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Communications to the Editor

In-Situ Formation of CdS Nanoarrays by Pore-Filling Nanoporous Templates from Degradable Block Copolymers

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For many complex devices in the applications of nanotechnology, it is preferable to assemble semiconductors, metals, or inorganic particles into nanostructures through templation at which the pore-filling process has been extensively exploited for the fabrication of hybridization system. The self-assembly of block copolymers offers a desirable route to form well-defined and ordered nanoscale morphologies by hybridization of inorganic and polymeric materials.[1−5] Thin films prepared from block copolymers driven by the self-assembly of immiscible constituted blocks possessing inherent morphologies are ideal for the formation of nanostructure hybrids with tens of nanometer dimensions.[6−13] Many studies have been achieved on the combination of semiconductor quantum dots (QDs) using various experimental approaches[14−17] not only for scientific reasons but also for their application as nanoelectronic devices,[18] biological labels,[19] and catalysts[20] and in many other regions of nanotechnology.

Nanoporous templates with well-oriented periodic arrays have numerous potential applications through the pore-filling process. The nanopores generated by scarifying the constituted blocks can thus serve as templates for the nanostructured inorganic materials in the applications of semiconductor materials such as CdS QDs by the pore-filling process. As a result, controlled capillary force for micron and submicron lithographical templates filled with micron-sized particles and nanoparticles has been extensively studied.[21,22] Russell and co-workers successfully used nanoporous templates from block copolymers to orient the tri-*n*-octylphosphine oxide (TOPO)-covered CdSe nanoparticles along the hexagonally packed cylindrical nanochannels.[23] They demonstrated a directed deposition method for the introduction of nanoparticles into the cylindrical nanochannels by using capillary force. They also fabricated an electrophoretic deposition to drive 11-mercaptoundecanoic acid (MUA)-covered CdSe nanoparticles into templates with nanoscale character; a specific quantum dot effect (QDE) due to overlapping nanoparticles can be found.[24] Consequently, the formation of nanostructure can be easily achieved by introducing nanoparticles into nanopores through capillary force or electrophoretic deposition, namely pore-filling methods.

In this study, templates with large-scale oriented cylindrical nanochannels from polystyrene-*b*-poly(L-lactide) (PS−PLLA) are used for the formation of hybridized thin films by various pore-filling processes. Our previous results suggested that the mechanism of induced orientation for PS−PLLA microdomains is strongly dependent upon the evaporation rate of solvent and its solubility between constituted blocks.[13] Owing to the degradable character of the polyester component,[25] the formation of the topographic nanopatterns of PS−PLLA by spin-coating provides a simple path to prepare thin-film templates for the pore-filling process. Hillmyer and co-workers demonstrated the ordered hydrophilic nanopores prepared by polylactide−poly(*N*,*N*-dimethylacrylamide)−polystyrene (PLA−PDMA−PS) can be easily filled with the water-soluble materials due to the wetting property of solution for the templates.[26] The objective of this study is to examine the features in the pore-filling process with semiconductor materials CdS into thin-film templates prepared from degradable diblock copolymer. The pore-filling process involves the thrust of capillary force driven from the tunable wetting property of solution for the templates. After the pore-filling process, CdS nanocrystals were in-situ generated by exposing the template incorporated with cadmium acetate ($CdAc_2$) to H_2S vapor. Various shapes of the cluster of CdS nanocrystals including tubular-like and cylinder-like CdS nanostructures in the templates can thus be obtained through different pore-filling processes. Consequently, the emission intensity of

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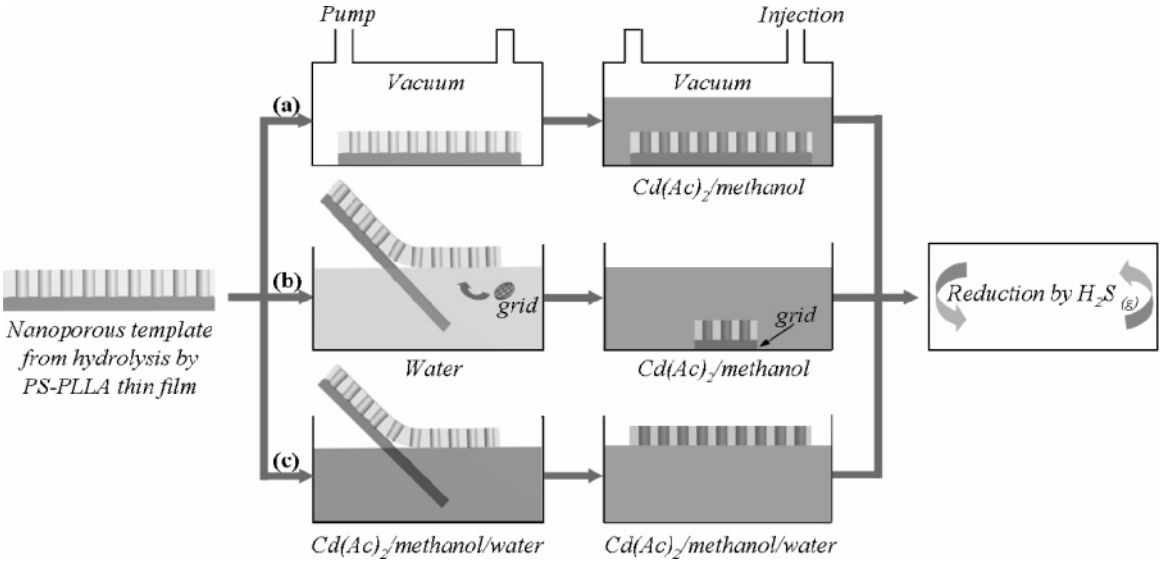

Figure 1. Schematic illustration of pore-filling processes by (a) air-block releasing, (b) directed capillary force (method 1), and (c) directed capillary force (method 2).

the CdS nanoarray can be modulated by the pore-filling process.

Experimentally, PS−PLLA diblock copolymer with PLLA volume fraction of 0.25 was prepared from free radical polymerization of styrene, resulting in a hydroxyl-terminated polystyrene, and then ring-opening polymerization of L-lactide in the presence of the macroinitiator.[27,28] Cylindrical nanostructures with perpendicular orientation were first formed onto glass substrate by spin-coating (1500 rpm) from 1.0 wt % dilute solution of 53 900 g/mol PS−PLLA at 50 °C (ca. 40 nm film thickness). Exposure of these films to UV radiation under vacuum for more than 10 min (at 254 nm) was conducted to increase the mechanical strength of the thin films so as to avoid the film-breaking damage during the hydrolysis process. Because the templates on glass substrate can easily cause fracture and delamination during hydrolytic process, the procedure for UV radiation is to increase the mechanical strength and adhesion of template as well.[29] The thin-film samples were placed in NaOH solution for 5 days to degrade PLLA and then dispersed in MeOH solution for washing residual degradation solution. The perpendicular hexagonal cylinder nanochannel arrays as evidenced by field-emission scanning electron microscopy (FE-SEM) was simply obtained by the hydrolysis process (see Figure S1 of Supporting Information).

Various pore-filling processes were designed to examine the pore-filling efficiency, as shown in Figure 1. In general, the cadmium ions (Cd^{2+}) are adsorbed within the pores of nanoporous PS template by means of the solution of $CdAc_2$. A 0.48 M solution of $CdAc_2$ was prepared by dissolving 3.2 g in 25 mL of methanol or water. Figure 1a illustrates that an air-extracting apparatus was designed to remove the air in the pores before the execution of pore filling. The template was located in a vacuum holder, and then the methanol solution of $CdAc_2$ was injected onto the template under vacuum. In contrast to the method of air-block releasing, two different pore-filling processes designated as directed capillary force (method 1) and directed capillary force (method 2) were used, as shown in parts b and c of Figure 1, respectively. As shown in Figure 1b, the template is removed from glass substrate with 1% HF solution, and then floated onto water surface, and finally collected by a copper grid. After drying in air overnight, the grid with nanoporous template was immersed into methanol or H_2O solution of $CdAc_2$ for 30 min. Then, the grid was removed from the solution and dried in air overnight. Figure 1c illustrates that the template is directly floated on a mixing solution of $CdAc_2$ (mixing ratios of methanol and H_2O was 5:1) for 3 h and then collected by carbon-coated glass. After the pore-filling process, the pore-filling templates were both washed with copious amounts of H_2O to remove any excess Cd^{2+} present on the outer surface of the template, and then the formation of CdS nanostructures was achieved by using H_2S vapor as reduction agent.

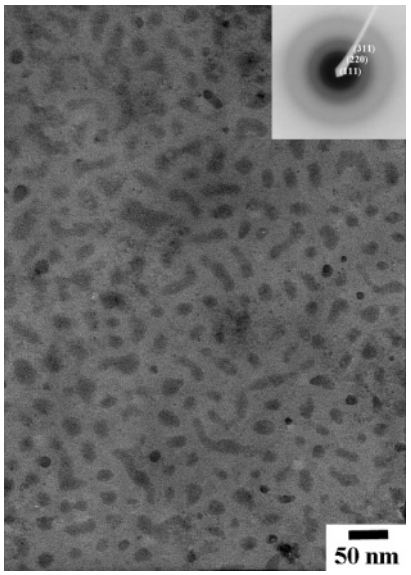

Figure 2. TEM image of templated CdS nanoarrays through the pore-filling process by air-block releasing. Inset shows the selected area electron diffraction pattern from the central region of the sample.

Figure 2 shows the TEM image of templated CdS nanoarrays through the pore-filling process by air-block releasing. The projected image reveals nanoarrays of CdS nanocrystals having size equivalent to the pore size of nanoporous templates, indicating that the reduced CdS nanocrystals are formed within the oriented cylinder nanochannels. For comparison, a controlled experiment without using vacuum for pore-filling process has been conducted; we immersed the template into the solution of $CdAc_2$ directly at similar conditions to the air-block releasing method. In contrast to the air-block releasing method, no significant CdS can be identified after reduction. We expect that the completion of the pore-filling process can also be

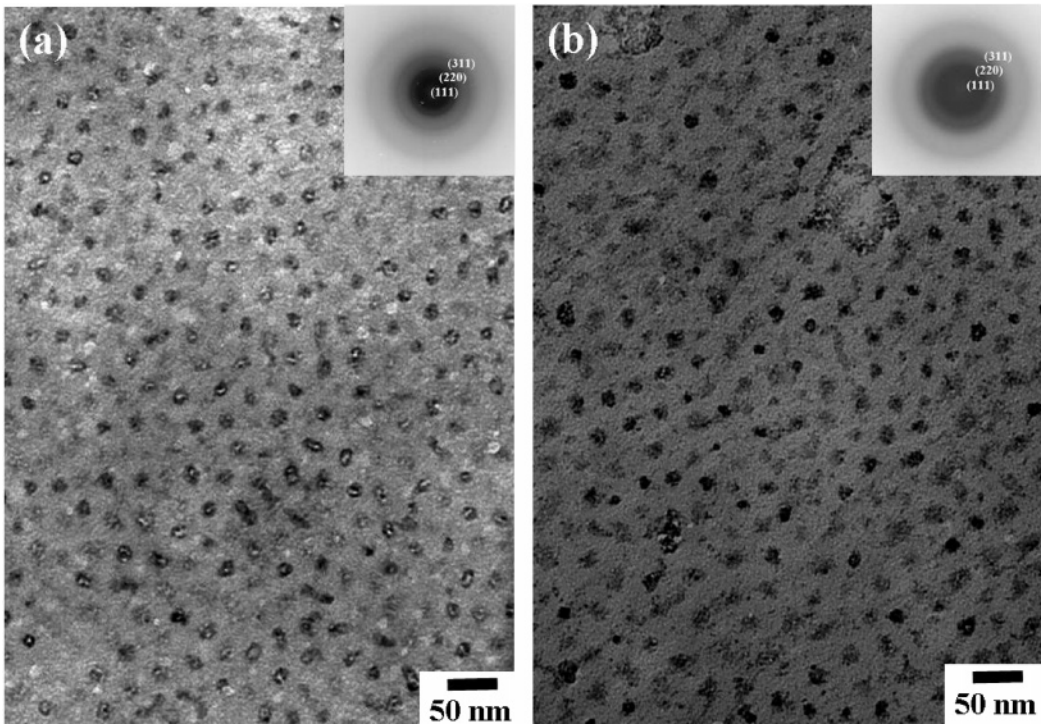

Figure 3. TEM images of templated CdS nanoarrays through pore-filling processes by (a) directed capillary force (method 1) and (b) directed capillary force (method 2). Inset shows the selected area electron diffraction pattern from the central region of the sample.

achieved through long-time immersion without using vacuum, as observed by Russell and co-workers.[30] We thus suggest that the time efficiency of the pore-filling process can be improved by the air-block releasing approach. Nevertheless, wormlike morphology of CdS nanocrystals can also be observed. We speculate that the formation of the wormlike texture is attributed to the inefficient filling so as to cause the occurrence of reduction on the surface. The formation of CdS nanocrystals was evidenced by selected area electron diffraction (SAED) experiments, as shown in the inset of Figure 2. On the basis of the β-CdS crystals, the interdomain distances, d_{hkl}, were identified as the reflections of (111), (220), and (311),[31,32] suggesting the occurrence of successful reduction by H_2S vapor (i.e., the in-situ formation of CdS nanocrystals within the nanoporous template).

Figure 3 shows TEM image of templated CdS nanoarrays through the pore-filling process by directed capillary force (method 1) at which the gray PS template is decorated with dark CdS nanocrystals on the inner walls of the bright regions of empty nanopores. We speculate that the formation of CdS shells might be attributed to the partial filling of going-through solution at which the nanopores of the template truly span the entire thickness of the films and the supporting grid provides the meshes for the going-through process. Similarly, the formation of β-CdS crystals was identified by electron diffraction results (inset of Figure 3a). Recently, a successful method similar to the described process mentioned above has been reported by Russell and co-workers; surface-functionalized CdSe nanorods can be formed for the practice applications by the so-called film flotation technique with diblock copolymer templates.[33] The capability of the pore-filling approach is attributed to the capillary force that is dependent upon the surface tension of wetting substrate (i.e., PS template) and the wetting tendency for the solution onto the substrate (i.e., the interfacial energy of PS and solution). As a result, the pore-filling efficiency is strongly dependent upon the mutual interaction of the solution prepared and the PS template. Here, methanol solvent is used to promote the wetting tendency of the solution of cdmium ions into PS template through capillary rise. In contrast to the use of methanol as solvent for pore filling, only template free of reduced CdS can be found in the template after filling by the aqueous solution of $CdAc_2$ (see Figure S2 of Supporting Information) because of the dewetting between water and PS template. Nevertheless, the thin film of PS template might not be able to address onto the simple methanol solution due to the low surface tension so as to cause the contraction of the thin-film template. Thus, the introduction of water into methanol solution is to enhance the surface tension for the deposition of the thin-film template uniformly floating on the surface of solution whereas the solution can still wet the PS template by appropriately adjusting the ratio of methanol and water as mixed solvent. Considering the enhancement of pore-fill efficiency, the nanoporous template is thus floated directly on the mixing solution of methanol and water so that CdS nanocrystals can completely fill the nanopores, as shown in Figure 3b. We believe that this methodology can be applied for the pore-filling approach with large-size template and is able to easily achieve uniform dispersion of CdS nanocrystals.

In addition, it is worthy of examination for the optical properties of the CdS nanocrystals in the template by ultraviolet absorption (UV) and photoluminescence (PL) emission experiments. For comparison, spherelike CdS nanoparticles were also fabricated by simply spin-coating of 0.48 M $CdAc_2$ methanol solution and then exposed to H_2S vapor. Spherelike CdS nanoparticles (ca. 10−20 nm on average) dispersed uniformly on the substrate (designated as CdS solid state) can be obtained (see Figure S3 of Supporting Information); no QDE can be found due to the large size of CdS nanoparticles (larger than 6 nm).[14] Figure 4 shows that the PL of nanoporous PS/CdS by directed capillary force (method 2) is higher than nanoporous PS/CdS by air-block releasing and CdS solid state. As shown, the air-extracting apparatus might not be good enough to completely release the air-block effect so as to cause the incomplete covering of CdS. Moreover, the observed increase

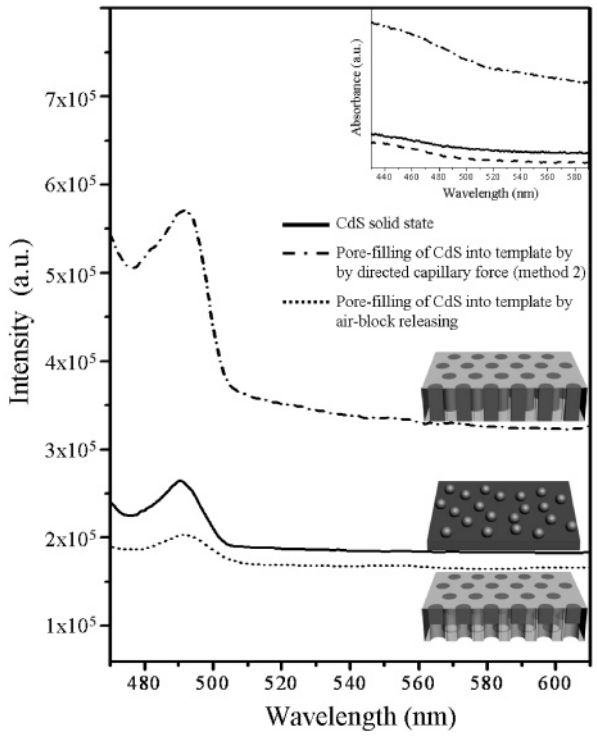

Figure 4. PL spectra of CdS solid state and templated CdS through pore-filling processes by air-block releasing and directed capillary force (method 2). The exciting length is at 450 nm. Inset shows corresponding UV−vis absorption spectra.

in emission intensity with a different pore-filling procedure suggests a greater density of CdS nanocrystals residing in the template. In line with no QDE from PL results, the onset absorption of UV spectrum in nanoporous PS matrix/CdS by directed capillary force also occurred at the same wavelength, ca. 512 nm (inset of Figure 4), but the absorption density was also quite different. Consistent with the emission results, confocal microscopy image observed that nanoporous PS/CdS by the directed capillary force (method 2) had higher brightness in macroscopic results (Figure S4 of Supporting Information).

In conclusion, the pore-filling process for the manufacturing of semiconductor nanoarrays by PS nanoporous templates proved to be an efficient method to place the in-situ formation of CdS nanoparticles into the nanopores of diblock copolymer templates. It is noted that the wetting property is critical to achieve a successful pore filling of solution because it determines the direction of the capillary force and also prevents the resistance in nanochannels caused by air-blocking. UV spectroscopy and PL were monitored after pore-filling deposition. In line with the UV absorption results, the photoluminescence of the templated CdS nanocrystals indicates great increase in optical activity, suggesting that the enhancement of emission intensity can be achieved by increasing the reduction amount of CdS through appropriate process for templation.

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Supporting Information Available: FE-SEM image of spin-coated PS−PLLA, TEM image of templated CdS nanoarray, TEM image of CdS nanoparticles, and confocal microscopy images of CdS. This material is available free of charge via the Internet at http://pubs.acs.org.

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