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# Spatial position control of pre-synthesized CdS nanoclusters using a self-assembled diblock copolymer template

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## Abstract

We report a method for fabricating ordered spatial arrangements of pre-synthesized CdS nanoparticles in thin block copolymer templates by first selectively dispersing these nanoparticles in one particular block of a diblock copolymer, in bulk, by means of dipole–dipole interactions and then using solvent selectivity to sequester CdS nanoparticles in the block copolymer thin film. A long-range, ordered morphology of CdS nanoclusters can be obtained by using patterned substrates with 400 nm shallow grooves. The incorporated nanoparticles retain the same luminescence characteristics as in the pure state.

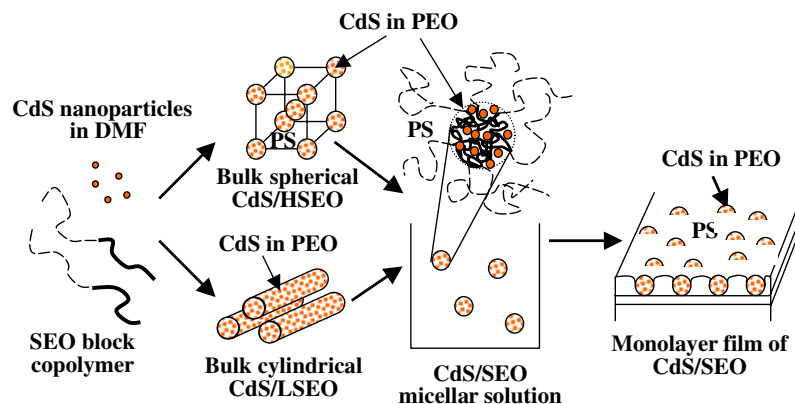
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(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The fabrication of periodically ordered, two-dimensional nanostructures on the scale of ten to a hundred nanometres is critically important as electronic and magnetic devices are continually miniaturized. A few attempts have been taken to arrange nanomaterials, such as semiconductor nanocrystals, as well as metal and metal oxide nanoparticles, into ordered structures for device applications [1–4]. A diblock copolymer chain consists of two chemically dissimilar blocks attached through a covalent bond. These diblock copolymers can microphase separate into various ordered nanostructures with periodic thicknesses between 10 and 100 nm [5], and therefore are good carriers for bringing nanoparticles into ordered structures, provided that strong interfacial interactions can be obtained. For instance, the sequestration of Au and SiO<sub>2</sub> nanoparticles in block copolymers in bulk form for photonic applications has been reported [6]. The incorporation of nanoparticles into block copolymers, however, would lead to more complicated block copolymer morphologies than their pristine state, as predicted by Balazs's group [7], which has used self-consistent field theory and density functional theory to describe the polymer and the nanoparticles, respectively; they have been able to predict the phase diagram and

morphological structure for both systems. On the other hand, thin films (less than 100 nm) of diblock copolymers can be used as lithographic templates for the production of high density nanostructures. For example, dense periodic arrays of holes and dots in silicon nitride [8], GaAs [9] and Au/Cr [10a] have been produced; magnetic cobalt dot arrays [11] on patterned substrates have been produced using polystyrene-*b*-polybutadiene, polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) and polystyrene-*b*-poly(ferrocenyldimethylsilane) block copolymer templates. Au, Ag [12] and magnetic Co [10b] nanowires can also be fabricated using a PS-*b*-PMMA block copolymer template. Alternatively, to control the spatial positions of nanoparticles with nanostructured block copolymers, a common approach has been to synthesize the nanocrystal clusters within microphase-separated diblock copolymer films. Quasi-regular arrays of Au clusters [13], Co and Fe arrays [14] and self-assemblies of both Au and Fe<sub>2</sub>O<sub>3</sub> nanoparticles [15] have all been synthesized using micellar polystyrene-*b*-polyvinylpyridine (PS-*b*-PVP). This approach has a limited ability to control the optoelectronic properties of the ordered nanoparticle arrays due to constraints imposed by the polymer matrix. Variation of the optoelectronic properties of the nanoparticles in the block copolymer matrix is essential for device applications.



**Scheme 1.** Fabrication of an ordered array of pre-synthesized nanoparticles using a block copolymer template by spin coating a micellar solution. Nanoparticles are held in the cores of the micelles.

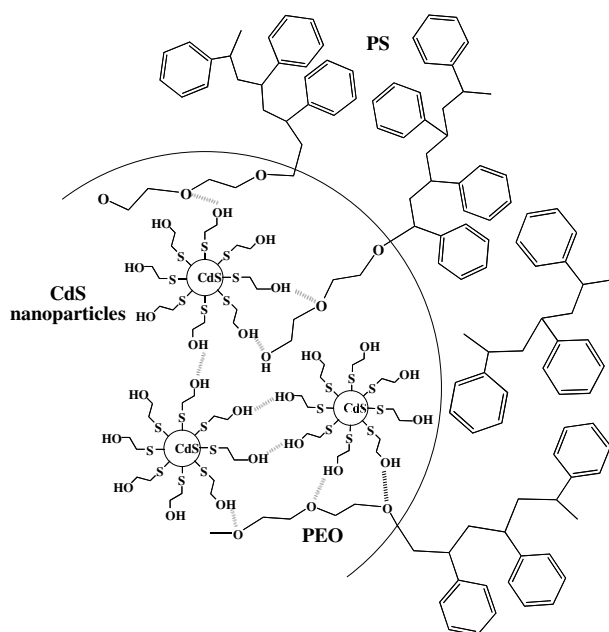
Another approach using block copolymer thin films as templates to control the spatial arrangement of pre-synthesized nanoparticles has recently been demonstrated in a few cases. Different sizes of pre-synthesized CdSe nanoparticles were screened by taking advantage of a capillary force with a nanoporous PS-*b*-PMMA template [16]. Sequestered CdSe nanoclusters within phosphine-containing domains of a diblock copolymer were also obtained [17]. Our laboratory has been able to selectively disperse surface-modified CdS nanoparticles in the PEO phase of polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO). We measured the size distribution of CdS nanoparticles using the absolute intensity of small-angle x-ray scattering results [18b] and demonstrated the morphological transformation of the block copolymer in the bulk form [18a] and thin film [18c]. In another case, hydrophilic or hydrophobic surface-modified TiO<sub>2</sub> were dispersed selectively in the PS or PMMA domain of PS-*b*-PMMA in bulk form, depending on the hydrophobic or hydrophilic nature of the surfactant [19]. To our knowledge, the sequestration of pre-synthesized nanoparticles in thin block copolymer films through dipole-dipole interactions between the ligands on nanoparticles and a particular block have not yet been reported.

In this paper, we report a method for fabricating an ordered spatial arrangement of pre-synthesized nanoparticles in thin block copolymer templates by first selectively dispersing these nanoparticles in one particular block of a diblock copolymer in a polar solvent, *N,N*-dimethylformamide, and then using non-polar solvent, toluene, to sequester CdS nanoparticles in the PS-*b*-PEO block copolymer thin film. This method is based on the fact that CdS nanoparticles surface modified by mercaptoethanol are hydrophilic and can be dispersed well in *N,N*-dimethylformamide (DMF). DMF, however, is a polar solvent that is a good solvent for PEO but a poor one for PS. Although toluene is also a good solvent for both PEO and PS, it is not appropriate to use toluene only to carry out the process because surface-hydroxylated CdS nanoparticles aggregate in the non-polar solvent, toluene. Therefore, a one-step process is not sufficient to produce an ordered spatial distribution using block copolymer thin films as templates. The method presented in this study can provide more flexibility in choosing a particular domain for nanoparticles containing matched surface ligands in a block copolymer thin film. The distance between nanoparticles is

tuned by varying the molecular weight of the other block of the diblock copolymer. Moreover, substrates with shallow grooves are used to confine the nanocomposites for a long-range-order morphology study. CdS nanoparticles are chosen in this study due to their inherently interesting electronic and photophysical properties [20].

## 2. Materials and methods

In the present study, CdS nanoparticles were synthesized by reacting cadmium acetate dihydrate (Cd(Ac)<sub>2</sub>·2H<sub>2</sub>O) and sodium sulfide (Na<sub>2</sub>S) with mercaptoethanol (HSC<sub>2</sub>H<sub>4</sub>OH) as a surfactant, following a modification of the kinetic trapping method. The average size of hydroxyl-ligand-modified CdS nanoparticles in *N,N*-dimethylformamide (DMF) is about 2.5 nm. PS-*b*-PEO (SEO) diblock copolymers, having a high molecular weight (MW) ratio of PS to PEO (MW<sub>PS</sub>/MW<sub>PEO</sub> = 125k/16.1k), termed HSEO, and a low ratio (MW<sub>PS</sub>/MW<sub>PEO</sub> = 19k/12.6k), termed LSEO, were used. Appropriate ratios of CdS and SEO were mixed in DMF. These mixtures were dried slowly under vacuum at 323 K and then maintained at 383 K for 24 h to obtain bulk CdS/HSEO and CdS/LSEO nanocomposites. 1 wt% micellar solutions of CdS/HSEO or CdS/LSEO were prepared by dissolving bulk CdS/HSEO or CdS/LSEO in toluene. Then, the micellar solutions were spin coated at 5000 rpm for 60 s at 25 °C on carbon-coated silicon wafers. After drying, the thin films were characterized by atomic force microscopy (AFM). The procedure used to prepare ordered CdS nanoparticles in a thin block copolymer template is demonstrated in scheme 1. In the initial stage, both mercaptoethanol-modified CdS nanoparticles and the SEO block copolymer are dissolved in DMF, which is a good solvent for the PEO domain. In DMF, surface-modified CdS nanoparticles were tethered to PEO chains by forming hydrogen bonds between the hydroxyl groups of mercaptoethanol and the ethylene oxide groups of PEO. After the solvent was removed, CdS nanoparticles are segregated in PEO domains of bulk SEO, as shown in figure 1 of the Supporting Information (available from [stacks.iop.org/Nano/16/683](http://stacks.iop.org/Nano/16/683)). Subsequently, we prepared 1% CdS/SEO toluene solution. In this approach, toluene is a good solvent for PS, but a poor one for surface-hydroxylated CdS/PEO composites, despite toluene being a good solvent



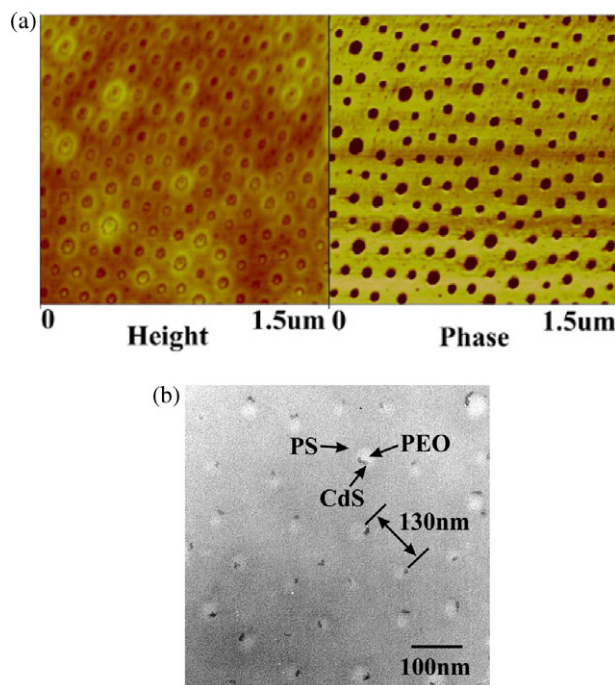
**Scheme 2.** CdS nanoparticles are dispersed selectively in the PEO block of PS-*b*-PEO block copolymer by dipole–dipole interactions.

for PEO. For a solubility test, we had prepared bulk CdS/PEO by the same approach. The colloidal solution of CdS/PEO in toluene appears to be cloudy, indicating a reduction of the solubility of PEO chains in toluene when incorporating CdS nanoparticles. This behaviour can be explained by two factors: first, the PEO chains in CdS/PEO domains are entangled by CdS nanoparticles via hydrogen bonds; second, the hydroxyl group on CdS nanoparticles sequestered in the PEO domains apparently changes the polarity of CdS/PEO, making it insoluble in a presumably good solvent, toluene, for PEO. As a result, a ‘spherical double-brush’ micellar structure could be produced in toluene, with a CdS cluster core and an inner PEO corona covered by an outer PS corona which forms the matrix, as demonstrated in our previous work [18c]. This micellar solution is then spin coated on a carbon-coated silicon wafer to form a micellar thin film. The CdS nanoparticles in each PEO domain are described as a CdS cluster in this study.

### 3. Results and discussion

Two cases of SEO are involved in the incorporation of CdS nanoparticles; they are bulk CdS/HSEO and CdS/LSEO nanocomposites. In bulk CdS/HSEO, spherical CdS/PEO phase is observed by PS matrix, and CdS/PEO cylinders are exhibited in the bulk CdS/LSEO system. The characteristics of bulk CdS/HSEO and CdS/LSEO nanocomposites were reported in our previous studies [18a, 18d]. As demonstrated in these two systems, CdS nanoparticles are selectively segregated in the PEO phase due to the dipole–dipole interactions between the hydroxyl groups on CdS and ethylene oxide groups on PEO chains, as shown in scheme 2.

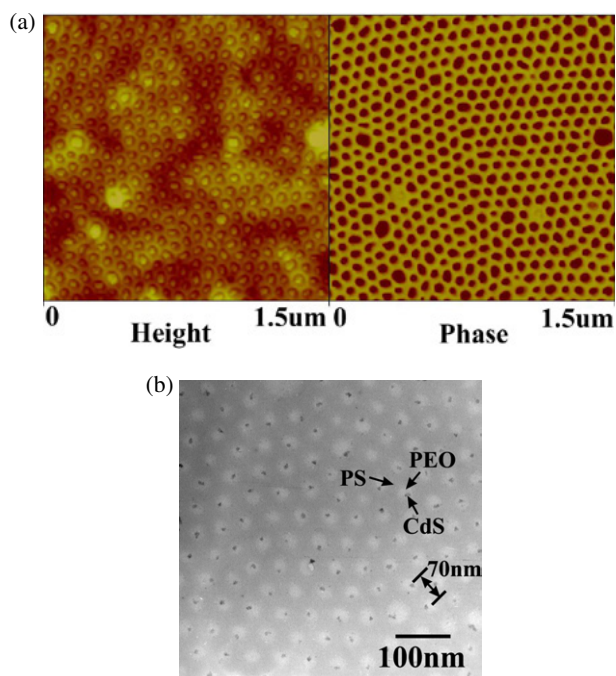
The thin film fabrication is carried out by dissolving CdS/HSEO or CdS/LSEO in toluene to form a micellar solution, which is then dried in air. Figure 1 shows AFM and TEM images of a thin film of CdS/HSEO. In figure 1(a),



**Figure 1.** (a) AFM image of a CdS/HSEO thin film supported on a carbon-coated silicon wafer. (b) TEM image of CdS/HSEO thin film after removal from a carbon-coated silicon wafer with 1% HF solution.

30–40 nm dark regions, representing ordered CdS-including PEO domains, appear in the height and phase contrast images. The inter-domain distance ranges from 120 to 140 nm. This also indicates that the microphase-separated CdS/HSEO thin film forms a monolayer thin film, since the thickness of the CdS/HSEO thin film is smaller than the size of the PEO domains (24.7 versus 30 nm). Figure 1(b) shows a TEM image of the CdS/HSEO thin film after it is removed from the carbon-coated silicon wafer with 1% HF solution. In figure 1(b), there are three distinct regions. The lightest regions, having circular shapes, are PEO domains, and the darkest regions located within the PEO domains are CdS nanoclusters. The matrix, which appears as an intermediate grey, is the PS domain. The contrast in the three domains is caused by differences in the electron density of Cd, ethylene oxide, and styrene. The TEM image shows conclusively that CdS nanoparticles are located mostly within the PEO domain, but close to the interface between PEO and PS domains of the monolayer film, and that the distance between CdS clusters in the nanostructure is about 130 nm. The formation of the structure does not depend sensitively on the film thickness. Thin monolayer films are easier to characterize, and have greater potential for optical applications.

In the case of a lower molecular weight PS block in LSEO, similar patterns appear, but again with a difference. Figure 2(a) shows the topology of the CdS/LSEO thin film in height and phase contrast images. Owing to the similar molecular weights of the PEO blocks in LSEO and HSEO, the size of the CdS-including PEO phase of the CdS/LSEO thin film is about 35 nm, which is close to that in the case of CdS/HSEO. The CdS/LSEO thin film is also a monolayer film because the thickness of the thin film of CdS/LSEO is about 30 nm.



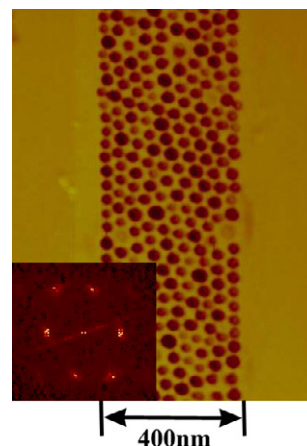
**Figure 2.** (a) AFM image of a CdS/LSEO thin film supported on a carbon-coated silicon wafer. (b) TEM image of a CdS/LSEO thin film after removal from carbon-coated silicon wafer with 1% HF solution.

Figure 2(b) shows a TEM image of the CdS/LSEO monolayer thin film after it is removed from the carbon-coated silicon wafer. The inter-domain distance between CdS-including PEO domains, however, is smaller than that in the CdS/HSEO thin film (70 versus 130 nm), due to the smaller molecular weight of the PS block in LSEO.

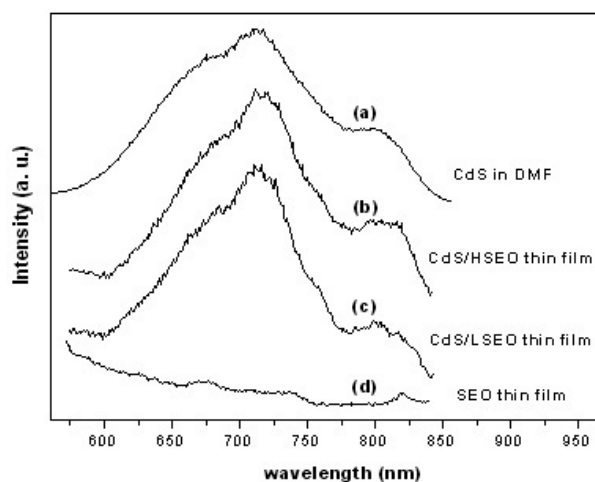
Close examination of figures 1(b) and 2(b) reveals that some CdS nanoparticles are not located in the centre of the PEO domains, but instead appear at the interface. Moreover, these CdS nanoparticles seem to clump together in the PEO domains. A few portions of CdS nanoparticles are not fully within the PEO domain and a small fraction of CdS close to the interface may be due to a reduction in interfacial energy [6, 21].

Long-range order in the block copolymer has been obtained by using substrate templating methods [11, 23, 24], but no previous experimental study on nanoparticles/block copolymers has been carried out. We have used substrates consisting of thermally oxidized silicon, patterned with square-wave-profile grooves (400 nm in width and 40 nm in depth), produced using electron beam lithography and reactive ion etching. Figure 3 shows phase contrast AFM images of an as-spun CdS/LSEO film on a patterned substrate containing these grooves. CdS/PEO domains within the 400 nm wide grooves orient parallel to the side of the groove, indicating that a long-range order of the nanocomposite has been obtained. The size of the CdS/PEO domains is about 36 nm. The distance between confined CdS/PEO domains within the grooves is about 55 nm, which is slightly smaller than that of CdS/PEO on the smooth substrate.

Figure 4 shows photoluminescence spectra of CdS in DMF and thin films of CdS/HSEO, CdS/LSEO, and pure LSEO. Photoluminescence spectra were obtained with a Hitachi F4500 fluorescence spectrophotometer at room temperature.



**Figure 3.** Phase contrast AFM images of a CdS/LSEO thin film on a patterned substrate with 400 nm wide grooves.



**Figure 4.** Photoluminescence spectra of CdS in (a) DMF, thin films of (b) CdS/HSEO and (c) CdS/LSEO, and (d) pure LSEO.

The photoluminescence of CdS in DMF has been reported previously [22]. CdS clusters sequestered in PEO domains of CdS/HSEO and CdS/LSEO thin films appear to retain their luminescence characteristics, as compared to those in DMF. The main peak, corresponding to the surface-trapped fluorescence, occurs at a wavelength of 715 nm, and it is caused by defects of CdS nanocrystals or the surface modification by mercaptoethanol. The minor peak at 818 nm may be due to another defect in the CdS nanoparticles or pure SEO.

#### 4. Conclusions

In conclusion, we have provided a method for controlling the spatial position of CdS nanoclusters using a specific interaction between surface ligands and one block of a self-assembled diblock copolymer template by first selectively dispersing these nanoparticles in one particular block of a diblock copolymer, in bulk, and then using solvent selectivity to sequester CdS nanoparticles in the block copolymer thin film. The inter-domain distance of the nanoclusters can be altered by changing the molecular weight of the other block of the diblock copolymer. Long-range order in CdS/LSEO thin films has been obtained using a patterned substrate. The incorporated

nanoparticles retain their luminescence characteristics, as in the pure state. The CdS nanoparticles can be replaced by other nanoparticles or quantum dots, as long as proper surface ligands can be found.

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