amine is attached to the quantum dot. The CH₂ next to the amine of the commercially available ODA-QD has a chemical shift of 2.36 ppm in CDCl₃. Based on these values, after each ligand exchange, we obtained this ratio by measuring the peak height relative to a line drawn through the base of the peak.

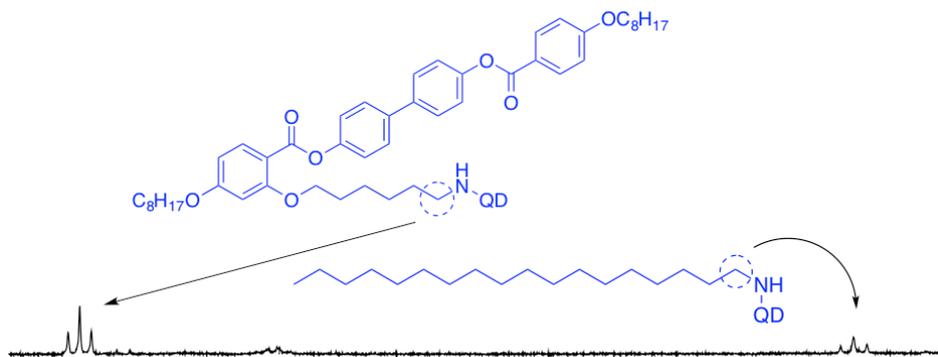


Figure 2. Overlaid ¹H NMR spectrum (500 MHz in CDCl₃) of mesogen functionalized QDs following ligand exchange at 0.4 wt. %.

One important part of this study was to investigate how the particle ligand ratio (mesogen:ODA on the surface) impacted final structure formation. To probe this effect we attempted to create particles with different ligand ratios by carrying out the ligand exchange in the presence of different ligand concentrations (0.4 – 0.05 wt%). We calculated the ratios of bound ligands by manually integrating the ¹H resonances of the triplets corresponding to the two H atoms attached to the amine-adjacent carbon atom in commercially-obtained ODA–QDs and LC–QDs (after the exchange) (Figure 2). Each ratio shown in the table represents the average of four different ligand exchanges.

Table 1 summarizes the results of this experiment. By increasing mesogen concentration during exchange, the final surface-bound ligand ratio decreased within our range of concentrations. Although we were able to coarsely tune the ligand ratio, the differences were found to have no measurable effect on the final diameter of the nano-assembled shells.

Wt% Mesogen	0.4	0.2	0.1	0.05
Mesogen : ODA	65:35	65:35	90:10	90:10

Table 1. Different average ratios of mesogen:ODA ligand bound to the QD surface for ligand exchanges performed in the presence of varying mesogen concentrations as determined by manually integrated ¹H NMR.

3. RESULTS & DISCUSSION

In the previous sections we described the synthesis of QDs functionalized with a mesogenic ligand (LC-QDs). These particles have been recently demonstrated to assemble into unique micro-capsules, or shells²², in which the rigid capsule

walls are composed of closely packed, ligand-stabilized QDs. The essential part of this process relies on the use of a nematic liquid crystal host phase. Particle assembly takes place by a Frank elasticity-induced sorting process at the isotropic to nematic phase transition¹⁹ when the system temperature falls below 34°C (Figure 3). As the initially well-dispersed composite system starts to go through the isotropic to nematic phase transition, nucleation and growth of ordered nematic domains occurs. During the transition, QDs tend to remain in the isotropic phase, expelled by growing nematic domains. These QDs are eventually pushed together at the shrinking domain interface and under the right conditions will stabilize into spherical shells.

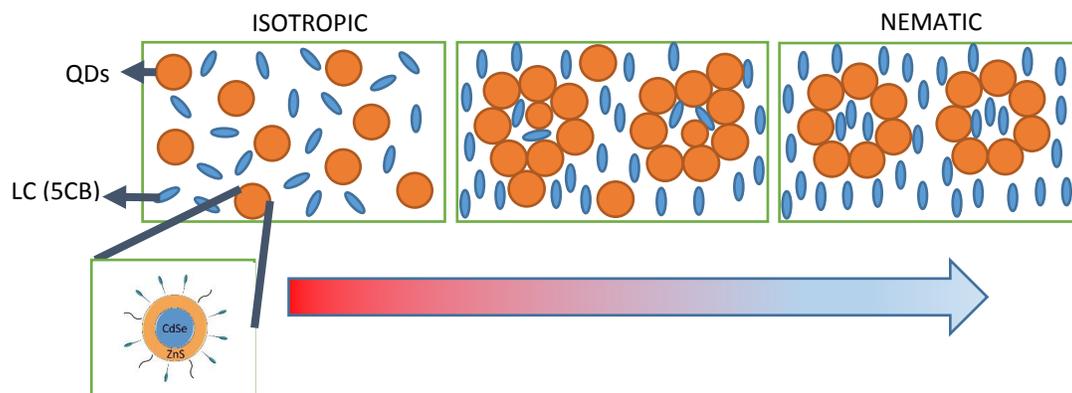


Figure 3. Diagram representing the process of nanoparticle shell formation. Particles are pushed together as they sort into shrinking nematic domains at the phase transition. The mesogenic ligands induce a short range attraction between particles, stabilizing large-scale QD structures templated by the phase interface.

In this paper we report that the size of the formed capsules can be controlled monotonically by changing two different factors, although the process seems relatively insensitive to the QD ligand ratio (Table 1). First, we increased the concentration of QDs in the host liquid crystal phase and we observed a significant increase in capsule diameter when the system was cooled through the phase transition at 200°C/min. Figure 4 shows characteristic fluorescence microscopy images of microshells formed at different QD concentrations demonstrating the size dependence, we measured shell sizes using ImageJ and found that higher concentrations of QD lead to larger shells on average. This result may be due to a jamming effect, in which the shrinking isotropic domains arrest at a certain size where the ligands can interact and form a reversible bond. Such a process should be sensitive to particle concentration at the shrinking phase interface.

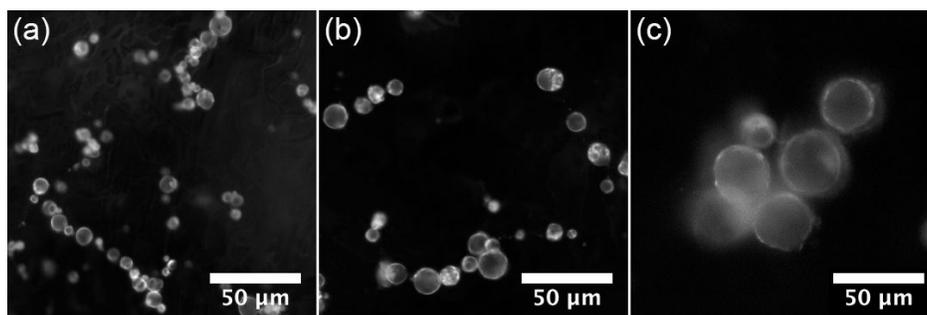


Figure 4. Fluorescence microscopy images of QD shells formed at a cooling rate of 200°C/min and three different initial QD concentrations, (a) 0.075 wt%, (b) 0.15 wt%, (c) 0.3 wt %.

Figure 5 shows representative images of microshells formed at different cooling rates, this time at a fixed particle concentration (0.3 wt%) (Figure 5). In this experiment, we observed that reducing the cooling rate through the liquid

crystal phase transition resulted in a significant size increase and we were able to form shells of very large size, up to 96 μm in diameter, as shown in Figure 5a. We observed the smallest capsules to form at fast cooling rates studied (200°C/min) and the largest structures at the slowest cooling rate of 7°C/min. Our qualitative observations of nematic phase nucleation and growth at the transition point indicate that the relationship between capsule length-scale and system cooling rate is closely related to phase transition dynamics, but this hypothesis requires further investigation.

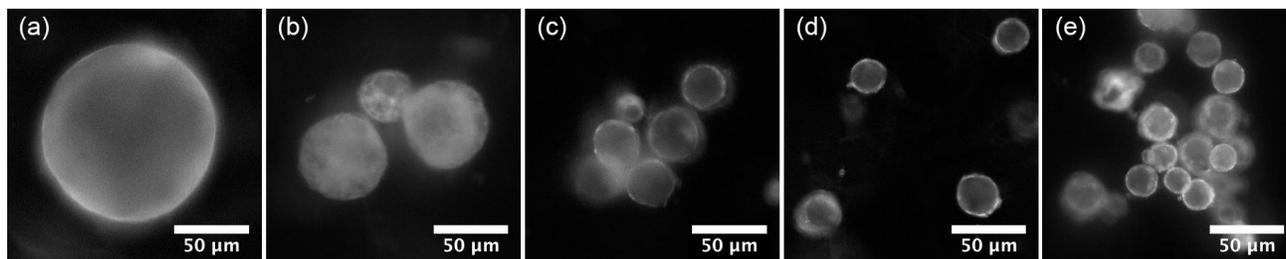


Figure 5. Fluorescence microscopy images of QD shells formed at 0.3wt% at 5 different cooling rates, (a) 7°C/min, (b) 15°C/min, (c) 20°C/min, (d) 30°C/min and (e) 200°C/min.

4. CONCLUSION

In previous work our group presented a new method to control the micro-scale assembly of nanoparticles using nematic liquid crystal as a host phase. For this purpose, we needed to modify the surface of the quantum dots with a mesogenic ligand. This step increased dispersion stabilization in the liquid crystal, while providing an attractive short-range interaction between particles. In this study, we explored the capsule formation process in more detail, including the effect of surface ligand ratios on microstructure formation. We formed QD shells over a surprisingly wide range of radii and demonstrated that initial nanoparticle concentration and cooling rate are key parameters affecting microstructure morphology. Since the particle assembly on the nanoscale can be stabilized by ligand-ligand interactions we can also hypothesize that interparticle packing with the microstructures can be controlled by varying ligand design. In future we plan to investigate the effect of different ligand designs on shell size and are also interested in using different phase transitions to generate more complex 2D and 3D liquid crystal nano-assemblies.

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