

**Spatial Position Control of CdS Nanoclusters using a Self-assembled  
Diblock Copolymer Template**

by

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# Report Documentation Page

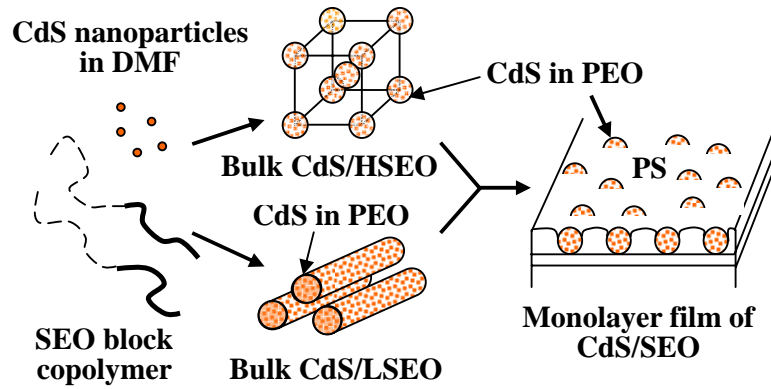
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14. ABSTRACT <b>Core-shell structured quantum dots (QDs) such as CdSe/ZnS and Au/CdSe/ZnS nanoparticles are synthesized, and enhanced photoluminescent properties are observed in these nanoparticles as compared to that of bare core nanoparticles. For controlling the spatial position of nanoparticles with block copolymers, it was found that the mercaptoethanol modified CdS nanoparticles have a preferential binding to the poly(ethylene oxide) block of polystyrene-b-poly(ethylene oxide) diblock copolymer, with a saturated concentration of 7% in volume fraction, and the composites have a better thermal stability. When CdS clusters have been sequestered into the PEO domain, the morphology of CdS/PS-b-PEO composite thin film was found to be transformed from cylinders to spheres by the presence of hydrogen bonds between surface-hydroxylated CdS and PEO. In another case Pyridine-modified CdSe nanoparticles were found to selectively disperse in the poly(4-vinylpyridine) block of polystyrene-b-poly(4-vinylpyridine) diblock copolymer, with their luminescence retaining as in the pure state. Moreover, the photoluminescence and electroluminescence of the dendritic copolyfluorene are dramatically enhanced when a few percentage of CdS nanoparticles was incorporated.</b>					
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## ***Abstract***

We report a method to fabricate 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 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.

The fabrication of periodically ordered, two-dimensional nanostructures on the scale of ten to a hundred nanometers 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.<sup>1-4</sup> 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 nanometers,<sup>5</sup> 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 by Thomas et al.<sup>6</sup> The incorporation of nanoparticles into block copolymers, however, would lead to more complicated block copolymer morphologies than their pristine state, as predicted by Balazs' group,<sup>7</sup> 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 of 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<sup>8</sup>, GaAs<sup>9</sup> and Au/Cr<sup>10a</sup> have been produced; magnetic cobalt dot arrays<sup>11</sup> 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<sup>12</sup> and magnetic Co<sup>10b</sup> 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 micro-phase separated diblock copolymer films.

Quasi-regular arrays of Au clusters,<sup>13</sup> Co and Fe arrays,<sup>14</sup> and self-assembly of both Au and Fe<sub>2</sub>O<sub>3</sub> nanoparticles<sup>15</sup> 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.

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. Taking advantage of capillary force, Russell et al. were able to screen different sizes of pre-synthesized CdSe nanoparticles with a nanoporous PS-*b*-PMMA template.<sup>16</sup> Schrock et al. sequestered CdSe nanoclusters within

phosphine-containing domains of a diblock copolymer.<sup>17</sup> 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), leading to a morphological transformation of the block copolymer in bulk form.<sup>18</sup> 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.<sup>19</sup> To our knowledge, the sequestration of presynthesized 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 letter, we report a method to fabricate 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 bulk, and then using solvent selectivity to sequester CdS nanoparticles in the block copolymer thin film. This method 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.<sup>20</sup>

In the present study, CdS nanoparticles were synthesized by reacting cadmium acetate dihydrate ( $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ ) and sodium sulfide ( $\text{Na}_2\text{S}$ ) with mercaptoethanol ( $\text{HSC}_2\text{H}_4\text{OH}$ ) 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 ( $\text{MW}_{\text{PS}}/\text{MW}_{\text{PEO}} = 125\text{k}/16.1\text{k}$ ), termed HSEO, and a low ratio ( $\text{MW}_{\text{PS}}/\text{MW}_{\text{PEO}} = 19\text{k}/12.6\text{k}$ ), termed LSEO, were used. Proper 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 the CdS/HSEO and CdS/LSEO nanocomposite films. 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 sec on carbon-coated silicon wafers. After drying, the thin films were characterized by atomic force microscopy (AFM). The procedure to prepare ordered CdS nanoparticles in a thin block copolymer template is demonstrated in Scheme 1. During 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. CdS nanoparticles are therefore selectively dispersed into the PEO domains



after evaporation of DMF. The CdS nanoparticles in each PEO domain are defined as a CdS cluster in this study. Subsequently, by using solvent selectivity, toluene, which is a good solvent for PS but a poor one for PEO, is used to form micelles with CdS/PEO-core and PS-shell structures in the solution. This micellar solution is then spin-coated on a carbon-coated silicon wafer to form a thin film.

Two cases of SEO are involved in the incorporation of CdS nanoparticles; they are CdS/HSEO and CdS/LSEO nanocomposites. Figure 1(a) and 1(b) show transmission electron microscopy (TEM) images without staining and differential scanning calorimetry (DSC) results of 14% CdS in HSEO (with respect to the weight of the PEO block), respectively. Judging by the electron density contrast, the dark spherical CdS-included PEO domains in HSEO display body-centered cubic or simple cubic structures, which have been described in detail elsewhere.<sup>18</sup> CdS nanoparticles are selectively dispersed in the PEO phase due to dipole-dipole interactions between the hydroxyl groups of mercaptoethanol and ethylene oxide, as shown in Scheme 2. Further evidence of the incorporation of CdS in PEO can be found in the thermal behavior of HSEO. DSC shows the melting temperature ( $T_{mPEO}$ ) to be a first-order transition with a zero first derivative of the heating curve, whereas the glass transition temperature ( $T_{gPEO}$ ) of amorphous PEO is a second-order transition with a zero second derivative of the heating curve. The bottom trace in Figure 1(b) shows that  $T_{mPEO}$  for

crystalline PEO of HSEO occurs at 42.9°C, with an undetectable glass transition. The top trace in Figure 1(b) shows that in CdS/HSEO,  $T_{mPEO}$  is depressed to an unobservable state, and  $T_{gPEO}$  appears at -56.6°C due to an increase in the portion of amorphous PEO, which results from crystallization inhibition by CdS. A similar melting point depression of PEO by nanoparticles has been reported in the case of PEO/montmorillonite nanocomposites.<sup>21</sup> In the case of 28% CdS/LSEO, Figure 1(c) shows that PEO domains incorporated with CdS display a cylindrical morphology. Figure 1(d) shows that hindered crystallization of PEO by CdS also occurs in the case of CdS/LSEO, but with a slight difference. A small dip (~40°C) in the DSC curve of CdS/LSEO may correspond to another population of non-integrally folded crystallites.<sup>22</sup>

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 2 shows AFM and TEM images of a thin film of CdS/HSEO. In Figure 2(a), 30 to 40 nm dark regions, representing ordered CdS-included 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 vs. 30 nm). Figure 2(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 2(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 gray, 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 3(a) shows the topology of the CdS/LSEO thin film in height and phase contrast images. Owing to the similar molecular weight of the PEO block in LSEO and HSEO, the size of the CdS-included 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 3(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-included PEO domains, however, is smaller than that in the CdS/HSEO thin film (70 vs. 130 nm), due to the smaller molecular weight of the PS block in LSEO.

Close examination of both Figure 2(b) and 3(b) reveals that some CdS nanoparticles are not located in the center of the PEO domains, but instead appear at the interface.

Moreover, these CdS nanoparticles seem to clump together in the PEO domains. This can be explained by the fact that there are two types of dipole-dipole interaction forces involved in the nanocomposite system. The first type is due to mutual dipole-dipole attractions between the hydroxyl groups of mercaptoethanol on CdS nanoparticles.

The second type occurs between the free hydroxyl groups of mercaptoethanol on CdS and poly(ethylene oxide). CdS nanoparticles clump together by the first type of dipole-dipole interaction, but small CdS clusters disperse in the PEO domain by the second type of dipole-dipole interaction. 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<sup>6, 23</sup> and the excluding effect brought by some small crystallization in the PEO domain.

Long-range order in the block copolymer has been obtained by using substrate templating methods,<sup>11, 25, 26</sup> 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 4 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 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 5 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. The photoluminescence of CdS nanoparticles has been reported previously.<sup>24</sup> 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 occurs at a wavelength of 715 nm, and it is caused by defects in CdS. The minor peak at 818 nm may be due to another defect in the CdS nanoparticles or pure SEO.

In conclusion, we have provided a method to control 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.

### ***Acknowledgment***

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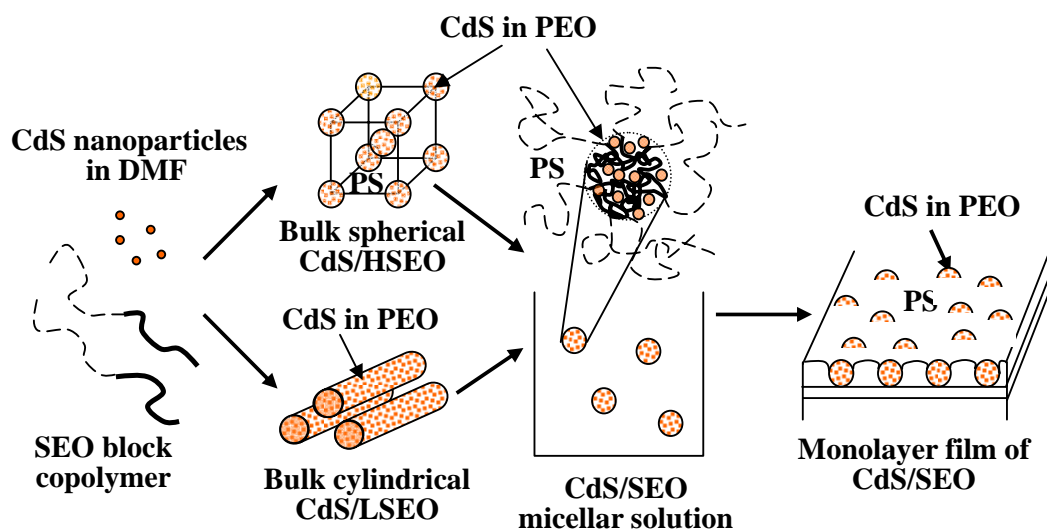
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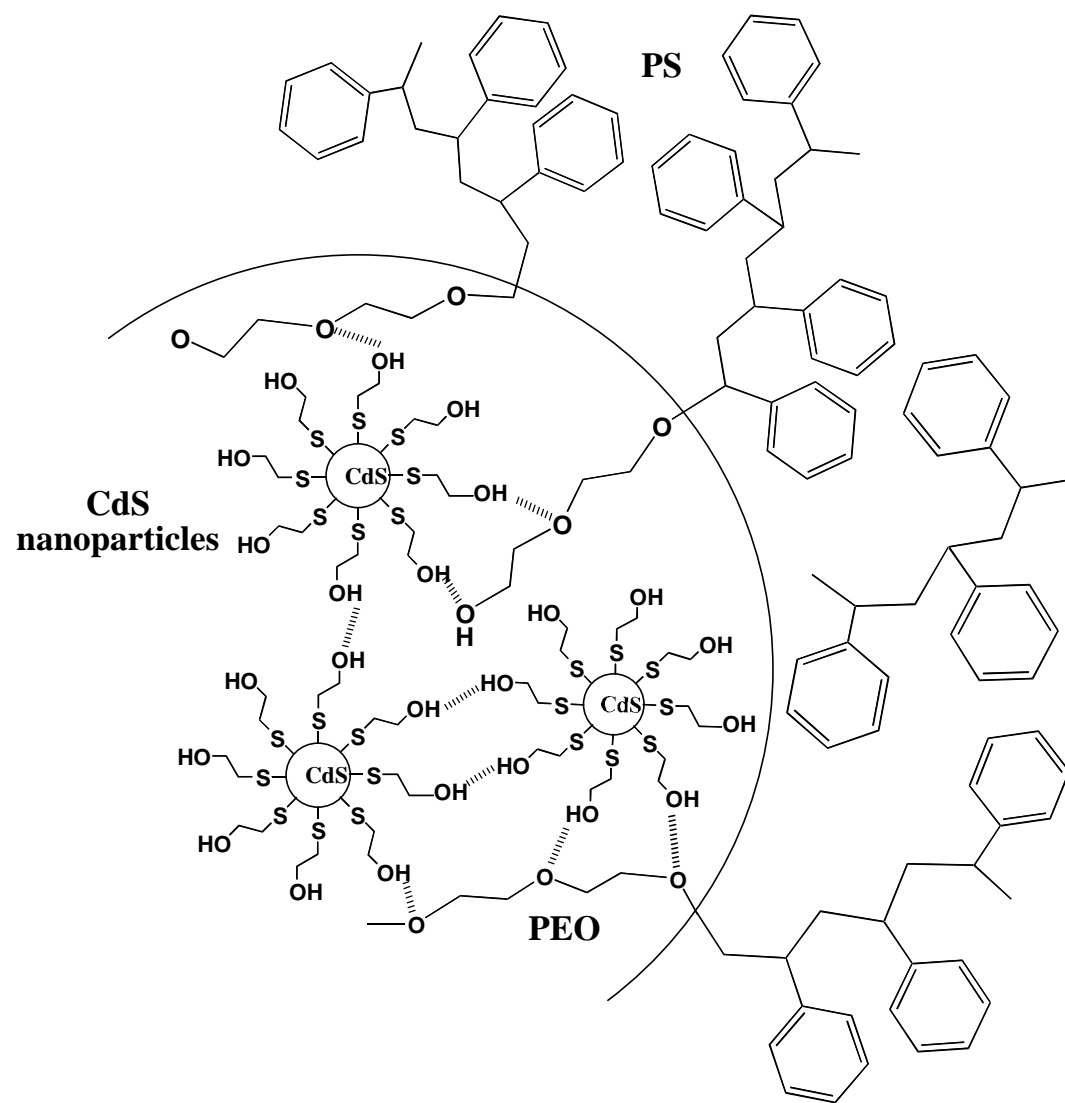


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**Scheme 1: Fabrication of an ordered array of pre-synthesized nanoparticles using a block copolymer template by spin-coating a micellar solution. Nanoparticles are held in the cores of the micelles.**



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



### Figure Captions:

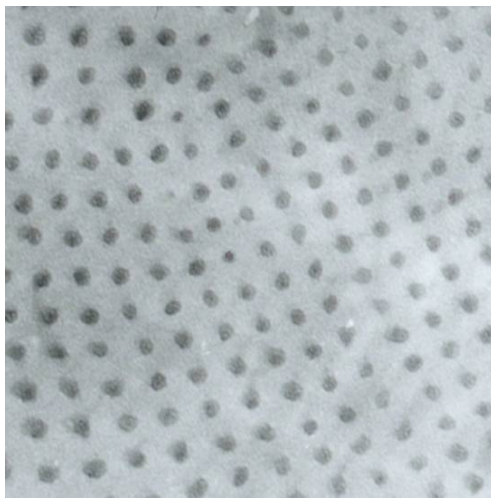
Figure 1 (a) TEM image of microtomed thin specimens from bulk CdS/HSEO (published previously, see reference 18) (b) DSC results of CdS/HSEO and pure HSEO. After being held at 150°C for 1 min and then quenched with liquid nitrogen, the samples were heated from -100°C to 150°C at 10°C/min. (c) TEM image of microtomed thin specimens from bulk CdS/LSEO. (d) DSC results of CdS/LSEO and pure LSEO.

Figure 2 (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.

Figure 3 (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.

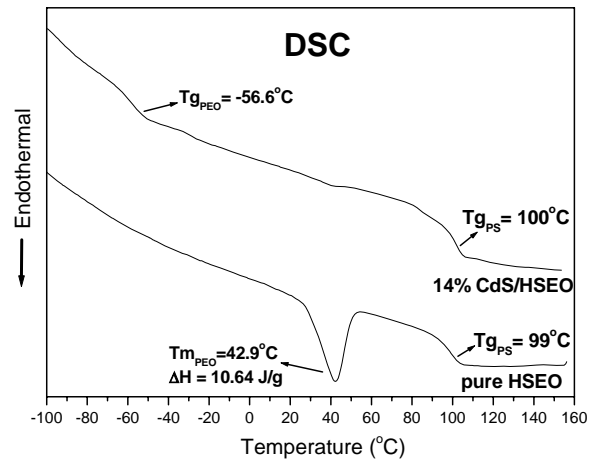
Figure 4 Phase contrast AFM images of a CdS/LSEO thin film on a patterned substrate with 400-nm wide grooves.

Figure 5 Photoluminescence spectra of CdS in (a) DMF, thin films of (b) CdS/HSEO and (c) CdS/LSEO, and (d) pure LSEO.

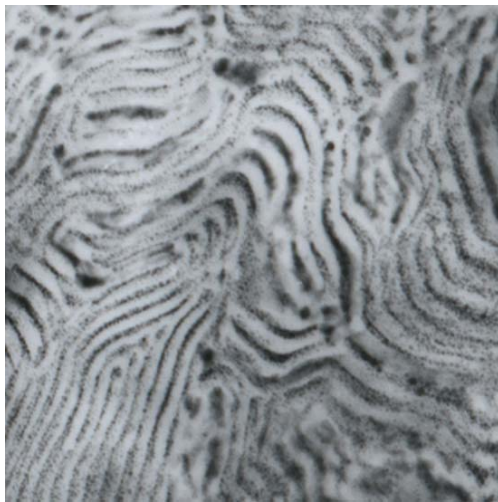


(a)

100nm

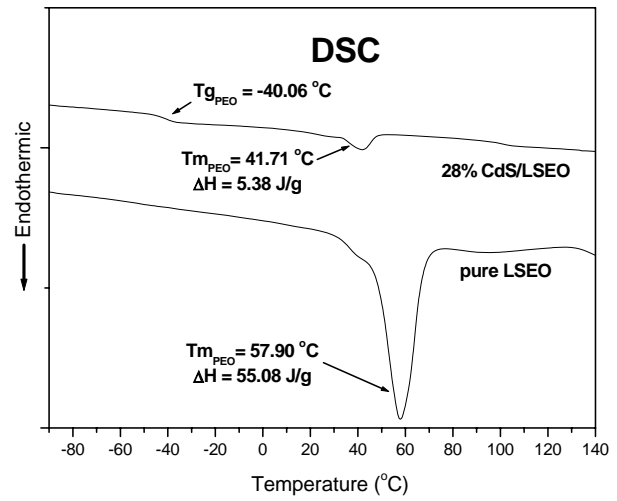


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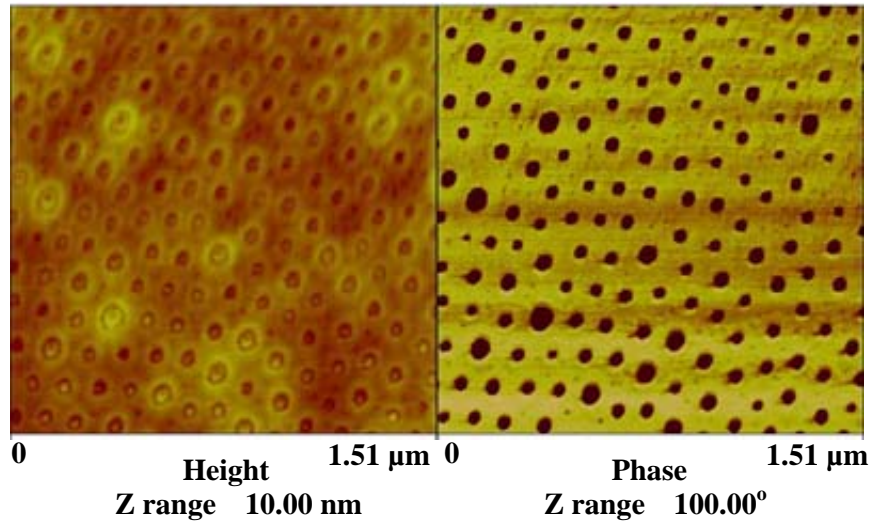
(c)

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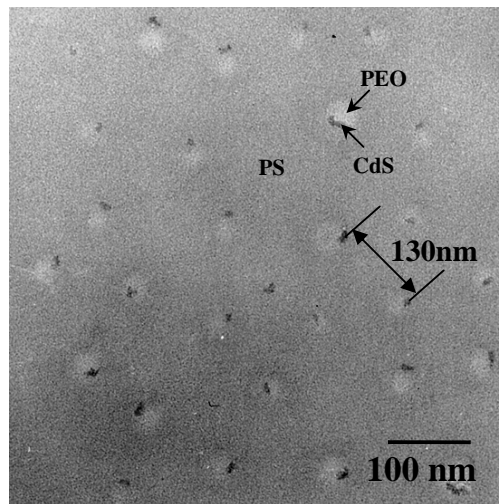


(d)

**Figure 1**

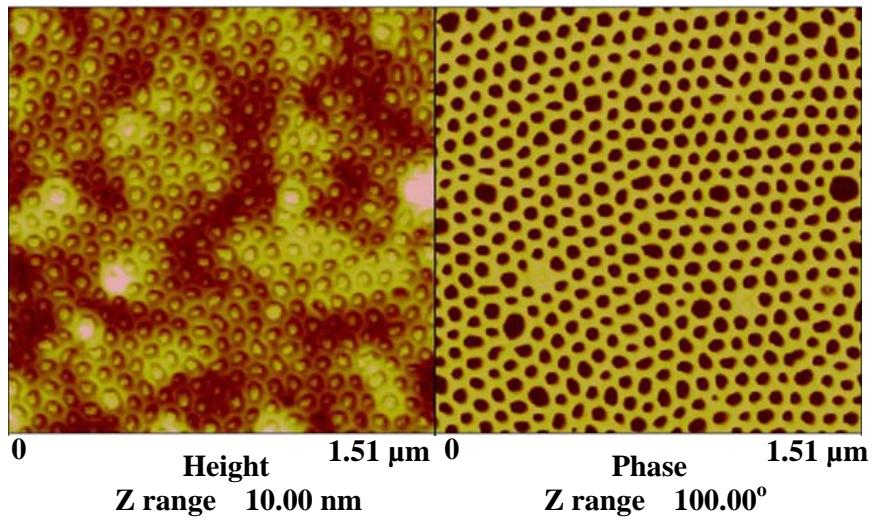


(a)

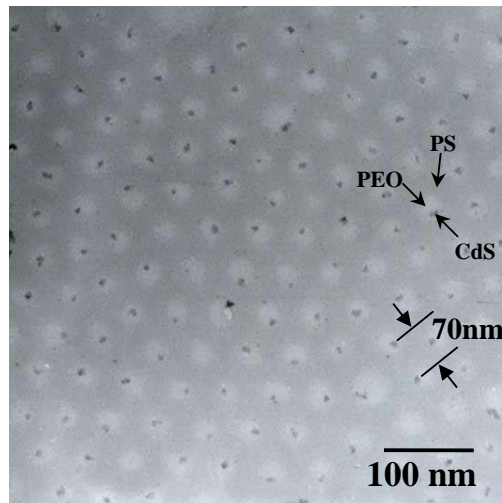


(b)

Figure 2



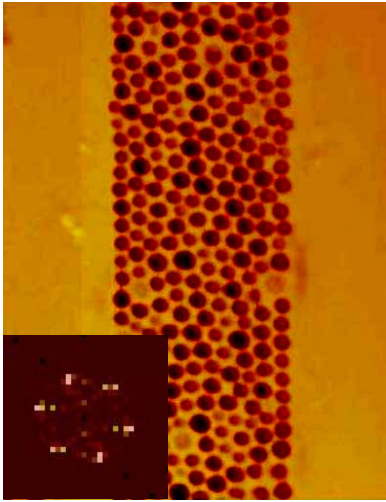
(a)



(b)

Figure 3

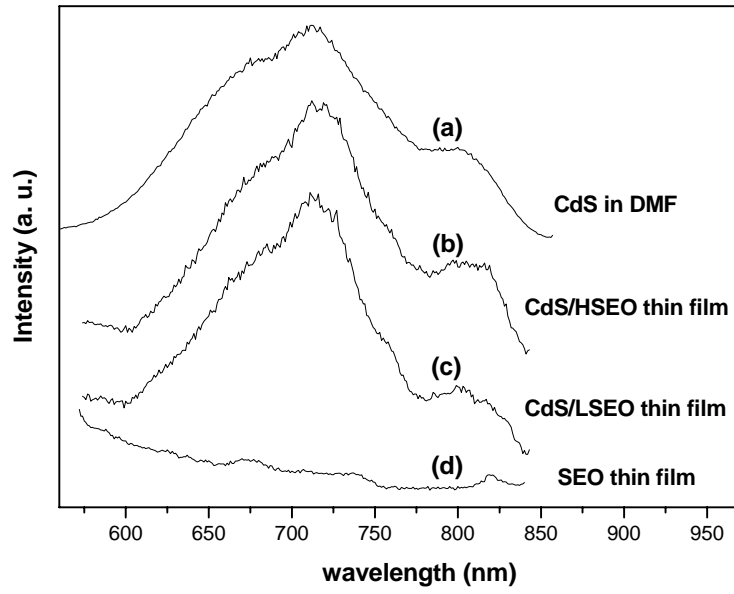
|



400 nm

Figure 4





**Figure 5**