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Block Copolymer-Templated Synthesis and Organization of Semiconductor Nanocrystals

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Summary: Templates formed by the self-assembly of amphiphilic block copolymers in selective solvents have been found to be instrumental in controlling critical parameters in semiconductor nanomaterials fabrication, including particle size, shape, and composition. These tunable nanoreactors exhibit rich polymorphism and have enabled the synthesis of a variety of nanostructures such as dots, wires, tubes, hollow spheres, and 2-D structures by growth-under-confinement at room temperature. The encapsulated particles have optical and electronic properties that are dependent upon physical dimensions and morphology, and exhibit inherent stability and functionalization flexibility, thus opening up promising prospects through their integration into functional optoelectronic and biological systems.

Keywords: block copolymer; nanoparticle; self-assembly; template; semiconductor

Introduction

Semiconductor crystals with sizes smaller than 10 nm, or having ~10–50 atoms along the crystal diameter, exhibit size- and shape-dependent optical and electronic properties due to discretization of the energy levels that is induced by quantum confinement effects.[1] These materials exhibit broad excitation by a wide range of wavelengths, high brightness, narrow and symmetric emission, photochemical stability, negligible photobleaching, and long fluorescence lifetime. These qualities render semiconductor nanocrystals valuable in diverse applications, such as photovoltaic devices and photodetectors, multiplexed DNA processing, and fluorescent biological labeling.

A variety of luminescent compound semiconductor nanocrystals and core-shell structures have been synthesized and functionalized following recent advances in colloidal chemistry. The most widely used synthesis technique involves particle growth and stabilization in coordination solvents that is carried out in small laboratory-scale batch reaction flasks under mechanical stirring to homogenize the solution, at rather high temperatures (around 300 °C).[2] However, in order to obtain monodisperse nanocrystal populations, instantaneous injection of the reactants, uniform nucleation over the entire mass of the coordination solvent, and perfect mixing are required. These conditions are difficult to achieve in practice, especially when processing of higher reaction volumes is desired. As a result, separation techniques are required following the synthesis, in order to narrow down the particle size distribution.[3] Furthermore, functionalization of the surface of the nanocrystals is challenging, and several post-processing steps are needed to strip out the growth capping agents and replace them with functional molecules.[4]

Nanostructured media generated by the self-assembly of amphiphilic molecules (e.g., surfactants, block copolymers) offer prescribed compartmentalization, local

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composition, local reactivity, and confinement, which confer advantages in nanomaterials synthesis and can help overcome some of the aforementioned drawbacks.[5] Monodisperse populations of typically spherical nanoparticles are being synthesized in self-assembled templates called reverse micelles or microemulsions (i.e., amphiphile-coated nanodroplets of one solvent dispersed into another, immiscible solvent). Nanoparticle synthesis in microemulsions can be classified into two types. The first is a single microemulsion type in which nanoparticles are produced by adding a reducing or precipitating agent, in the form of gas or liquid, to a microemulsion containing the primary reactant dissolved in its droplets, and the second is the double or multiple microemulsion type, in which two or more microemulsions, each containing respective reactants, are mixed together to exchange content. The microemulsion droplets undergo numerous collisions and thereby the reactants are brought into contact and react to form solid particles.[6]

In an early (1982) work on ultrafine particle synthesis in microemulsions, monodisperse Pt, Pd, Rh, and Ir particles in the 3–5 nm size range were prepared by reduction (with hydrogen or hydrazine) of metal salts dissolved in the water pools of reverse micelles.[7] Semiconductor nanoparticles were synthesized for the first time in such systems in 1984, when Aerosol-OT (AOT) water-in-isooctane reverse micelles were used to generate platinized colloidal CdS.[8] Since then, many researchers have used this methodology to synthesize and study a variety of semiconductor nanocrystals, mainly CdS, CdSe, and ZnS.[6,9] Recently, Quinlan et al.[10] expanded the technique to synthesize ZnSe nanoparticles by a reaction between zinc perchlorate hexahydrate and sodium selenide in AOT reverse micelles. Although the crystalline quality of the resulting nanocrystals was good, the particles exhibited a relatively broad size distribution as indicated by the resulting photoluminescence spectra, which is mainly attributed to inherently fast dynamics of droplet coalescence of the AOT-based microemulsions,[11] leading to droplet clusters and polydisperse particle populations.[9] These limitations prompted us to consider structured media stabilized by macromolecular amphiphiles.

We highlight here research where we employed templates formed by self-assembly of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) amphiphilic block copolymers (BCs) as confined-growth environments. These systems exhibit remarkable stability owing to slow dynamics of domain interaction, and well-defined structural order consisting of spherical, cylindrical, or planar domains. As a result, they provide superior control over size, morphology, and stability of the synthesized compound semiconductor nanostructures in the quantum confinement regime. BC-directed growth, functionalization, and spatial arrangement of a variety of nanomaterials has been recently investigated,[12–14] e.g., mesoporous materials,[15] metal nanoparticles,[16–18] CdS nanorods,[19] and polymorphic ZnSe and CdSe nanostructures.[20–23]

Results and Discussion

The reaction templates were formed following the self-assembly of PEO-PPO-PEO BCs in a mixture of solvents with different polarity. Under these circumstances, the dual affinity of the BC, consisting of polar PEO and less-polar PPO blocks, results in a variety of thermodynamically stable structures with different morphologies, including oil-in-water (''normal'') and water-in-oil (''reverse'') micelles in solution, and various normal and reverse lyotropic liquid crystals (LLCs) (micellar cubic, hexagonal, lamellar).[24–26] For synthesis of compound semiconductor (MeX, e.g., Me = Zn, Cd, Pb and X = Se, S) nanocrystals, the metal-containing compound was pre-dissolved selectively in one of the two solvents, and the group-VI precursor was fed externally into the system either in the form of a hydride gas (H_2X) or

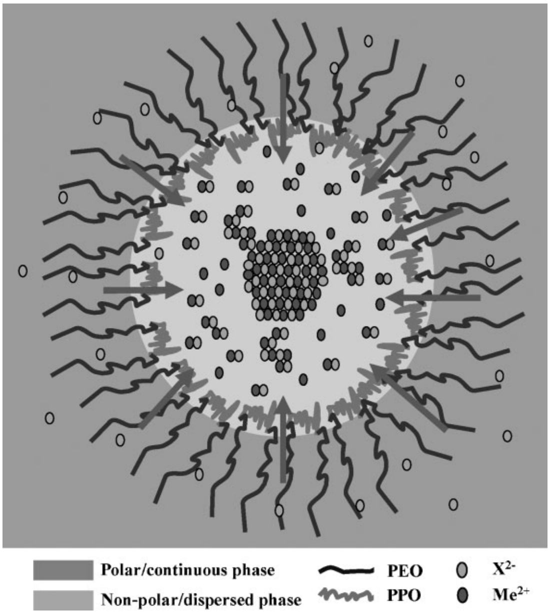

Figure 1.
Mechanism of MeX compound nanocrystal formation in a self-assembled BC domain. The gas reactant (e.g., H_2X) is fed into the system, diffuses into the domain, and reacts with the metal compound that is pre-diluted in the dispersed phase. The MeX nuclei (clusters) formed in each domain grow by surface reactions until exhaustion of the limiting metal reactant, and by particle-particle coalescence, leading to the formation of a single nanocrystal per domain.

as a compound that is soluble in the continuous phase. Figure 1 depicts the growth of a MeX quantum dot (QD) inside a spherical PEO-PPO-PEO micelle. H_2Se gas was brought into contact with the micellar system consisting of a diethylzinc-loaded heptane dispersed phase, diffused through the BC interfaces into the nanodomains, and reacted there with diethylzinc to yield ZnSe QDs at room temperature. In this case, formamide was used as the continuous phase since it does not react with diethylzinc and is sufficiently polar to be immiscible with heptane, thus enabling domain formation by BC self-assembly. The concept of template-gas contacting is beneficial since it allows interaction between the reactants without destabilizing the self-assembled system, whereas introduction of the second reactant by mixing with another liquid would have possibly induced undesirable transitions in the thermodynamic equilibrium, thus changing the characteristics of, or even completely destroying, the templating nanodomains.

Reaction and particle growth are terminated when the limiting reactant inside the nanodomains is exhausted. This allowed for tuning of the nanocrystal size by changing the initial concentration of the metal compound in the dispersed phase. The size control is reflected by the blue shift in the photoluminescence (PL) peak as the particles get smaller.[20] Figure 2a shows PL spectra of ZnSe QDs synthesized in a PEO-PPO-PEO/heptane/formamide microemulsion system for three different concentrations of diethylzinc in heptane. According to the spectra, there is a systematic blue shift of the emission peak as the concentration decreases, indicating a decrease of the average nanocrystal size. The synthesized QDs exhibit remarkable photostability, as their PL spectra remained unchanged over a period of several months after synthesis, owing to slow droplet-droplet interaction of

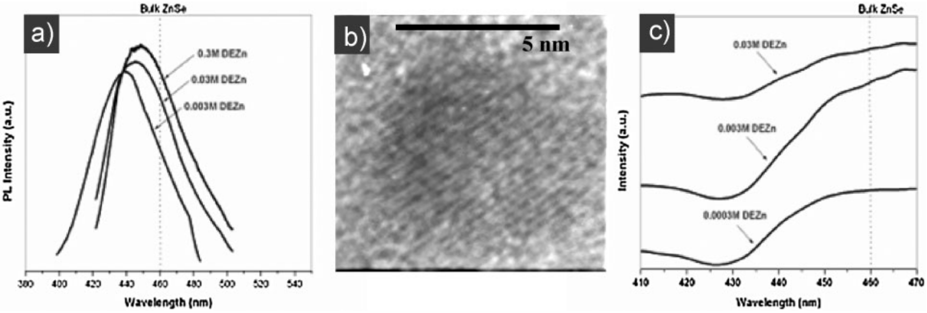

Figure 2.

ZnSe QDs grown inside PEO-PPO-PEO-stabilized oil-in-formamide microemulsions. (a) PL spectra corresponding to different diethylzinc (DEZn) concentrations in the domains, (b) HR-TEM of a ZnSe QD, (c) Optical transmission spectra for three QD populations corresponding to different diethylzinc concentrations.

the templating system. Figure 2b is a high-resolution TEM image of a ZnSe QD with a diameter of 6 nm, prepared by using a diethylzinc-in-heptane concentration of 0.3M. The resulting particles are single-crystalline. Their size is in good agreement to the one estimated by simple calculations based on system parameters, which indicates that a single nanocrystal is formed in each domain. An analogous blue shift, as the concentration of the metal compound decreases, is demonstrated in the optical transmission spectra shown in Figure 2c.

MeX nucleation occurs simultaneously at different locations inside each microemulsion droplet domain, followed by cluster growth through surface reactions. Eventually, cluster diffusion within the domain enables the formation of a single nanocrystal by particle-particle coalescence. Cluster merging proceeds spontaneously inside each domain because there is no inhibitor to prevent individual clusters from agglomerating. This was confirmed by carrying out the reaction between H_2Se gas and diethylzinc in heptane without involving templates, which resulted in formation of large particle agglomerates due to lack of stabilization. Evidence of efficient coalescence between crystalline clusters/particles is provided by Figure 3, which shows a HR-TEM image of two spherical ZnSe nanocrystals coalescing in heptane using a high concentration of Zn^{2+}. A close observation reveals that the crystallographic planes are continuous from one particle to the other, confirming that after coalescence the resulting particle is monocrystalline in nature, and not a polycrystalline aggregate. It is noteworthy that beyond a certain size, formation of a spherical particle by coalescence is not feasible due to lack of sufficient energy release per unit mass, favoring the formation of dumbbell-shaped particles (Figure 3), in contrast to smaller-sized nanocrystals that are spherical (Figure 2b).

Formation of single-crystalline particles at macroscopically room temperature is attributed to annealing associated with the energy released during coalescence of the small nanocrystals and clusters to form

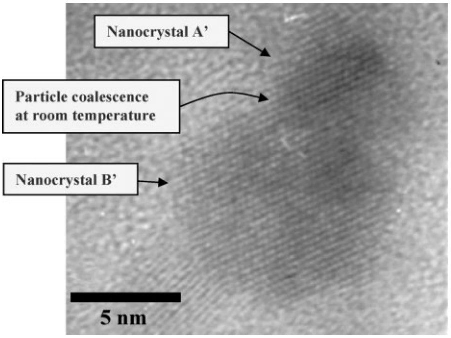

Figure 3.

HR-TEM image of the coalescence of two spherical ZnSe nanocrystals formed using a high Zn^{2+} concentration. The resulting particle is monocrystalline as revealed by the continuity of the crystallographic planes, and not a polycrystalline aggregate.

the final particle, due to formation of new Zn–Se bonds that minimizes the number of unsaturated surface bonds and the total free energy of the structure.[21] The annealing is aided by the reaction exothermicity and by the depression of the melting point with particle size.[27] Due to the melting point depression, the annealing can proceed at much lower temperatures than the ones required for annealing of bulk crystals. Modeling of thermal effects during cluster and nanocrystal coalescence in the templates discussed here indicates that the energy release during coalescence is sufficient to locally raise the temperature of the resulting nanocrystals and enable annealing, before energy dissipation by conduction to the surrounding medium can cool the nanocrystals back to room temperature. The net energy released during this process is small and localized thus the macroscopically observed temperature of the system remains constant at room temperature.

Besides the ability to tune the particle size, control over the shape and morphology of semiconductor nanocrystals is equally critical, since it affects their properties and determines their applicability. Novel structures that confine electron-hole pairs in one or two dimensions have attracted attention for fundamental studies as well as for their potential applications as interconnects and functional units in nanoelectronics.[28] One-dimensional nanocrystals in particular, such as nanowires and nanotubes, represent the smallest dimension for efficient transport of electrons and excitons, thus can be ideal building blocks for hierarchical assembly of functional electronic and photonic configurations.[29] The use of microemulsions as templates can provide facile control of the crystal size, as discussed above, yet the spherical morphology of these self-assembled domains does not allow for the formation of particles other than QDs and related spherical structures. Ordered, LLC structures formed by PEO-PPO-PEO self assembly can offer the means to overcome this limitation. To this end, a variety of 0-, 1-, and 2-dimensional domains were formed and employed to confine nanocrystal growth and produce semiconductor structures with analogous morphologies.

Figure 4 shows a partial isothermal phase diagram for the PEO-PPO-PEO/heptane/formamide system, demonstrating structural polymorphism that is induced by a variation of the concentration of the individual components.[21] At equilibrium, the single-phase samples were clear and macroscopically homogeneous, while the two-phase samples were either homogeneous but opaque, or macroscopically heterogeneous/phase separated. Under polarized light, microemulsion solution (L_1) and cubic LLC samples (I_1) appeared isotropic/non-birefringent, while hexagonal (H_1) and lamellar (L_a) LLC samples were anisotropic/birefringent[30,31] (Figure 4).

Additional templating systems were also employed, such as the PEO-PPO-PEO/water/p-xylene system,[31] which enabled nanocrystal growth in the aqueous phase that was pre-loaded with a water-soluble metal compound (e.g., metal acetate). Tuning of the growth environment is essential for particle post-processing and integration into applications. For optoelectronics, a compatibility of nanocrystals with common organic solvents is required, whereas for biological applications, nanocrystals must be soluble in water.[32] Growing nanocrystals in the aqueous nanodomains allows for *in situ* incorporation of appropriate surface-decorating agents in the water domains upon synthesis, to render the nanocrystals soluble and stable in water for applications in biological systems.

Figure 5 shows a variety of nanostructures grown in LLC phases with different domain morphologies. ZnSe QDs with an average diameter of 3 nm were grown in the oil dispersed cubic LLC phase of the PEO-PPO-PEO/heptane/formamide system (Figure 5a). Particle monodispersity was enhanced by increasing BC content, thus ensuring a more efficient stabilization, while size tuning was achieved by changing the metal concentration in the dispersed phase and/or by manipulating the BC-to-

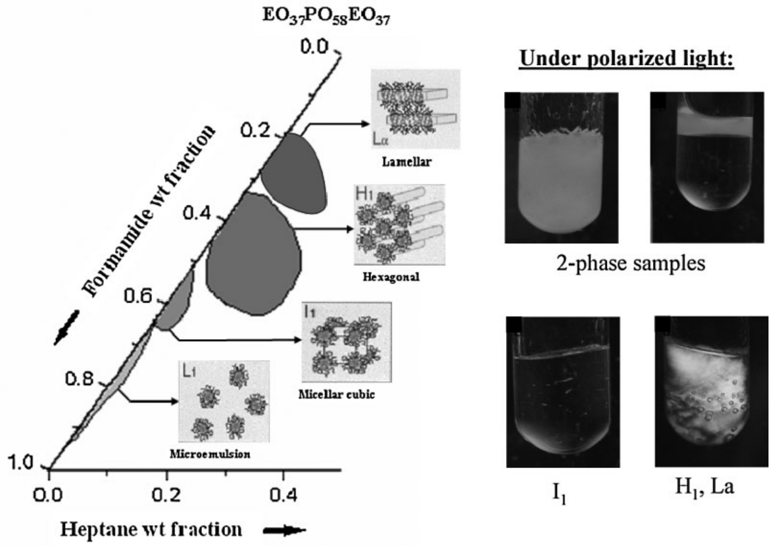

Figure 4.
Phase diagram of the $EO_{37}PO_{58}EO_{37}$/heptane/formamide system at room temperature depicting the microemulsion (L_1), micellar cubic LLC (I_1), hexagonal LLC (H1), and lamellar LLC (L_a) phases. The appearance of the corresponding samples under polarized light is shown on the right.

dispersed phase mass ratio within the phase region of interest, thus changing the size of the domains.[21] Changing the templating system to PEO-PPO-PEO/water/p-xylene enabled nanoparticle synthesis in water.[23] Figure 5b shows QDs grown in the reverse micellar cubic LLC (I_2) phase by a reaction between H_2Se gas, which is brought into contact with a thin film of the LLC, and zinc acetate that is pre-dissolved into the water dispersed phase.

Employing the cylindrical domains of the normal hexagonal region (see Figure 4), crystal growth was confined in one direction to produce nanowires. Figure 5c shows ZnSe nanowires with an average diameter of 3 nm that appear to be arranged parallel to each other following the arrangement of the hexagonal templating structure.[21] It is noteworthy that synthesis of compound semiconductor nanowires with diameters well below the quantum confinement threshold, as done here, is practically difficult to achieve by typical chemical vapor deposition (CVD) techniques, which produce nanowires having diameters of several tens of nanometers.[33] As shown in Figure 5c, the separation distance between adjacent nanowires is approximately constant, with an average value of about 6 nm. Since the expected length of the PEO blocks is about half this distance,[34] this indicates that after evaporation of the solvents, the surface of the nanowires is coated by a single BC layer with the PEO pointing outwards, thus sterically hindering nanowire aggregation.

Employing the lamellar LLC (L_a) phase of the same system enabled the generation of 2-dimensional, self-supported nanolaminates,[23] as shown in Figure 5d. According to this TEM image, the nanolaminates extend up to $\sim$2 μm along the growth plane, whereas their thickness is estimated to be in the order of the BC polar lamellae thickness (i.e., approximately 7 nm[35] or smaller). The nanoplates grow preferentially parallel to each other following the morphology of the lamellar domains, and are separated by BC layers. All the synthesized structures are optically active and exhibit quantum confinement due to their reduced

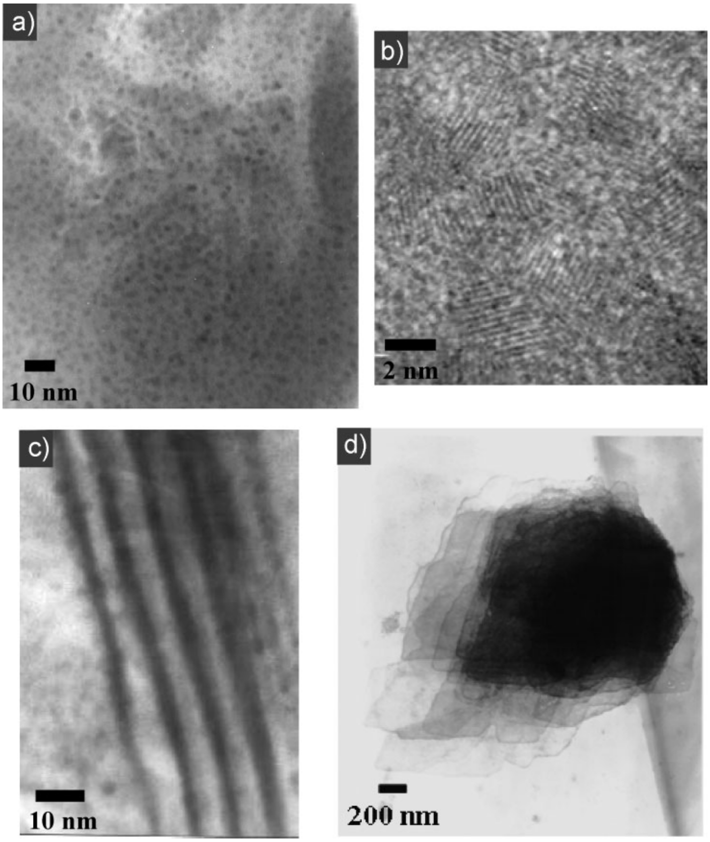

Figure 5.
ZnSe nanostructures grown under confinement in self-assembled BC templates. (a) QDs in normal cubic LLC (I_1) of the PEO-PPO-PEO/heptane/formamide system, (b) QDs in reverse cubic LLC (I_2) of the PEO-PPO-PEO/water/p-xylene system, (c) nanowires in the hexagonal LLC (H_1) phase of the PEO-PPO-PEO/heptane/formamide system, and (d) nanoplates in the lamellar LLC phase of the PEO-PPO-PEO/water/p-xylene system.

critical dimensions, as realized by the blue shift of their respective PL peaks compared to bulk values (data not shown here).

The formation of prescribed nanostructures in BC-stabilized LLC templates (as highlighted above) proceeds through space-restricted coalescence inside each domain. Initially, the metal compound is introduced into the dispersed phase, followed by mixing of all the components and homogenization of the LLC gel (by, e.g., repeated centrifugation in alternating directions). A thin layer of the resulting LLC is brought into contact with the hydride gas, which diffuses into the domains and spontaneously reacts with the metal compound. Coalescence of the clusters and small particles that are formed upon reaction is confined by the structure of the domain originating from BC self-assembled (see Figure 6), resulting in particle with an analogous morphology.[22] In addition to imposing the supramolecular organization that guides the nanocrystal shape selection, we speculate that the BCs actively aid the cluster coalescence into nanoparticles by a mechanism that involves the expulsion (phase separation) by the polymer coils of the clusters when they grow above a certain size (relative to the polymer coil), and thus pushing them to the core of the nanodomain to grow long/flat structures.

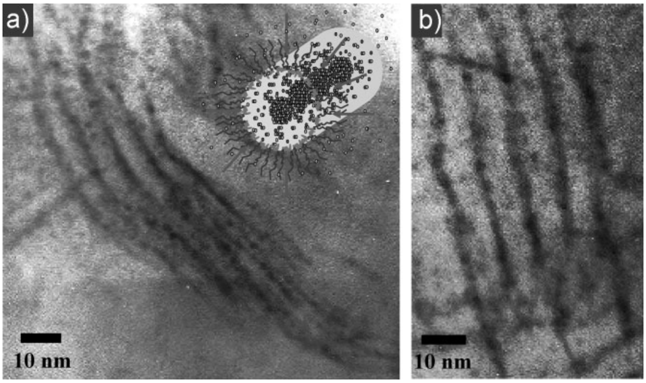

Figure 6.
Early stages of 1-dimensional coalescence. ZnSe clusters/particles are formed and organized after reaction of H_2Se gas and dielthylzinc inside the cylindrical domains of a PEO-PPO-PEO/heptane/formamide hexagonal LLC (H_1) system. Particle coalescence is confined by the morphology of the nanodomains and it proceeds unidimensionally with time to yield ZnSe nanowires (shown in Fig. 5c).

New prospects can be opened up for the nanoparticle and semiconductor communities by the great variety of structures, including novel ones, that are formed by employing the amphiphilic BC templates discussed here. In addition to the morphologies shown in Figure 5, ZnSe nanotubes were synthesized for the first time,[36] as well as vesicle-like hollow spheres by employing the PEO-PPO-PEO/water/p-xylene system,[23] while 2-dimensional, disk-like quantum wells were also formed into the PEO-PPO-PEO/heptane/formamide lamellar phase.[21] These advancements have triggered new theoretical studies investigating the behavior of these materials,[36] and may pave new directions regarding nanomaterials fabrication and integration into functional units.[37]

Conclusions

Templates formed by self-assembly of amphiphilic block copolymers in the presence of two immiscible solvents can direct the growth of zero-, one- and two-dimensional crystalline nanostructures with critical dimensions that fall below the quantum confinement threshold. They also enable tuning of particle size, chemical composition, and growth environment (organic or aqueous), qualities that are of great importance as they determine the application capabilities of the resulting materials. Synthesis proceeds under ambient conditions and, since it is based upon self-assembly, it does not require mechanical mixing or other externally-interfering procedure to ensure uniform nanocrystal nucleation and growth, thus has a high potential for scalability. In addition, the templating domains can act as functionalization vessels, as they can accommodate a variety of molecules in the dispersed phase (e.g., thiols, mercapto-acetic acid) to decorate the nanocrystal surfaces upon growth and enable post-processing targeting specific applications, while they provide enhanced stability to the encapsulated structures due to slow interactions of the copolymer blocks that sterically hinder nanocrystal aggregation.

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[1] A. P. Alivisatos, *Science* **1996**, *271*, 933.
[2] C. B. Murray, D. J. Norris, M. G. Bawendi, *J. Am. Chem. Soc.* **1993**, *115*, 8706.

[3] C. B. Murray, C. R. Kagan, M. G. Bawendi, *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.

[4] H. Mattoussi, J. M. Mauro, E. R. Goldman, G. P. Anderson, V. C. Sundar, F. V. Mikulec, M. G. Bawendi, *J. Am. Chem. Soc.* **2000**, *122*, 12142.

[5] C. J. Brinker, *MRS Bull.* **2004**, *29*, 631.

[6] Y. Li, C.-W. Park, *Langmuir* **1999**, *15*, 952.

[7] M. Boutonnet, J. Kizling, P. Stenius, *Colloids Surf.* **1982**, *5*, 209.

[8] M. Meyer, C. Wallberg, K. Kurihara, J. H. Fendler, *J. Chem. Soc. Chem. Commum.* **1984**, *2*, 90.

[9] H. Zhao, E. P. Douglas, B. S. Harrison, K. S. Schanze, *Langmuir* **2001**, *17*, 8428.

[10] F. T. Quinlan, J. Kuther, W. Tremel, W. Knoll, S. Risbud, P. Stroeve, *Langmuir* **2000**, *16*, 4049.

[11] P. Alexandridis, J. F. Holzwarth, T. A. Hatton, *J. Phys. Chem.* **1995**, *99*, 8222.

[12] B. A. Rozenberg, R. Tenne, *Prog. Polym. Sci.* **2008**, *33*, 40.

[13] J. U. Kim, B. O'Shaughnessy, *Macromolecules* **2006**, *39*, 413.

[14] M. K. Gaines, S. D. Smith, J. Samseth, M. R. Bockstaller, R. B. Thompson, KÃ. Rasmussen, R. J. Spontak, *Soft Matter* **2008**, *4*, 1609.

[15] A. Jain, U. Wiesner, *Macromolecules* **2004**, *37*, 5665.

[16] T. Sakai, P. Alexandridis, *Nanotechnology* **2005**, *16*, S344.

[17] T. Sakai, P. Alexandridis, *Langmuir* **2005**, *21*, 8019.

[18] T. Sakai, P. Alexandridis, *Chem. Mater.* **2006**, *18*, 2577.

[19] C. S. Yang, D. D. Awschalom, G. D. Stucky, *Chem. Mater.* **2002**, *14*, 1277.

[20] G. N. Karanikolos, P. Alexandridis, G. Itskos, A. Petrou, T. J. Mountziaris, *Langmuir* **2004**, *20*, 550.

[21] G. N. Karanikolos, P. Alexandridis, R. Mallory, A. Petrou, T. J. Mountziaris, *Nanotechnology* **2005**, *16*, 2372.

[22] G. N. Karanikolos, P. Alexandridis, T. J. Mountziaris, *Mater. Sci. Eng. B* **2008**, *152*, 66.

[23] G. N. Karanikolos, N. L. Law, R. Mallory, A. Petrou, P. Alexandridis, T. J. Mountziaris, *Nanotechnology* **2006**, *17*, 3121.

[24] R. Ivanova, B. Lindman, P. Alexandridis, *Langmuir* **2000**, *16*, 9058.

[25] R. Ivanova, B. Lindman, P. Alexandridis, *J. Colloid Interface Sci.* **2002**, *252*, 226.

[26] L. Yang, P. Alexandridis, *Langmuir* **2000**, *16*, 4819.

[27] A. N. Goldstein, C. M. Echer, A. P. Alivisatos, *Science* **1992**, *256*, 1425.

[28] Y. N. Xia, P. D. Yang, Y. G. Sun, Y. Y. Wu, B. Mayers, B. Gates, Y. D. Yin, F. Kim, Y. Q. Yan, *Adv. Mater.* **2003**, *15*, 353.

[29] Y. Huang, X. F. Duan, Q. Q. Wei, C. M. Lieber, *Science* **2001**, *291*, 630.

[30] P. Alexandridis, *Macromolecules* **1998**, *31*, 6935.

[31] P. Alexandridis, U. Olsson, B. Lindman, *Langmuir* **1998**, *14*, 2627.

[32] N. Gaponik, D. V. Talapin, A. L. Rogach, A. Eychmuller, H. Weller, *Nano Lett.* **2002**, *2*, 803.

[33] X. T. Zhang, Z. Liu, Y. P. Leung, Q. Li, S. K. Hark, *Appl. Phys. Lett.* **2003**, *83*, 5533.

[34] P. Alexandridis, U. Olsson, B. Lindman, *Macromolecules* **1995**, *28*, 7700.

[35] B. Svensson, P. Alexandridis, U. Olsson, *J. Phys. Chem. B* **1998**, *102*, 7541.

[36] B. Goswami, S. Pal, C. Ghosh, P. Sarkar, *J. Phys. Chem. C* **2009**, *113*, 6439.

[37] R. A. Vaia, J. F. Maguire, *Chem. Mater.* **2007**, *19*, 2736.