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<https://doi.org/10.1021/la0629274>

Langmuir, 23, 4, pp. 1612-1614, 2007-02-01

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Ordered CdSe Nanoparticles within Self-Assembled Block Copolymer Domains on Surfaces

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Received October 5, 2006. In Final Form: January 10, 2007

Hierarchical, high-density, ordered patterns were fabricated on Si substrates by self-assembly of CdSe nanoparticles within ~20-nm-thick diblock copolymer films in a controlled manner. Surface-modified CdSe nanoparticles formed well-defined structures within microphase-separated polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) domains. Trioctylphosphine oxide (TOPO)-coated CdSe nanoparticles were incorporated into PS domains and polyethylene glycol-coated CdSe nanoparticles were located primarily in the P2VP domains. Nearly close-packed CdSe nanoparticles were clearly identified within the highly ordered patterns on Si substrates by scanning electron microscopy (SEM). Contact angle measurements together with SEM results indicate that TOPO-CdSe nanoparticles were partially placed at the air/copolymer interface.

Introduction

Engineering the self-assembly of inorganic nanoparticles within block copolymer nanodomains is useful for the design of periodic structures to form materials with enhanced mechanical strength as well as to achieve unique optical, electronic, and magnetic properties on the nanometer scale. The technological relevance of these nanoscale materials is linked to a fundamental understanding of the structural characteristics to afford a reliable prediction of, for example, the photonic properties needed to tailor the materials for various applications. Several experimental processes and theoretical models have been developed for the incorporation of inorganic nanoparticles into polymeric nanostructures.^{1–10} On the basis of theoretical predictions of the cooperative self-assembly of nanoparticles and block copolymers,^{11–13} Bockstaller et al.⁶ demonstrated pattern formation using mixtures of hydrophobic nanoparticles and block copolymers. More recently, the work of Russell and co-workers⁷ showed that the pattern of block-copolymer domains in films could be influenced by nanoparticles. In addition, Kramer and co-workers⁸ showed that polymer-grafted Au nanoparticles can be located either inside the block-copolymer domains or at the interface of

the two block-copolymer domains. Precise control of the position of the nanoparticles within block-copolymer films is important for developing organized hybrid materials to obtain practical functionality. In many of those applications, including the above-mentioned photonic band gap devices, nanostructured solar cells, magnetic storage media, and biomedical devices, it is important to fabricate highly ordered patterns of nanoparticles on surfaces. Several conventional fabrication methods, including standard photolithography,^{14,15} electron beam lithography,^{16,17} and other lithographic techniques,^{18–20} have been employed to generate well-organized nanostructures. However, these approaches are often sophisticated and limited in terms of minimum achievable feature sizes.

In this letter, we report a study that set out to examine whether nanoparticles could be loaded heavily within domains of a phase-segregated diblock copolymer film on a solid surface such that the particles would be close-packed on one length scale while the diblock polymer remained cleanly phase-separated on a second length scale. We demonstrate the formation of highly ordered hierarchical structures on solid surfaces by controlling the surface hydrophobicity of nanoparticles within ~20-nm-thick diblock copolymer films. High-resolution scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were made of the CdSe-diblock copolymer hybrid films and were used to identify individual CdSe nanoparticles within the highly ordered patterns on solid substrates in which the spatial location of the nanoparticles was determined by their surface ligands. Moreover, contact angle experiments supported the determination of the location of TOPO-CdSe nanoparticles.

Diblock copolymer poly(styrene-*b*-2 vinyl pyridine) (PS-*b*-P2VP) ($M_w(\text{PS}) = 52.4 \text{ kg/mol}$, $M_w(\text{P2VP}) = 28.1 \text{ kg/mol}$, PDI = 1.11, Polymer Source Inc., Canada) and tri-*n*-octylphosphine oxide (TOPO)-coated CdSe nanoparticles (TOPO-CdSe, core diameter 4 nm, Evident Technologies, NY) were used in our

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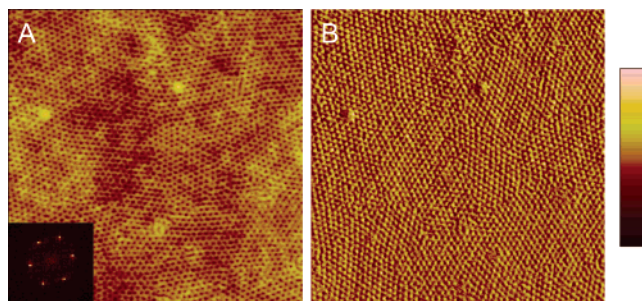


Figure 1. AFM (A) height and (B) phase images of a CH_2Cl_2 vapor-annealed TOPO-CdSe/PS-*b*-P2VP film on a Si substrate. Image size: 2500 nm \times 2500 nm. Z range: 10 nm, 30°. The inset in A is a Fourier transformation of the height image.

study. Films with thicknesses of 20 ± 2 nm were prepared by spin coating toluene solutions of a mixture of 0.3 wt % PS-*b*-P2VP and 0.05 wt % TOPO-CdSe on silicon substrates. Prior to use, Si wafers were immersed in freshly prepared piranha solution (3:1 v/v $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$) for 10 min. Then they were rinsed with excess Milli-Q water, acetone, and toluene and immediately dried in a nitrogen stream. (*Piranha solution should be handled with extreme caution. It has been reported to detonate unexpectedly.*) Before and after the TOPO-CdSe/copolymer films were annealed in saturated dichloromethane vapor for 4 h at 25 °C,²¹ the samples were kept under vacuum for 16–20 h to remove the solvent. In agreement with the literature,⁷ we found that solutions of TOPO-CdSe nanoparticles and the block copolymer were stable at room temperature; aggregation caused by ligand exchange was not observed.

Atomic force microscopy (AFM) height and phase images of an annealed TOPO-CdSe/PS-P2VP film with a thickness of ~ 20 nm are shown in Figure 1. AFM measurements were made using a Digital Instruments Dimension 5000 AFM (DI/Veeco, Santa Barbara, CA) operated in tapping mode using silicon probes (Mikromasch, resonance frequencies in the range of 175–350 kHz, free amplitude 20–25 nm). Before annealing, the mixed nanoparticle/copolymer films presented quasi-hexagonal micellar patterns on Si substrates (Supporting Information Figure S1).^{22,23} In Figure 1A, a highly ordered array of microphase-separated domains of P2VP in a PS matrix is observed for the annealed films on Si substrates. Using Fourier transformation of the AFM images (Figure 1A inset), the lattice spacing of the hexagonal packing domains was found to be 40 ± 1 nm for the TOPO-CdSe/copolymer films. The ordered structure is similar to that of the annealed pure PS-*b*-P2VP films on Si surfaces (Supporting Information Figure S2). However, the pronounced increase in height and phase contrast indicates that the hard nanoparticles were incorporated into the PS phase (Figure 1B, bright areas).⁷

Figure 2 shows scanning electron microscopy (SEM, S-5200, Hitachi microscope operated at 5 kV) images of CH_2Cl_2 vapor-annealed films on silicon wafers. First, the Figure illustrates a significant degree of regular diblock phase segregation. PS domains are about 40 nm in diameter. The second important observation is that TOPO-CdSe nanoparticles with diameters of 4 to 5 nm are distinctly identified within the PS domains. This location of TOPO-CdSe particles is expected as a result of the hydrophobic modification of TOPO groups on the surface of

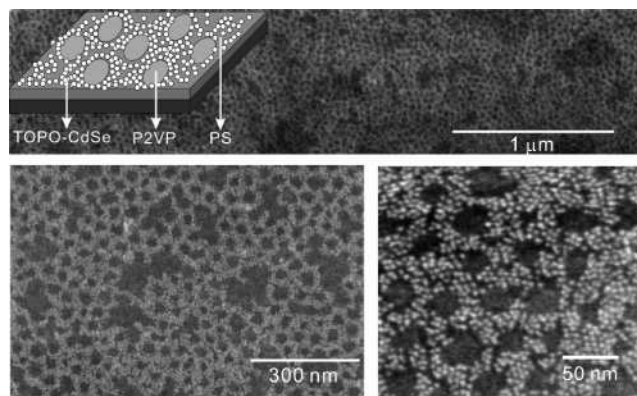


Figure 2. SEM micrographs of an annealed PS-*b*-P2VP/TOPO-CdSe film on Si at 5 kV acceleration voltage. The inset scheme shows the packing of the nanoparticles.

Table 1. Advancing Water Contact Angles Measured on Si Substrates, PS-*b*-P2VP Films, and PS-*b*-P2VP/TOPO-CdSe Ordered Pattern Films

	freshly cleaned Si substrate	PS- <i>b</i> -P2VP films	PS- <i>b</i> -P2VP/TOPO-CdSe films
contact angles (deg)	12 ± 2	90 ± 5	105 ± 5

CdSe particles, which increase the favorable molecular interactions between PS blocks and the nanoparticles, in preference to P2VP/TOPO-CdSe (block–nanoparticle) or PS/P2VP (block–block) interactions.

As can be seen in the inset to Figure 2 (lower right image), the CdSe particles are nearly close-packed and exhibit a high degree of local order. A pairwise correlation plot for these particles can be found in Supporting Information. As others have shown, a low degree of particle loading does not interfere with the diblock pattern formation (Figure S3).⁸ However, Figure 2 shows the remarkable result that greater than 75% lateral loading of particles into single domain types can be accomplished while retaining the majority of the diblock-induced long-range order. Some long-range-order defects were observed in the nanoparticle/copolymer mixed films. Further vapor annealing did not improve the ordering of the particles within the PS domains but resulted instead in the collapse of the ~ 20 -nm-thick films. This indicates that such films are not stable for long periods of vapor annealing. Therefore, the CdSe particles may not obtain sufficient mobility to form ideal hexagonal structures on surfaces.

Advancing contact angles of freshly treated Si substrates, pure diblock copolymer films, and highly ordered nanoparticles/copolymer pattern films were measured with water at room temperature (Table 1). Pure copolymer films showed hydrophobic behavior due to the preferential adsorption of the P2VP blocks to the hydrophilic silicon surfaces with most of the PS chains staying close to the air interface.^{24,25} After adding the TOPO-CdSe nanoparticles to the PS-*b*-P2VP copolymer, the patterned films showed even higher hydrophobicity. This is reasonable if the alkyl chains of TOPO molecules are exposed to the air–polymer interfaces. Consider that the adsorption energy of a nanoparticle at an air–polymer interface is given by $E_a = \pi R^2 \gamma_{\text{poly/air}} (1 - |(\gamma_{\text{CdSe/poly}} - \gamma_{\text{CdSe/air}})/\gamma_{\text{poly/air}}|)$, where R is the radius of the nanoparticles and $\gamma_{\text{poly/air}}$, $\gamma_{\text{CdSe/poly}}$, and $\gamma_{\text{CdSe/air}}$ are the interfacial tensions of polymer–air, nanoparticles–polymer, and nanoparticles–air, respectively. Here, $R = 2.5$ nm, $\gamma_{\text{poly/air}}$

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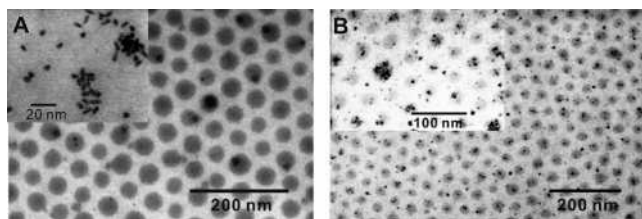


Figure 3. Bright field TEM images of (A) low and (B) high concentrations of PEG-CdSe in PEG-CdSe/PS-*b*-P2VP films. The inset in A shows the PEG-CdSe nanoparticles without polymer films.

$= 36 \text{ mN/m}$,²⁶ $\gamma_{\text{CdSe/poly}} \approx 25 \text{ mN/m}$,²⁷ and $\gamma_{\text{CdSe/air}} = 33 \text{ mN/m}$,⁷ which gives $E_a \approx 100k_B T$. Therefore, it is expected that the particles should be found at the polymer–air interface.

The clearly resolved CdSe nanoparticles in SEM images and the increasing hydrophobicity of nanoparticles/polymer mixture films indicate that the TOPO-CdSe nanoparticles were at least partially located at air–polymer interface.

Further reference samples of hydrophilic coated CdSe nanoparticles and PS-*b*-P2VP mixed films were analyzed by TEM. Polyethylene glycol-coated CdSe nanoparticles²⁸ (PEG-CdSe) with diameters of $\sim 5 \text{ nm}$ (Figure 3A inset) were cast from 0.05 mg/mL chloroform solution on carbon-supported TEM grids. Figure 3A shows a typical TEM micrograph of spin-coated films prepared from 0.025 mg/mL PEG-CdSe and a 0.3 wt % PS-*b*-P2VP chloroform solution on carbon-supported TEM grids. After vapor annealing in CH_2Cl_2 for 4 h and drying at 70°C for 16–20 h, a well-defined micropattern structure of diblock copolymer was detected over a large area without the prominent presence

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of CdSe particles. Dark domains in Figure 3A represent P2VP domains in the PS matrix (bright area). Upon increasing the PEG-CdSe concentration to 0.25 mg/mL, the nanoparticles were mostly found in P2VP domains, as illustrated in the TEM micrographs shown in Figure 3B. Particles did not situate at phase boundaries apparently because of the strength of the favorable PEG–P2VP interaction.¹²

In summary, we have demonstrated the fabrication of highly ordered hierarchical structures on Si substrates using the self-assembly of CdSe nanoparticles within PS-*b*-P2VP diblock copolymer films in a controlled manner. TOPO-CdSe nanoparticles were incorporated into PS domains, and PEG-CdSe nanoparticles were located mostly in P2VP domains. Individual CdSe nanoparticles can be clearly identified within the highly ordered patterns on Si substrates. Low particle loading allows the diblock pattern to form unimpeded. Interestingly, at higher loading even in ranges where strong particle–particle packing forces come to bear, the longer length scale self-assembly of the diblock system was only slightly affected. Contact angle measurements together with SEM results indicate that TOPO-CdSe nanoparticles were partially placed at the air–copolymer interface.

Acknowledgment. The NSERC (312497), NIH (IR21EB003101-01), ONR (N00014-05-10765), ARO-MURI (W911NF-04-1-0191), Canada Research Chair Program, and NSF (CHE-0404579) are acknowledged for financial support.

Supporting Information Available: AFM images of neat copolymer and nanoparticles/copolymer films before annealing and a histogram of the nanoparticle center-to-center distance pairwise correlation plot. This material is available free of charge via the Internet at <http://pubs.acs.org>.

LA0629274