



Pergamon

Materials Research Bulletin, Vol. 34, No. 3, pp. 463–469, 1999
Copyright © 1999 Elsevier Science Ltd
Printed in the USA. All rights reserved
0025-5408/99/\$—see front matter

PII S0025-5408(99)00030-6

CdS MINERALIZATION OF HEXAGONAL, LAMELLAR, AND CUBIC LYOTROPIC LIQUID CRYSTALS

Paul V. Braun¹ and Samuel I. Stupp^{1,2*}

¹Department of Materials Science and Engineering, Beckman Institute for Advanced Science and Technology, and Materials Research Laboratory, University of Illinois Urbana-Champaign, Urbana, IL 61801, USA

²Department of Chemistry, University of Illinois Urbana-Champaign, Urbana, IL 61801, USA

(Communicated by P. Laibinis)

(Received April 2, 1997; Accepted August 14, 1998)

ABSTRACT

Growth of CdS was studied in three different liquid crystalline phases demonstrating the versatility of liquid crystal templating of inorganic solids. Semiconductor growth in a hexagonal liquid crystal yielded a nanostructure with hexagonal symmetry, a lamellar liquid crystal yielded a lamellar nanostructure, and a cubic liquid crystal (consisting of spherical micelles) yielded a hollow, spherical product. The product grown in the hexagonal liquid crystal contains rod-like pores of 3 nm diameter, spaced 8 nm apart in a hexagonal lattice. The product grown in the lamellar liquid crystal consists of CdS sheets 5 nm thick, with 2 nm spaces between layers, which presumably contain the organic template. Both these superlattices have virtually identical symmetries and characteristic dimensions as the liquid crystal in which they were formed. The mineralization of the cubic phase yielded hollow spheres of CdS, 20–100 nm in diameter, 1–5 times the diameter of the micelles making up the liquid crystal. © 1999 Elsevier Science Ltd

KEYWORDS: A. nanostructures, B. crystal growth, D. crystal structure

Invited paper presented at the Materials Research Society Symposium on Interfacial Effects and Organization of Inorganic-Organic Composite Solids, March 31–April 2, 1997, San Francisco, CA.

*To whom correspondence should be addressed. Present address: Northwestern University, Materials Science & Engineering, 2225 N. Campus Drive, Evanston, IL 60108.

INTRODUCTION

The formation of inorganic and organic nanostructures is an area of intense research [1]. Over the last 5 years researchers have engineered a variety of materials with specific nano-morphologies with the expectation of novel properties. Mesoporous ceramics [2,3], nanophase metals and ceramics [4], nanostructured organics [5], and semiconductors [6–8] are all examples of this work. Improved properties, and even new properties, ranging from mechanical [4] to waste remediation [9] have been observed for these nanomaterials. Not only are the characteristic dimensions of these systems smaller than those obtainable by lithographic techniques, but they are attainable through bulk synthesis in most cases (obviously not possible via lithography). An interesting feature in the synthesis of many of these materials is their self-assembling nature. The mesoporous ceramics, nanostructured organics, and nanostructured semiconductors all rely on the self-assembly of organic molecules to generate the desired final product. Organic systems can create nanostructures through a designed aggregation or bonding of specific molecular segments or functional groups. In some ceramics and semiconductors, on the other hand, nanostructure formation is mediated by organic templates [10]. The mesoporous ceramics form via a co-assembly process of organic and inorganic precursor, while the semiconducting systems are templated by a preformed matrix.

Mineral growth in a preformed matrix, such as a liquid crystal, offers the possibility of defining structure through control of the characteristic dimensions and symmetry of the matrix. As we have previously reported, a hexagonal liquid crystal based on oligoethylene oxide ($\overline{10}$ oleyl ether[(EO) $_{\overline{10}}$ oleyl] [6,8], and a lamellar liquid crystal formed by oligovinyl alcohol ($\overline{23}$ oleyl ester [7] have successfully templated the growth of CdS. The hexagonal liquid crystal yielded product with a hexagonal nanostructure, and the lamellar product with a lamellar structure. (EO) $_{\overline{10}}$ oleyl is also known to form a lamellar liquid crystal, which also may have the potential to template a lamellar product. The mineralization of CdS in the lamellar phase was studied in this regard. Other lyotropic phases such as a variety of bicontinuous and cubic liquid crystals [11–13], may also yield interesting mineral nanostructures. We investigated precipitation of CdS in a body centered cubic phase using as the mesogen a triblock copolymer of poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) [(EO) $_{\overline{106}}$ (PO) $_{\overline{70}}$ (EO) $_{\overline{106}}$]. When mixed with water, the PO segment is only weakly solvated, while the EO is highly solvated. As a result, when hydrated the molecule forms micelles that close pack, forming a cubic phase [14].

EXPERIMENTAL

All materials were used as received, and deionized water was used throughout. Cadmium (II) acetate dihydrate and cadmium (II) nitrate tetrahydrate were purchased from Aldrich, and H₂S gas was obtained from MG Industries and saturated with water by passing through an aerator before entering the reaction flask. (EO) $_{\overline{10}}$ oleyl was obtained courtesy of ICI, and (EO) $_{\overline{106}}$ (PO) $_{\overline{70}}$ (EO) $_{\overline{106}}$ was obtained courtesy of BASF. The mesophases were formed by mixing the amphiphile with an aqueous salt solution. The volume ratio of amphiphile to 0.1 M aqueous salt solution and amphiphile type was varied to yield the desired liquid crystal. The hexagonal liquid crystal was formed from equal volumes of aqueous solution and (EO) $_{\overline{10}}$ oleyl [15], the lamellar one from 22% aqueous solution and 78% (EO) $_{\overline{10}}$ oleyl [15], and the cubic liquid crystal from 40% aqueous

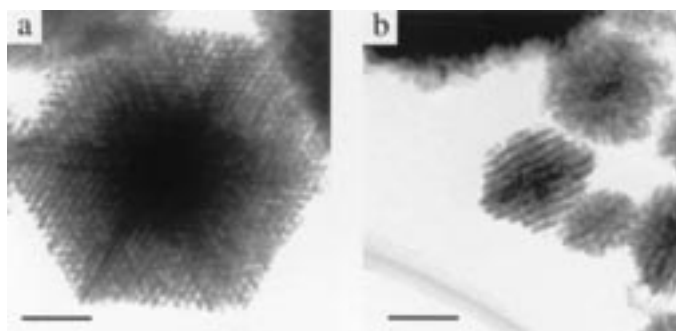


FIG. 1

TEM micrographs of CdS grown in the (a) hexagonal liquid crystal and (b) lamellar liquid crystal (bar = 50 nm).

solution and 60% $(EO)_{106}(PO)_{70}(EO)_{106}$ [14]. The $(EO)_{10}$ oleyl systems were homogenized by heating them above their isotropization temperatures ($\sim 75^{\circ}\text{C}$), mixed for a few minutes, and then allowed to cool to room temperature. The $(EO)_{106}(PO)_{70}(EO)_{106}$ system does not undergo isotropization below 100°C , so it was mechanically mixed and then left for several days to allow diffusion to complete the homogenization. Nanostructured CdS was then generated by flowing hydrated H_2S over the cadmium salt-doped liquid crystals. The resulting semiconductor-mesophase composite was washed three times by dispersing the material in a 50/50 vol% solution of diethyl ether/ethanol via sonication, followed by centrifugation and removal of the clear supernatant, thus removing reaction by-products and amphiphile.

RESULTS AND DISCUSSION

CdS growth in the hexagonal, lamellar, and cubic phases all yield interesting but widely differing nanostructures. As we have previously reported, CdS grown in the hexagonal phase very clearly exhibits a hexagonal nanostructure, which is most evident when $\text{Cd}(\text{NO}_3)_2$ is used as the dopant (Fig. 1a) [8]. The lamellar phase did not generate mineral with a superlattice structure when $\text{Cd}(\text{CH}_3\text{CO}_2)_2$ was used as the precursor salt; however, the use of the nitrate salt successfully templated a lamellar superlattice (Fig. 1b). Mineral growth in the cubic phase was performed using both the acetate and nitrate cadmium salts. The acetate salt yields hollow spheres, 20–100 nm in diameter (Figs. 2,3), while the nitrate salt only yields disordered particles. The hollow sphere morphology can be observed both by TEM and SEM. When the sample is tilted in the stage, the shape and observed structure does not change, as expected for a sphere (Fig. 2a–c). If the particles were corpuscular in shape, their appearance would change as a function of sample tilt in the microscope. The strongest evidence for their hollow nature is the dark edges of the sphere observed in TEM micrographs. If each sphere were solid, the TEM would show greater scattering from the center than the edges, making the center appear darker. In the SEM, the spheres also scatter the most electrons from their edges, and appear somewhat transparent in their centers, providing further proof of their hollow nature (Fig. 3).

From the SAXS experiments (Fig. 4), both the structure and d-spacings of each of the phases were determined. As expected, 100, 110, and 200 reflections are observed for the

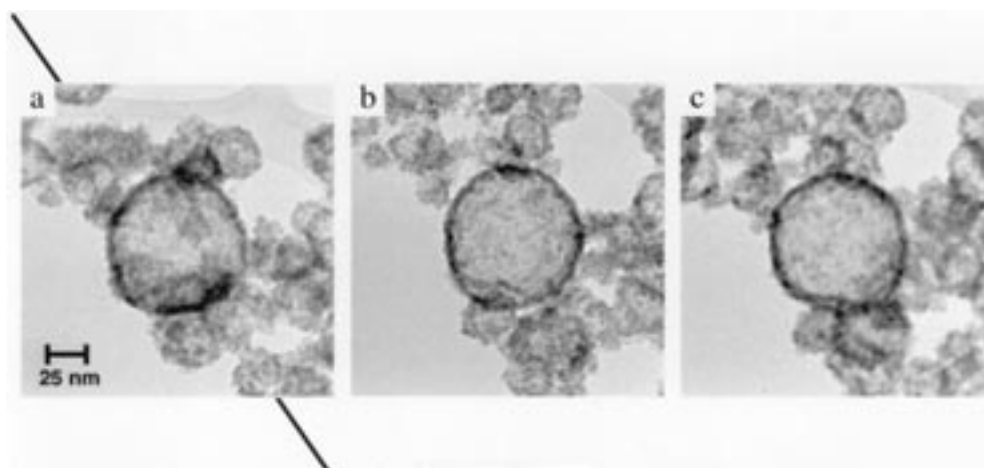


FIG. 2

TEM tilt series of the hollow CdS spheres grown in the acetate-doped cubic phase. The axis of tilt is marked with a black line: (a) -45° , (b) 0° , and (c) 45° .

hexagonal phase, 100 and 200 reflections are observed for the lamellar phase, and 110 and 200 reflections are observed for the cubic phase (indicative of a bcc structure). The lattice constants for the three phases were found to be 8 nm for the hexagonal phase, 6 nm for the lamellar phase, and 23 nm for the cubic phase. More explicitly, the hexagonal liquid crystal consists of a hexagonal array of rod-like objects containing a hydrophobic interior (oleyl) and a hydrophilic exterior (EO + H₂O). The lamellar phase consists of alternating layers of hydrophobic and hydrophilic regions while the cubic appears to be a bcc arrangement of spherical hydrophobic domains (PO) separated by a “sea” of hydrophilic. We believe the CdS

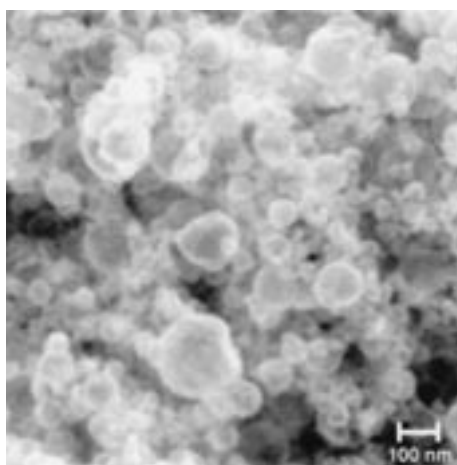


FIG. 3

SEM micrograph of CdS grown in the acetate-doped cubic phase.

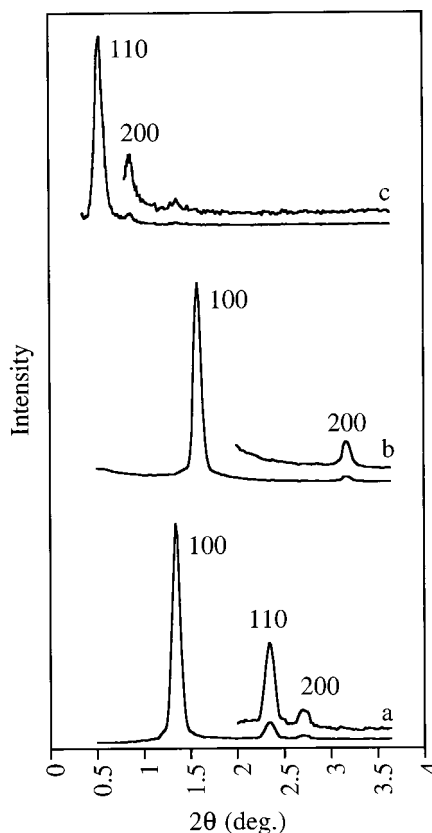


FIG. 4

SAXS data from the (a) hexagonal, (b) lamellar, and (c) cubic phases (offset is $\times 5$ for all three samples).

only grows in the hydrophilic regions of the liquid crystal, leading to the interesting nanostructures formed (the precursor salts are excluded from the hydrophobic regions). This argument explains the nanostructure obtained from the hexagonal and lamellar liquid crystals, where there is a high degree of fidelity between the CdS superlattice dimensions and the lattice of the respective liquid crystal. The hollow spheres formed by mineralization of the cubic phase could be the result of mineral growth around one or more of the micelles making up the phase. This process would in part explain their hollow morphology, as the mineralization is known to be excluded from the hydrophobic cores of the micelles.

The characteristic dimension (diameter) for hollow CdS spheres product obtained from the $\text{Cd}(\text{CH}_3\text{CO}_2)_2$ -doped cubic phase is 20–100 nm, which is 1–5 times the diameter of the micelles making up the cubic phase. It does not appear in this case the mineral nanostructure is a direct template of the liquid crystal. In addition, this nanostructure is absent from the CdS when the cubic phase is doped with $\text{Cd}(\text{NO}_3)_2$ as the precursor salt. This result is important when taken in the context of our previous results in which the use of the nitrate salt led to a nanostructure with enhanced order [8]. In essence, the use of the nitrate salt allows the

growing mineral to access a thermodynamically lower energy morphology, which is a nanostructure commensurate with the structure of the liquid crystalline matrix. The inability of the nitrate salt to “sharpen” the order in the cubic system is not surprising, because, as was observed in previous studies, the nitrate salt only improves the registry between the nanostructure and the liquid crystal and does not result in a new nanostructure. In the cubic system, the spheres are not copies of the liquid crystal; thus, there is no registry to improve. The mineralization of the cubic phase must lead to local rearrangements of the liquid crystal, causing the hollow sphere morphology observed.

A potentially significant difference between the cubic phase and the other phases studied (hexagonal and lamellar) is the connectivity of the hydrophilic and hydrophobic portions of the liquid crystal. In both the lamellar and hexagonal phases, these regions are continuous in at least one direction. In the cubic phase, however, the hydrophobic regions are confined to discrete micelles. This confinement may cause a difference in templating ability relative to the other phases. For all templating phases, as the mineral nucleates and grows, it is necessary to expel some molecules from the volume occupied by the mineral. For both the lamellar and hexagonal phases it is possible for a molecule to diffuse away from the growing mineral without ever exposing its hydrophobic (oleyl) or hydrophilic (EO) segments to domains of opposite nature. In contrast, in the cubic phase, when a molecule is forced away from the growing mineral, it must leave its micelle and expose its hydrophobic (PO) segment to the polar surroundings (EO + H₂O), a high energy situation. As already stated, the nitrate salt allows the mineral phase to access a lower energy configuration, which in the lamellar and hexagonal systems resulted in a high degree of fidelity between the template and semiconductor nanostructure. That a hollow sphere morphology is not observed in the cubic system when the nitrate salt is used is not surprising, given that both the hollow morphology is not a direct template of the liquid crystal and the formation of the spheres requires the mesophase to go through a high energy intermediate state. The spherical morphology when Cd(CH₃CO₂)₂ is used as the semiconductor precursor must be due to a subtle kinetic balance, which we do not understand at this time.

SUMMARY

Mineralization in lyotropic liquid crystals results in the formation of previously unattainable CdS nanostructures. All three morphologies observed—the hexagonal array of pores, the layers, and the hollow spheres—appear to be linked to the liquid crystalline matrix in which they were grown. The ability to define the structure of hard minerals such as a semiconductor with soft organic structures at room temperature provides a new methodology for the formation of interesting nanostructures. This strategy is a potential source of new properties using controlled syntheses.

ACKNOWLEDGMENTS

This work was supported in part by the U.S. Department of Energy, Division of Materials Science grant DEFG02-96ER45439 through the University of Illinois at Urbana-Champaign, Frederick Seitz Materials Research Laboratory. The authors acknowledge the Beckman Institute for Advanced Science and Technology for a graduate fellowship granted to P.V.B.

REFERENCES

1. *Chem. Mater.* **8**, 1569–1882 (1996) (special issue on nanostructures).
2. C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, and J.S. Beck, *Nature* **359**, 710 (1992).
3. J. Liu, A.Y. Kim, L.Q. Wang, B.J. Palmer, Y.L. Chen, P. Bruinsma, B.C. Bunker, G.J. Exarhos, G.L. Graff, P.C. Rieke, G.E. Fryxell, J.W. Virden, B.J. Tarasevich, and L.A. Chick, *Adv. Colloid Interface Sci.* **69**, 131 (1996).
4. R.W. Siegel, *Sci. Am.* **275**, 74 (1996).
5. S.I. Stupp, V. LeBonheur, K. Walker, L.S. Li, K.E. Huggins, M. Keser, and A. Amstutz, *Science* **276**, 384 (1997).
6. P.V. Braun, P. Osenar, and S.I. Stupp, *Nature* **380**, 325 (1996).
7. P. Osenar, P.V. Braun, and S.I. Stupp, *Adv. Mater.* **8**, 1022 (1996).
8. V. Tohver, P.V. Braun, M.U. Pralle, and S.I. Stupp, *Chem. Mater.* **9**, 1495 (1997).
9. X. Feng, G.E. Fryxell, Q.-L. Wang, A.Y. Kim, J. Liu, and K.M. Kemner, *Science* **276**, 923 (1997).
10. S.I. Stupp and P.V. Braun, *Science* **277**, 1242 (1997).
11. R.G. Laughlin, *The Aqueous Phase Behavior of Surfactants*, Academic Press, San Diego, CA (1994).
12. K. Fontell, *Colloid. Polym. Sci.* **268**, 264 (1990).
13. *Nonionic Surfactants, Physical Chemistry*, ed. M.J. Schick, Marcel Dekker, New York (1987).
14. G. Wanka, H. Hoffmann, and W. Ulbricht, *Macromolecules* **27**, 4145 (1994).
15. I. Lo, A.T. Florence, J.-P. Treguier, M. Seiller, and F. Puisieux, *J. Colloid Interface Sci.* **59**, 319 (1977).