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COMMUNICATIONS

Surface-Functionalized CdSe Nanorods for Assembly in Diblock Copolymer Templates

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Nanoparticles are central to fundamental studies and applications in nanoscience and nanotechnology, due to their novel electronic, luminescent, and magnetic properties that are not present in the bulk.[1−3] Metallic and semiconductor nanoparticles can be prepared as spheres, rods, or multi-arm objects, and significant control over size and size distribution can now be achieved in a number of nanoparticle compositions.[4] To take full advantage of the unique properties of nanoparticles requires a spatial control on both the nanometer length scale of the particles as well as much larger length scales associated with arrays and assemblies. A variety of methods to achieve such control over spherical nanoparticles have been reported, including close-packed superlattices,[5] lithographic methods,[6] and self-assembly techniques.[7−9] Outside the scope of liquid crystalline ordering,[10,11] comparatively little control has been achieved over assembly of rod-like particles.

Changing the shape of nanoparticles from isotropic spheres to anisotropic rods alters their properties and potential applications.[12] For example, CdSe nanorods are interesting for photovoltaic applications since the long axis of the rod provides a continuous channel for transporting electrons, an advantage over spherical nanoparticles where electron hopping between particles would be required.[13] However, effective methods to manipulate nanorods are comparatively few and limited in scope. Moreover, the ligand surface modification of CdSe nanorods is much more limited than that of spherical particles. To use nanorods to their full potential in applications, surface functionalization is necessary to gain control over their lateral distribution and positional orientation.

Here we describe the synthesis of poly(ethylene oxide)-functionalized CdSe nanorods that are ideally suited for assembly in diblock copolymer templates. Polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymer thin films were used to generate templates of two types, one with cylindrical nanoscopic pores standing perpendicular to an underlying substrate, and the other with nanoscopic channels lying parallel to an underlying substrate.[14,15] The PEO-covered CdSe nanorods, 20−60 nm in length and 7−8 nm in diameter, were assembled selectively within the nanometer scale channels and pores of these templates. These assemblies were prepared by floating the polymer template onto an aqueous solution of the nanorods. In this process, the nanorods become trapped within the channels and pores. The length of the nanorods relative to the channel or pore width controlled the orientation and lateral position of the nanorods.

The nature of the ligands on the nanorods was found to be critically important to the success of the assembly. Alkane-covered CdSe nanorods prepared by state-of-the-art techniques[16] are not compatible with this aqueous flotation method, and attempts to perform similar assemblies in organic solvents are complicated by swelling of the template and the low surface tension of organic solvents. Functionalization of CdSe nanorods with PEO ligands provides nanorod solubility in water, enabling the assembly by the flotation method described here. Moreover, the surface activity of PEO that directs the nanorods to the water−air interface proved to be of key importance for the assembly process. Other water-dispersible CdSe nanorods, for example, those covered with 11-mercaptoundecanoic acid (MUA),[17] are not integrated into the templates using these flotation procedures.

To prepare PEO-covered CdSe nanorods, alkane-covered rods (50 mg) were refluxed in anhydrous pyridine (2 mL) for 24 h, then precipitated into hexane. The pyridine-covered nanorods were heated to 60 °C for 10 h in a methanolic solution of thiol-terminated PEO (MW 2100) to give a dark red homogeneous solution. The PEO-covered CdSe nanorods were purified by precipitation into ether; these nanorods displayed solubility properties characteristic of PEO, dispersing effectively in water, chloroform, toluene, and methanol. The ^{1}H NMR spectrum of the nanorods in $CDCl_3$ clearly showed PEO (methylene resonance at 3.7 ppm), and the UV−vis spectrum in chloroform showed a band edge absorption centered at 650 nm. Absorption at ~650 nm is identical to the alkane-covered nanorods in chloroform, indicating that the ligand exchange altered only the solubility properties of the nanorods, rather than their spectral absorption properties.

PS-*b*-PMMA thin film copolymer templates on silicon wafers were prepared with 30 nm wide channels (from 260 000 g/mol PS-*block*-PMMA with 50 wt % PS) or 30 nm diameter pores (from 140 000 g/mol PS-*block*-PMMA with 68 wt % PS). The templates were floated onto aqueous HF (5 vol %) and retrieved with a 400 mesh TEM copper grid. The template-covered copper grid was then floated onto an aqueous solution of PEO- or MUA-covered CdSe nanorods, with the template film facing down into the nanorod solution. The templates were left on the nanorod solutions for 10−12 h, then removed and washed with water. Transmission electron microscopy (TEM) (JEOL 2000FX) was used to examine the resulting distribution of nanorods in the templates.

The film flotation method used in these studies, depicted in Figure 1, exposes the pores and channels of the templates only to the surface of the aqueous nanorod solution. Immediately after removal of the template from the aqueous nanorod solution, the PEO-covered CdSe nanorods are found to accumulate both within the channels and on PS surface of the template. However, rinsing with water removes the nanorods from the PS surface, leaving nanorods only within the channels. This was observed for all four of the nanorod samples investigated, specifically those with average lengths of 20, 25, 35, and 60 nm. Two representative images of the 25 and 35 nm nanorods in lamellar templates are shown in Figure 2a and 2b. These images also reveal the tendency of the nanorods to align along the channel walls. It should be stressed that the separation distance between the confined nanorods, as dictated by the distance between the channels, is not limited to that shown in Figure 2, but rather is adjustable by choice of diblock copolymer molecular weight, in which higher molecular weight diblock copolymers provide larger separation distances.

10.1021/ja058615p CCC: $33.50

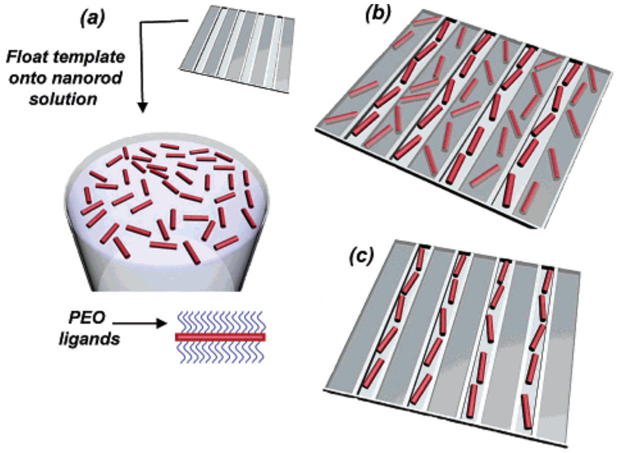

Figure 1. Schematic of assembly process: (a) flotation of template onto aqueous solution of PEO-covered nanorods; (b) PEO-covered nanorods within the channels and on the PS template surface; (c) nanorods isolated in the channels following rinsing of the template.

Nanoporous templates prepared from PS-*b*-PMMA diblock copolymers having cylindrical microdomains were also used in nanorod assembly experiments. When the nanorod length is smaller than the diameter of the pores in the template, the nanorods segregate within the cylindrical pores after the template is floated onto the aqueous nanorod solution and washed with water. The efficiency of this assembly is apparent in Figure 2c, where CdSe nanorods 20 nm in length have assembled within a template having 30 nm diameter pores. Each of the pores contains several nanorods, and no preferred orientation of the nanorods is observed, due to the symmetry of the pore cross-section. As the rod length exceeds the pore diameter, penetration of the rods into the pores becomes difficult, and the density of rods in the template is considerably lower as shown in Figure 2d.

In contrast, water-soluble MUA-covered CdSe nanorods could not be deposited into copolymer templates with any measure of success. MUA-covered nanorods appear only sporadically on the template films, as shown in the TEM image of Figure 2e. In addition, MUA-covered nanorods show no selectivity for either domain of the templates. This result demonstrates that water solubility of the nanorods, while needed to enable the desired assembly, is not sufficient to drive the process. Rather, the surface activity of PEO is required[18] to aid the segregation of the nanorods to the water−air interface, where they are absorbed by the templates. The entrapped PEO-covered CdSe nanorods are held effectively by the template, rather than removed by rinsing with water, due to their affinity for the water−air interface. Moreover, the channels and pores in the copolymer templates are hydrophobic and, as such, are not wet by water.[19] On the other hand, the PEO-covered nanorods resting on the polystyrene film are removed easily by rinsing. The lack of surface activity in the MUA-covered nanorods leaves no driving force for assembly into the template material using this convenient flotation technique.

In summary, PEO-covered CdSe nanorods were prepared for the purpose of their application to a film flotation technique with diblock copolymer templates. This methodology enables an assembly of the nanorods into the templates. The PEO ligand coverage on the nanorods was found to be especially effective for achieving the desired assembly, as other water-soluble rods covered with carboxylate ligands proved unsuitable due to surface energy considerations. This methodology causes a sequestration of the nanorods into defined regions of a patterned surface, an area of importance when considering electronic and photoactive applications of nanorods of this type.

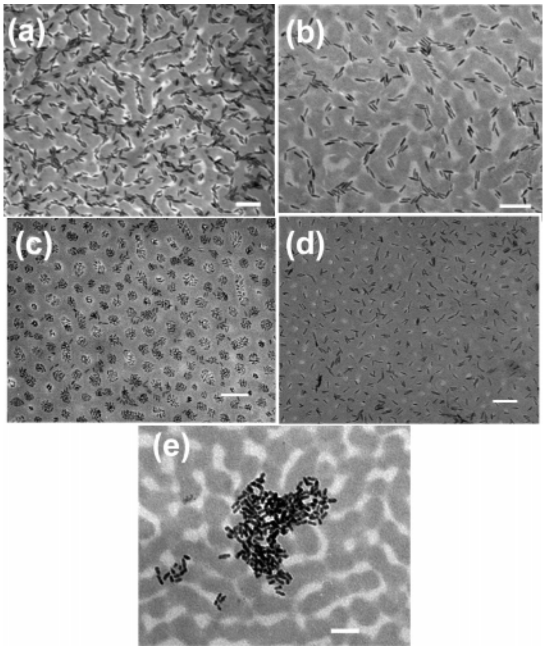

Figure 2. TEM micrographs showing distribution of CdSe nanorods on lamellar and cylindrical templates after washing with water: (a) 25 nm (in length) PEO-covered nanorods in lamellar template; (b) 35 nm PEO-covered nanorods in lamellar template; (c) 20 nm PEO-covered nanorods in cylindrical template; (d) 40 nm PEO-covered nanorods in cylindrical templates; and (e) attempted assembly using 25 nm MUA-covered nanorods with lamellar template. Scale bars = 100 nm.

Acknowledgment. The authors acknowledge support from an NSF-CAREER award (CHE-0239486), the DOE (DE-FG-02-96ER45), the NSF-supported MRSEC at UMass Amherst (DMR 9400488), an Army Research Laboratory MURI award, and the Army Research Office (W911NF041 0233).

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JA058615P