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Counterion Effects in Liquid Crystal Templating of Nanostructured CdS

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There have been several investigations on the synthesis of inorganics in molecular assemblies such as reverse micelles,[1−4] LB films,[5] vesicles,[5] and block copolymers.[6] Synthetic methodologies are also known for the formation of mesoporous materials[7,8] based on the coassembly of surfactants and ionic species. After calcination these lead to the formation of mesoporous oxides[9−11] or nonoxides such as SnS_2.[12] Typically, such mesoporous solids have periodic nanometer scale pores, and the mechanism of their formation involves a dynamic coassembly process of electrostatic charge matching in solution between ionic surfactants and precursors to inorganic solids.

In contrast, we reported recently on the synthesis of nanostructured CdS templated directly with ion-doped liquid crystals.[13,14] In both cases the mesoporous solid copied the symmetry and dimensions of its precursor mesophase. In the first case the hexagonal phase of oligoethylene oxide (10) oleyl ether doped with cadmium acetate or cadmium chloride was utilized. In the other system, nanostructured particles consisting of alternating sheets of CdS and oligomeric vinyl alcohol-based amphiphile were generated. In our present study we investigated the effect of different salt counterions on the synthesis of nanostructured CdS in a hexagonal liquid crystal. The salts studied were cadmium sulfate, cadmium perchlorate, and cadmium nitrate. In all precipitations the salt concentration was 0.1 M. In the methodology used here and in our previous work, H_2S gas diffuses into the gellike mesophase leading to the formation of nanostructured CdS (Scheme 1). After precipitation was complete, the resulting CdS−mesophase composite was washed repeatedly with diethyl ether/ethanol (50/50) to remove byproducts and unbound amphiphile. Most importantly, as evidenced by transmission electron microscopy, the periodic nanostructure is not disrupted by this procedure. This is in contrast to the synthesis of nanosized semiconductors in phase-separated copolymers,[6] which would not exist in ordered arrays after the block copolymer template is removed. The characterization techniques included optical microscopy, X-ray diffraction, transmission and scanning electron microscopies, and elemental analysis.

All ion-doped mesophases showed similar birefringent textures under the optical microscope. As shown in

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Scheme 1. Steps in the Synthesis of the Nanostructured CdS: (1) Self-Assembly of Aqueous Ionic Solution and Amphiphile into a Lyotropic Mesophase; (2) Mineralization of the Liquid Crystal Induced by Diffusion of a Gaseous Reagent (H_2S)

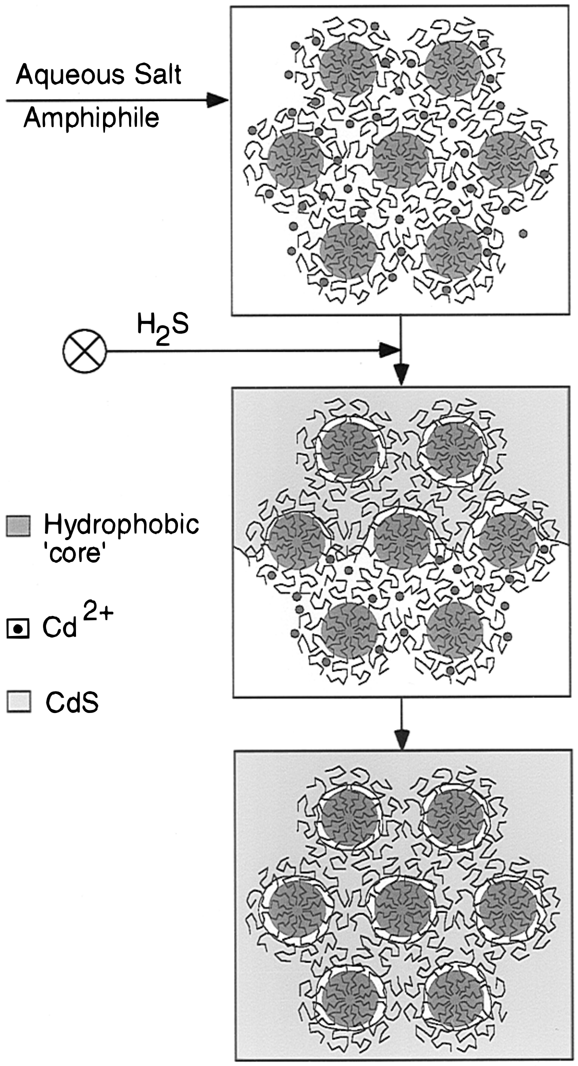

Figure 1 the isotropization temperature of the mesophase doped with 0.1 M cadmium acetate or cadmium chloride was approximately 3 °C lower than that of the undoped mesophase (77 °C). However, the graph also shows the isotropization temperature of the mesophase doped with 0.1 M cadmium nitrate dropped only by approximately 1 °C. With increasing ionic concentrations the isotropization temperatures continued to drop for all mesophases. Interestingly, doping the mesophase with 0.1 M cadmium sulfate led to a significant decrease in isotropization temperature (approximately 10 °C). On the basis of these observations we infer that acetate, chloride, and especially nitrate counterions at 0.1 M concentration do not significantly disrupt the order parameter of the mesophase. However, a significant disruption appears to occur in the presence of sulfate counterions even at 0.1 M salt concentration. In great contrast, the isotropization temperature of the mesophase doped with 0.1 M cadmium perchlorate increased by 3−4 °C, suggesting a stabilization of this hexagonal mesophase.

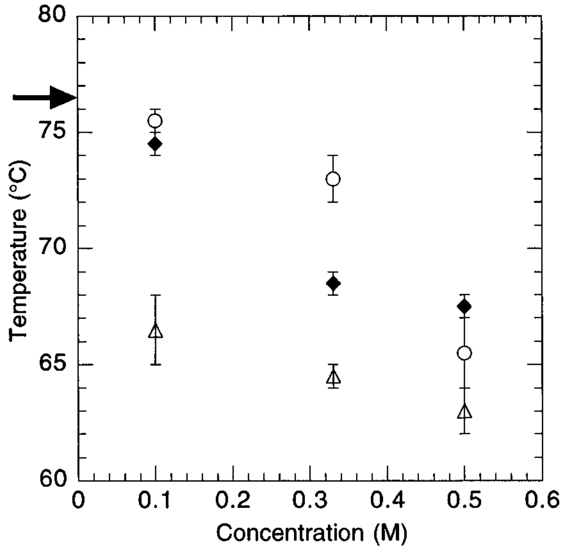

Figure 1. Graph of isotropization temperatures of hexagonal mesophases doped with various cadmium salts at different molarity concentrations (◆, cadmium acetate; ○, cadmium nitrate; △, cadmium sulfate). Arrow at left indicates the isotropization temperature of the undoped mesophase.

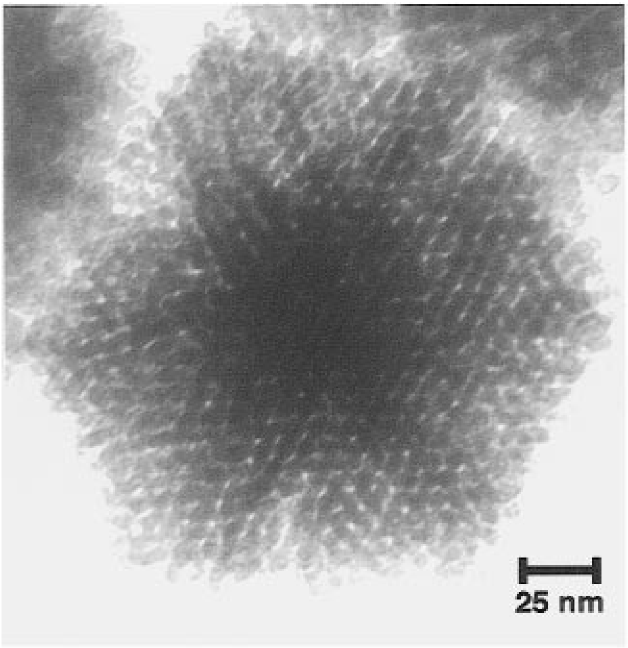

Figure 2. TEM micrograph of nanostructured CdS particle precipitated from a hexagonal mesophase template doped with cadmium nitrate. Similar order was observed in particles precipitated from cadmium perchlorate.

The CdS colloids precipitated from cadmium perchlorate and especially cadmium nitrate-doped mesophases revealed an ordered nanostructure with significantly improved definition relative to those synthesized using cadmium acetate or cadmium chloride as the ionic precursors[13] (Figures 2 and 3). In addition to the improved order and definition in the nanostructure, some CdS colloids precipitated from cadmium perchlorate and cadmium nitrate exhibited hexagonal faceting, and thus their shape also expressed the symmetry of the liquid crystal (Figure 4). On the other hand, the use of cadmium sulfate as a precursor salt did not result in CdS colloids with a regular, ordered porosity in the nanostructure (Figure 3). In all the nanostructured colloids, the array of hexagonally arranged channels corresponding to the hydrophobic domains of the oligoethylene oxide oleyl ether assemblies showed a uniform

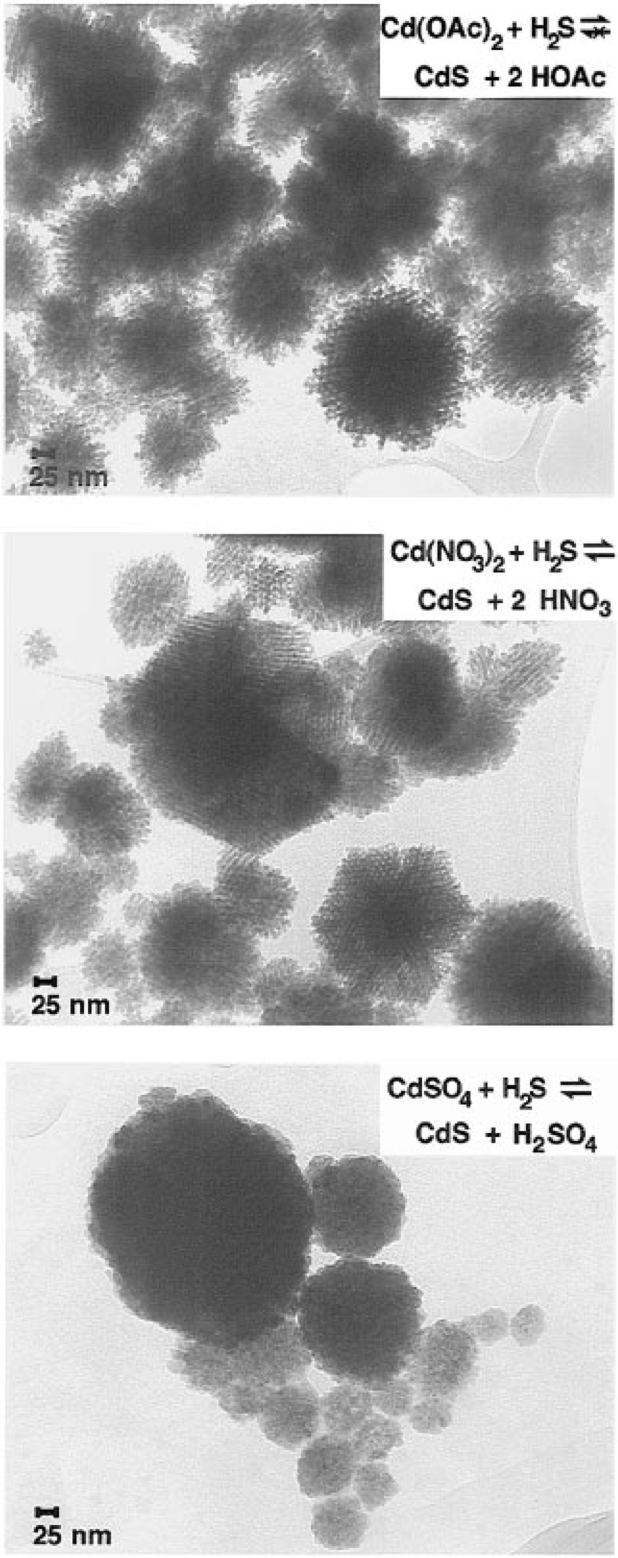

Figure 3. TEM micrographs of nanostructured CdS particles precipitated in the same liquid crystalline phase, but using different cadmium precursor salts.

intercore spacing of ~8 nm. In the case of hexagonally shaped particles the rows of channels were parallel to the particle edges, indicating the facets of the hexagonally shaped colloid match the expected lattice planes of the templating mesophase.

X-ray diffraction scans of all the doped mesophases showed the characteristic (100) and (110) reflections corresponding to a hexagonal phase. These signature peaks remained after CdS precipitation had taken place. (*d* spacings were always 65 and 36 Å.) In undoped mesophases, a weak third peak corresponding to the (200) reflection was also observed, further confirming the existence of a hexagonal phase. In all samples analyzed an intercore spacing of ~8 nm between cylindrical micelles was estimated from the diffractogram. This X-ray analysis indicates that addition of the cadmium salts used (including cadmium sulfate) does not significantly disrupt the long-range hexagonal packing of molecular assemblies before precipitation. The addition of H_2S and formation of acid byproducts do not disrupt the mesophase structure either, thus confirming its existence at all stages of CdS synthesis. Consequently, the precipitation and growth of the nanostructured CdS occurs in a preordered matrix of cylindrical micelles. Elemental analysis shows that ~1 wt % carbon (5 vol % organic) remains in the CdS colloids precipitated from cadmium nitrate after work up. This result indicates that less organic material remains in the nanostructured particles after growth relative to the cadmium acetate preparation (approximately 3 wt % carbon, 15 vol % organic).[13] The difference in carbon content can be attributed to the smaller average particle size of CdS precipitated from cadmium acetate relative to that from cadmium nitrate. As a result, more surface area is available for adsorption of amphiphile on CdS precipitated from cadmium acetate.

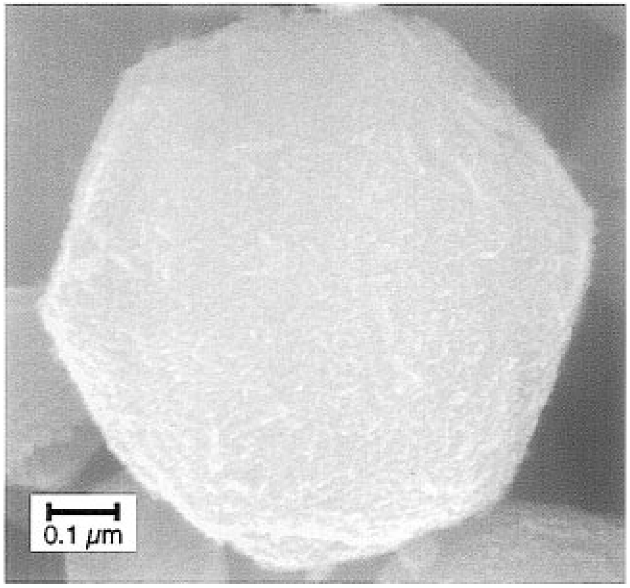

Figure 4. SEM micrograph of nanostructured CdS with hexagonal faceting precipitated from a hexagonal mesophase template doped with cadmium perchlorate.

Cadmium nitrate, cadmium perchlorate, cadmium chloride, and cadmium acetate precursors yielded CdS with the common wurtzite crystal structure[15] (Figure 5), and cadmium nitrate yielded the product with the greatest degree of crystalline order. Interestingly, X-ray diffraction scans indicate that the use of cadmium sulfate results in CdS with a cubic zinc blende crystal structure as opposed to wurtzite, which has hexagonal symmetry. All X-ray diffraction results of crystal structures reported here were confirmed by electron diffraction.

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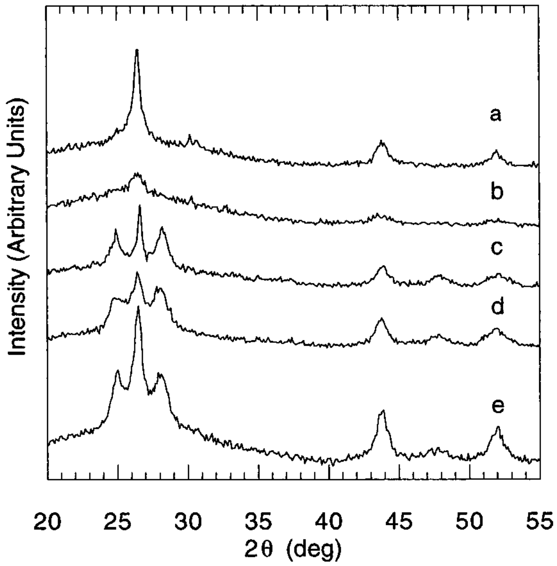

Figure 5. Powder X-ray diffraction on CdS precipitated from liquid crystals doped with different cadmium precursor salts: (a) cadmium sulfate, (b) cadmium acetate, (c) cadmium chloride, (d) cadmium perchlorate, (e) cadmium nitrate.

Our system does not rely on electrostatic charge matching between organic surfactant and inorganic precursor ions. However, we have found the chemical nature of anions in the cadmium salt does affect the stability and degree of order in the mesophase template as well as the resulting order and crystal lattice of the precipitated inorganic colloids. X-ray diffraction scans confirmed long-range hexagonal order for all the doped mesophases, yet not all resulted in hexagonally nanostructured particles. The significantly lower isotropization temperature in the case of cadmium sulfate doping suggests this salt reduces the stability of the hexagonal mesophase. To investigate the effects of mesophase stability on the resulting periodic nanostructure, precipitations were carried out at elevated temperatures (32 ± 2 and 52 ± 2 °C) using cadmium nitrate-doped mesophases. Although both temperatures are below the isotropization temperature for a 0.1 M cadmium nitrate-doped mesophase, periodic nanostructures were not observed. These results suggest the stability of the ion-doped mesophase as affected by counterion selection or temperature is an important factor in the formation of periodic nanostructures. As mentioned before, CdS grown from cadmium sulfate has a zinc blende as opposed to wurtzite structure. It is interesting that a nonperiodic nanostructure is only observed in the one preparation that yields the less common zinc blende crystal structure. We do not understand at the present time the possible links between these two observations.

Cadmium nitrate and perchlorate showed significant improvement over cadmium acetate in the structural definition of the periodic nanostructure. A factor in this difference is the stronger acidity of the byproduct for perchlorate and nitrate counterions. These acid byproducts result in dissolution of unfavorable high-energy morphologies such as small particles and nonperiodic nanostructure in which the mesoporosity of the CdS is not commensurate with the liquid crystal template. Also, these salts do not destabilize the mesophase, an important factor in the formation of periodic nanostructures. In the case of cadmium acetate there was little ripening, resulting in small particles with less periodicity. In addition to the improved periodicity, X-ray powder diffraction of cadmium nitrate-derived CdS also showed the greatest degree of crystallinity.

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