

Template-Controlled Synthesis of Wire-Like Cadmium Sulfide Nanoparticle Assemblies within Core–Shell Cylindrical Polymer Brushes

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A controlled fabrication of wire-like assemblies of cadmium sulfide (CdS) nanoparticles has been developed based on a template technique. Well-defined amphiphilic core–shell cylindrical polymer brushes were used as single molecule templates, utilizing the coordination of cadmium ions with carboxylate groups in the core of the brush. Formation of CdS nanoparticles inside the polymer brush was carried out via the reaction of the coordinated Cd^{2+} ions with H_2S . This route resulted in wire-like CdS nanoparticle assemblies of about 4–5 nm in diameter and about 170 nm long. After the formation of the CdS nanoparticles, the polymer brush resumes its original chemical structure and morphology and therefore can be used as template again. The obtained polymer–semiconductor nanocomposite is soluble and stable in organic solvents, and potential applications may be found due to the quasi-1D structure of the assembly of CdS nanoparticles. In principle, the present synthetic approach is of general applicability to various metals, metal chalcogenides, and oxides.

Introduction

The synthesis and study of inorganic nanoparticles has become a major interdisciplinary research area in recent years,^{1–5} resulting from their numerous applications in various areas. Particularly, research on semiconductor nanoparticles with size-dependent optical and electronic properties is motivated by potential uses in the fields of nonlinear optics,^{6,7} light-emitting devices,⁸ solar cells,⁹ biological labels,^{10,11} electronics,^{12,13} and catalysis,¹⁴ among others.⁴ When the particle approaches a size of a few nanometers, its diameter is comparable to or less than that of the bulk semiconductor exciton (the exciton diameter of cadmium sulfide is

5–6 nm¹⁵), such that quantum confinement of electron–hole pairs increases the band gap relative to that in the bulk materials. Therefore, the control of particle size allows tuning of the band gap to give the desired electronic and optical properties. Research has led to the fabrication of a number of devices.

Many synthetic methods for the preparation of inorganic nanoparticles have been reported, including controlled precipitation,¹⁶ seeded growth,¹⁷ and confined synthesis in structured templates.^{3,4} Template-directed synthesis represents a straightforward route to nanoparticles. In this approach nanoparticles are generated in situ with the morphology complementary to that of the template. A number of templates have been used, including hard solid templates such as zeolites,¹⁸ glasses,¹⁹ layered solids,²⁰ molecular sieves,^{21,22} alumina membranes,⁵ and self-organized media such as micelles (of surfactants and block copolymers)^{23–30} and vesi-

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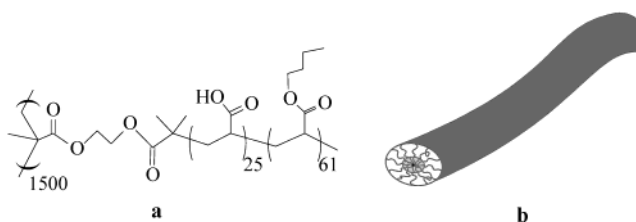
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cles.^{31–33} In the case of hard solid templates, the fabricated nanoparticles are embedded inside the matrix and thus it is hard to remove the templates after the synthesis. It is also difficult for the further processing of the nanoparticles. In contrast, templates such as micelles and vesicles can produce and stabilize dispersed nanoparticles which simplifies postprocessing. Ordered (such as hexagonal) arrays of nanoparticles have been obtained via a polymeric micellar route, and the templates can be removed completely by oxygen plasma.^{29,34} However, the instability of these templates limits their potential applications. Once the templates decompose under harsh conditions (such as elevated temperatures or change of solvent), the nanoparticles will lose their stabilization layer and may undergo aggregation.

Recently, fabrication of inorganic nanoparticles in solid polymer matrixes has attracted more and more attention^{35–42} because the combination of inorganic nanoparticle and polymer provides a simple route to stable and processable materials integrating the promising properties of both components. However, these composites normally cannot be redissolved while preserving the colloidal state of nanoparticles. Among polymeric templates, the single polymer molecule represents an important type because isolated nanocomposites based on a single molecule can be obtained, which have very desirable processing characteristics. Dendrimers,⁴³ DNA,^{44,45} and polyelectrolytes⁴⁶ have been used as single molecule templates for inorganic nanoparticle synthesis. Basically, all the applications based on single polymer molecule can be applied to the single molecule–nanoparticle composite as well. For example, a single DNA molecule was used as a template for the growth of a conductive silver nanowire, which was used as a nanocircuit to connect macroscopic electrodes.⁴⁴

Very recently, Schmidt et al. succeeded in synthesis of gold nanoclusters and nanowires using polymer

Scheme 1. (a) Chemical Structural Formula of the Polymer Brush Used in the Present Paper, [AA₂₅-*n*BA₆₁]₁₅₀₀; and (b) Its Schematic 3-D Structure



brushes with poly(2-vinylpyridine) core and polystyrene shell as templates.⁴⁷ However, the length distribution of those brushes was broad because they were synthesized via conventional radical polymerization of block macromonomer. Thus, control of the length of fabricated linear nanocluster assemblies or nanowires could not be achieved.

In this paper we describe the use of an amphiphilic core–shell cylindrical polymer brush with a poly(acrylic acid) (PAA) core and a poly(*n*-butyl acrylate) (P*n*BA) shell as template for the synthesis of wire-like assemblies of cadmium sulfide (CdS) nanoparticles. The structure of the polymer brush is shown in Scheme 1. It is well-defined in both length and diameter. Obviously this amphiphilic core–shell polymer brush can be regarded as a unimolecular cylindrical micelle, thus it has the advantages of both micellar templates and single molecular templates. Compared to block copolymer micelles, it has a much better stability against the change of exterior environment because one end of the side chain is linked to the backbone of the polymer brush via a strong covalent bond. Moreover, the shell of the polymer brush protects the fabricated nanoparticles from aggregation, which cannot be achieved by other single molecule wire-like templates such as polyelectrolyte and DNA.

In our method, the amphiphilic polymer brush acts as both a nanoreactor for the formation of CdS nanoparticles and a template to direct the distribution of nanoparticles inside the polymer. The core of the polymer brush carries carboxylate groups (after neutralization of PAA) capable of coordinating with Cd²⁺ ions. The coordinated Cd²⁺ ions were subsequently sulfidized to form a string of nanoparticles along the backbone of the polymer brush. Both chains of separated nanoclusters and continuous nanowires could be obtained, which are of equal interest.⁴⁵ The hydrophobic shell of the polymer brush offers the solubility of the final composite in organic solvents, in addition to the stabilization of nanoparticles.

The combination of precise size control, solubility, stability, and easy processing makes the cylindrical polymer brush a unique template for the preparation of wire-like assemblies of semiconductor nanoparticles.

Experimental Section

All chemicals were of analytical grade and used as received without further purifications. The synthesis of polymer brushes was reported earlier.^{48,49} The degree of polymerization (DP) of

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the backbone was determined by membrane osmometry and the DP of side chains was calculated from monomer conversion of polymerization.

The synthesis of CdS nanoparticles inside the core-shell polymer brush proceeded as follows. First, 29.7 mg of the polymer brush, [AA₂₅-*n*BA₆₁]₁₅₀₀ (containing 0.077 mmol of acrylic acid), was dissolved in 20 mL of a mixture of methanol and chloroform (*v/v* = 1/1). Then 75 μ L of 1.0 M NaOH aqueous solution was added to neutralize the polymer core. After stirring for 6 h, 0.042 mmol of CdAc₂·2H₂O (0.133 M solution in methanol) was added and the reaction mixture was stirred overnight. A transparent solution was obtained.

To remove the uncoordinated Cd²⁺ ions, dialysis was tried first. This was done in a mixture of methanol and chloroform (*v/v* = 1/1) using regenerated cellulose membrane tube (molecular weight cutoff = 6–8000). The solvent was changed every 3 days. After 20 days of dialysis, free Cd²⁺ salt was still observed via scanning force microscopy (SFM), indicating that dialysis is a very slow process. To remove the residual free Cd²⁺, precipitation was carried out by addition of water. The precipitate was washed with methanol twice, and finally redissolved in 30 mL of methanol/chloroform (*v/v* = 1/1) mixture. The turbid dispersion of the polychelate of the polymer brush and Cd²⁺ ions was stable in this solvent for several hours without appreciable precipitation, however, most polychelates settled to the bottom 1 day later. The supernatant was used to check the purity of the polychelate, and no free Cd²⁺ salt was observed by SFM.

The turbid dispersion of the polychelate was bubbled with N₂ for 1 h to remove the oxygen, and then H₂S was introduced under N₂ atmosphere. The color of the dispersion turned yellow instantly, indicating the formation of CdS. An optically clear solution was finally obtained, which was bubbled with N₂ for 3 h. The yellow solution was stable over several months.

Scanning force microscopy (SFM) images were recorded on a Digital Instruments Dimension 3100 microscope operated in tapping mode. The samples were prepared by dip-coating from dilute solutions of the polymer brush, polychelate (supernatant), and hybrid of the polymer brush and CdS nanoparticles in methanol/chloroform (*v/v* = 1/1) mixture onto freshly cleaved mica.

Transmission electron microscopy (TEM) images were taken on a LEO 922 OMEGA electron microscope operated at 200 kV (Figures 2a and b, and 3b–d), or a Zeiss CEM 902 electron microscope operated at 80 kV (Figure 3a). A 5- μ L droplet of a dilute solution, with the concentration similar to that for SFM samples, was dropped onto a copper grid (300 mesh) coated with a carbon or Formvar/carbon film, followed by drying at room temperature. The same sample was also used for electron diffraction (ED) measurements, which were carried out on a Philips CM 20 TEM operated at 200 kV. Energy-dispersive X-ray (EDX) analysis was performed on a LEO 1530 field emission scanning electron microscope using an X-ray detector. The samples were obtained by applying a drop of a dilute solution onto a silicon wafer followed by drying at room temperature.

UV/visible absorbance spectra of samples in methanol/chloroform (*v/v* = 1/1) were recorded on a Perkin-Elmer Lambda 15 UV/visible spectrophotometer. The spectrum from a quartz cuvette containing solvent was subtracted from all sample spectra.

Results and Discussions

Advances in living polymerizations enable us to synthesize polymers with well-defined structures and sizes. An amphiphilic cylindrical polymer brush with hydrophilic poly(acrylic acid) (PAA) core and hydrophobic poly(*n*-butyl acrylate) (*Pn*BA) shell, used as the

template in this paper, was synthesized via combination of anionic polymerization and atom transfer radical polymerization (ATRP), as reported in our previous paper.⁴⁸ A brief description of the polymer synthesis is given as follows. The backbone of the polymer brush, poly(2-hydroxyethyl methacrylate) (PHEMA), was synthesized via anionic polymerization of the silyl-protected monomer (2-(trimethylsilyloxy)ethyl methacrylate) followed by the cleavage of the protecting trimethylsilyloxy groups. Through esterification of the all pendant hydroxy groups of PHEMA with α -bromoisobutyryl bromide, ATRP initiating groups were attached to the backbone. Sequential ATRP of *tert*-butyl acrylate (*t*BA) and *n*-butyl acrylate (*n*BA) initiated by the pendant α -bromoester groups on the backbone formed the block copolymer (*Pt*BA-*b*-*Pn*BA) side chains. Finally, the selective hydrolysis of the *tert*-butyl groups of the *Pt*BA block resulted in the amphiphilic core-shell cylindrical polymer brush. Because of the living/controlled nature of both anionic polymerization and ATRP, the length of brush as well as the diameters of core and shell are well-defined. As shown in Scheme 1a, the polymer brush used here has 1500 block copolymer arms consisting of 25 acrylic acid units in the core block and 61 *n*-butyl acrylate units in the shell block (defined as [AA₂₅-*n*BA₆₁]₁₅₀₀). The polydispersity indices (M_w/M_n) of the backbone and the polymer brush are 1.08 and 1.29, respectively.

A typical scanning force microscopy (SFM) image of the polymer brush is shown in Figure 1a. Wormlike cylinders are clearly visible. A statistical analysis of the SFM image shows that the number- and weight-average lengths of the polymer brushes are L_n = 166 nm and L_w = 180 nm, respectively, with a polydispersity index L_w/L_n = 1.08, which is identical to the polydispersity index of the backbone. As shown in Figure 1a, one can easily see the core-shell structure in the phase image but not in the corresponding height image. The difference in hardness between the relatively hard PAA (glass transition temperature, T_g = 106 °C⁵⁰) core and the very soft *Pn*BA (T_g = -54 °C⁵¹) shell provides the apparent contrast in the phase image, thus the core-shell structure shown in the right side of Figure 1a should correspond to that of the polymer brush. Because of the very low glass transition temperature of *Pn*BA, the shell of the polymer brush is totally collapsed on mica at room temperature and thus its height is undetectable.⁴⁸ The SFM image clearly shows that these polymer brushes are structurally well-defined single molecule templates for the nanoparticle fabrication, and the controls of both the dimension of nanoparticle and the length of wire-like nanoparticle assembly can be achieved.

Our approach in using the cylindrical polymer brush as template for the synthesis of CdS nanoparticles includes three steps, as illustrated in Scheme 2. In the first step (a→b), the PAA core of the polymer brush was neutralized using NaOH. It has been reported that the conversion of carboxylic acid to sodium carboxylate results in large increases in both the extent and rate of transition metal ion uptake.⁵² Afterward, Cd²⁺ ions were introduced into the core of the polymer brush via ion

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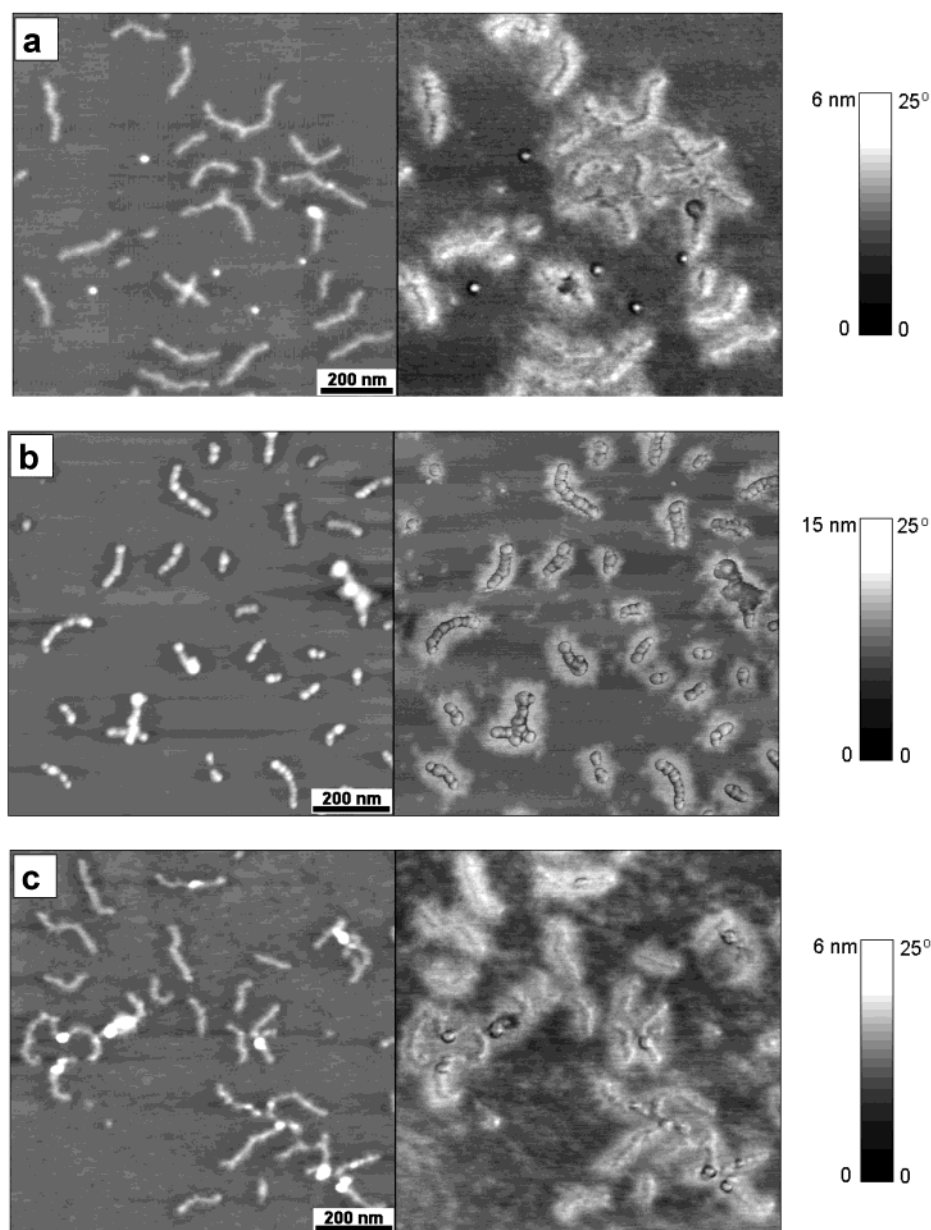


Figure 1. Tapping mode SFM images (left, height; right, phase) of (a) the polymer brush, [AA₂₅-*m*BA₆₁]₁₅₀₀; (b) the polychelate of the polymer brush and Cd²⁺ ions; and (c) the hybrid of the polymer brush and CdS nanoparticles. All the samples were measured on mica.

exchange between Cd²⁺ and Na⁺ (step 2: b→c). The uncoordinated Cd²⁺ ions were removed by either precipitation or membrane dialysis, then the composite of the polymer brush and Cd²⁺ ions, named as polychelate,⁵³ was obtained. In the final step (c→d), H₂S gas was introduced into the dispersion of the polychelate, and CdS nanoparticles were produced, indicated by the instant color change from colorless to yellow. The size of the resulting particles was limited by the amount of Cd²⁺ ions within the polychelate, which in principle can be controlled by varying the core size of the polymer brush, the neutralization extent of the core, and the amount of cadmium salt used.

SFM measurements showed that there was no apparent change in the morphology of the polymer brush before and after neutralization. However, after loading

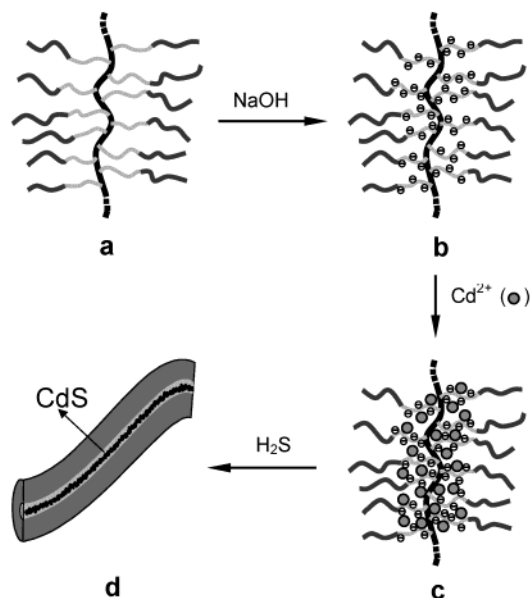
of Cd²⁺ ions, the morphology of the polymer brush changed dramatically. A peculiar “pearl necklace” structure of the polychelate was observed in the SFM image, as shown in Figure 1b. This structure may stem from the “cross-linking” of side chains induced by the coordination between divalent Cd²⁺ ions and monovalent carboxylate groups from different side chains. Similar phenomena were also observed in the polychelate of another polymer brush and Fe³⁺ ions,⁵⁴ and in Fe²⁺ loaded microporous membranes containing PAA grafts in the pores.⁵⁵ In contrast, monovalent ions such as Na⁺ did not induce the formation of the “pearl necklace” structure, simply because the “cross-linking” of different side chains cannot happen. Particularly, the morphology

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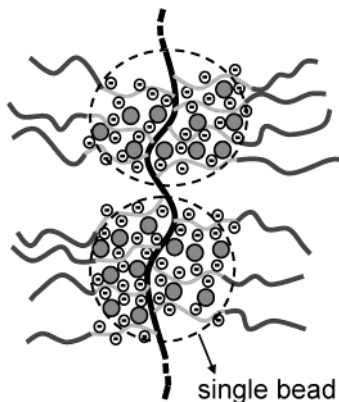
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Scheme 2. Schematic Illustration of the Synthesis of Wire-Like Assembly of CdS Nanoparticles Inside the Cylindrical Polymer Brush: (a) Polymer Brush with PAA Core and PnBA Shell; (b) Neutralized Polymer Brush with Poly(sodium acrylate) Core (Na^+ Is Not Shown); (c) Polychelate of the Brush and Cd^{2+} Ions; and (d) Hybrid of the Brush and Wire-like Assembly of CdS Nanoparticles



Scheme 3. Schematic Illustration of the “Pearl Necklace” Structure of the Polychelate



change was observed solely in the core region, supporting that the Cd^{2+} ions coordinate selectively with the core block of the polymer brush. Moreover, the height of the polychelate is more than two times that of the pure polymer brush, indicating that the loading of Cd^{2+} ions stiffens the polymer brush significantly. Scheme 3 depicts the structure of the polychelate.

The pearl-necklace-like morphology was also observed in the SFM image of pure polymer brushes with PnBA core and polystyrene (PS) shell on mica.⁵⁶ However, in that case the driving force for the morphology formation is different from that for polychelates. On substrate mica, the PS tails in the block copolymer brushes tend to aggregate due to dewetting of PS on mica. While

aggregation of PS occurs, the PnBA chain fragments remain tightly adsorbed on the substrate, leading to the necklace-like morphology. In contrast, smooth contours were observed for the polymer brushes with PAA core and PnBA shell on mica (as shown in Figure 1a), because both PAA and PnBA are tightly adsorbed on the substrate due to their attractive interactions with mica. Thus, the formation of the “pearl necklace” structure of polychelates can be attributed to the “cross-linking” of side chains by Cd^{2+} ions.

Removal of uncoordinated free Cd^{2+} ions via precipitation (or dialysis) ensures that the CdS nanoparticles form solely inside the polymer template. Because of the linking of side chains by Cd^{2+} ions, the solubility of the polymer brush decreased. After precipitation, the purified polychelate could not be completely redissolved in the same solvent for the pure polymer brush, and only a turbid dispersion was obtained. Without stirring, most polychelates precipitated out in 1 day. The supernatant of the polychelate dispersion was used for SFM characterization. One can see more short brushes in the SFM image of the polychelate (Figure 1b), as compared to that of the polymer brush (Figure 1a). This is because long polymer brushes in the polychelate dispersion are easier to precipitate so that there are more short brushes in the supernatant.

After the formation of CdS nanoparticles the “pearl necklace” structure disappeared (Figure 1c), and the morphologies of the obtained hybrid of the polymer brush and CdS nanoparticles was almost the same as that of the pure polymer brush, indicating that the “cross-linking” of side chains induced by inter-side-chain coordination via bridging Cd^{2+} ions vanished. Additionally, the height of the hybrid is similar to that of the polymer brush, indicating that the CdS nanoparticles formed inside the polymer brush must be very small such that they did not change the overall dimension of the polymer template significantly. As expected, the polymer brushes recovered their original solubility after the formation of CdS nanoparticles, and a clear yellow solution was obtained. This yellow solution was stable for several months (stored in a dark place with stirring), remaining free of precipitate or turbidity.

Without staining, the contrast for the polymer brush is too weak to render an image via transmission electron microscopy (TEM). However, a good contrast was observed when Cd^{2+} ions were loaded, as shown in Figure 2a. Wormlike dark domains in the bright-field TEM image of the polychelate present direct proof for the successful coordination of Cd^{2+} ions with carboxylate groups in the core of the polymer brush. The diameter of the wormlike objects is about 5–6 nm, which should correspond to that of the core of the polymer brush. A closer examination of the TEM image of the polychelate (Figure 2b) clearly shows a string of spherical dark grains, which again confirms the “pearl necklace” structure of the polychelate as shown in the SFM image (Figure 1b).

Figure 3 shows some typical TEM images of the hybrid of the polymer brush and CdS nanoparticles on different substrates. Compared to that of the polychelate, a higher contrast was observed due to the formation of CdS nanoparticles. Wire-like assemblies (with a diameter of 4–5 nm) of CdS nanoparticles were clearly

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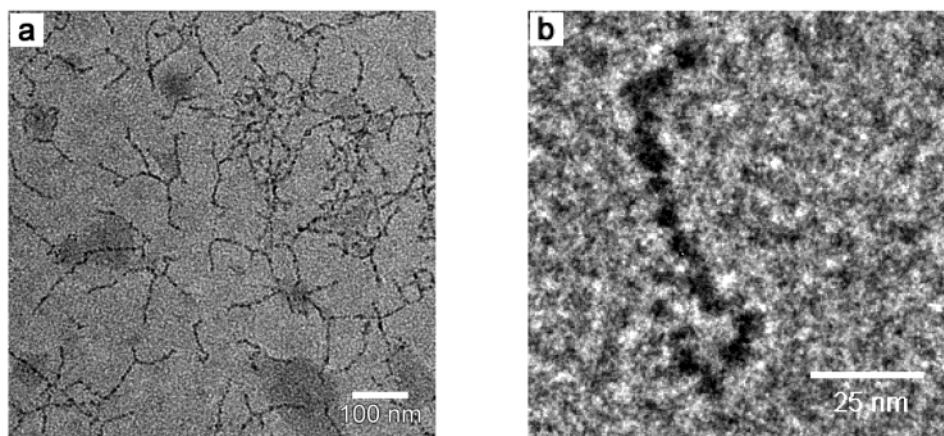


Figure 2. Nonstained TEM images of the polychelate of the polymer brush and Cd^{2+} ions on Formvar/carbon-coated copper grids.

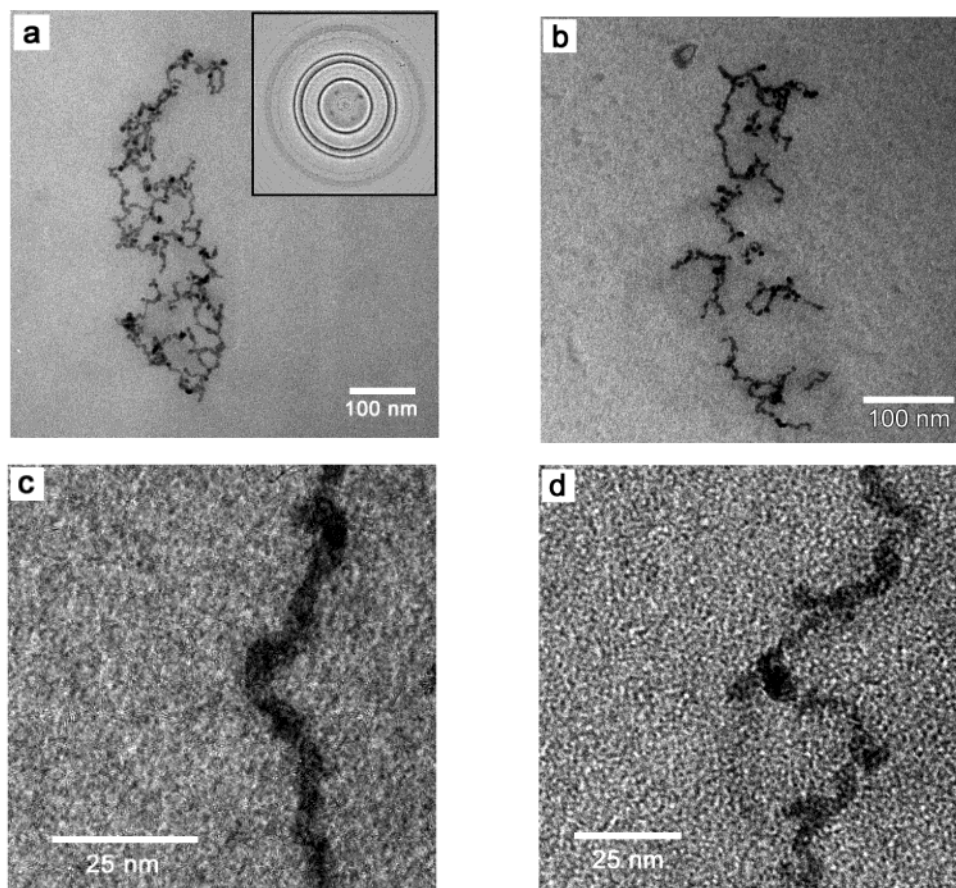


Figure 3. Nonstained TEM images of wire-like assembly of CdS nanoparticles: (a) on Formvar/carbon-coated copper grid; and (b–d) on carbon-coated copper grid. Inset in Figure 3a is the electron diffraction pattern.

visible. The diameter of these wire-like assemblies is slightly less than that of the core of the polychelate, indicating the more compact structure of CdS nanoparticles. Both continuous nanowires with regular shape (Figure 3c) and wire-like assemblies of discrete nanoparticles (Figure 3d) are observed. Although the precursors of CdS nanoparticles, Cd^{2+} ions, are confined in separated “beads”, CdS can diffuse and grow to form a continuous phase due to its weaker bonding to the carboxylic acid groups compared to that of Cd^{2+} . The nucleation, growth, and interconnection of CdS nanoparticles inside the polymer brush is a complex process, and further investigation is needed to control the

distribution of the nanoparticles along the polymer brush. Nevertheless, the carboxylic acid coordination sites are regenerated after the formation of CdS nanoparticles; therefore, it is possible to perform multi-loading of Cd^{2+} ions followed by the treatment with H_2S . Thus, the discrete CdS nanoparticles might be further connected to generate continuous nanowires.

The electron diffraction pattern of the CdS nanoparticles, as shown in the inset of Figure 3a, supports the presence of a polycrystalline structure, which is often obtained in template-directed methods.⁵ The d spacings calculated from the rings in the electron diffraction pattern are 3.29, 2.02, and 1.73 Å, which correspond to

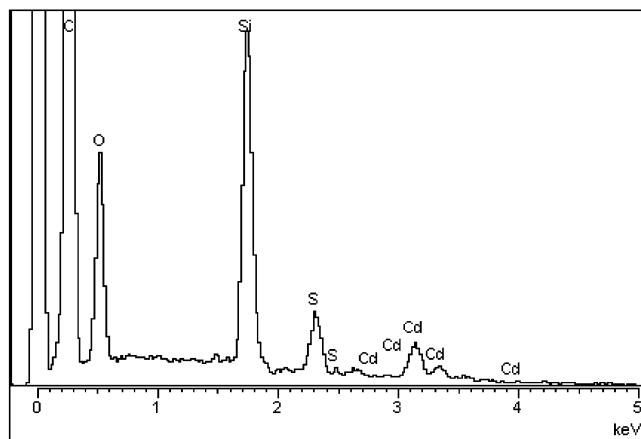


Figure 4. EDX spectrum of the hybrid of the polymer brush and CdS nanoparticles.

the reported d spacings for lattice planes (111), (220), and (311) of the cubic (zinc blende) phase of CdS.^{57,58}

Elemental analysis of the hybrid was carried out using the energy-dispersive X-ray (EDX) analysis of a scanning electron micrograph. Figure 4 shows the EDX spectrum of the hybrid of the polymer brush and CdS nanoparticles, which confirms the presence of cadmium and sulfur. The average atom ratio of Cd/S over the selected area is 1.1, quite close to the theoretical value.

It is known that CdS particles larger than about 6 nm (the size of an exciton in the bulk) start to absorb at the wavelength of about 515 nm. With decreasing particle size, the absorption threshold shifts to shorter wavelengths as a result of quantum confinement effects. Figure 5 shows the UV/visible absorption spectrum of the hybrid of the polymer brush and CdS nanoparticles. Considering the pure polymer brush has no absorption in the observed wavelength range,⁵⁴ the absorption shown in Figure 5 can be attributed exclusively to the CdS nanoparticles. The absorption spectrum illustrates characteristics similar to those of CdS colloids formed via other techniques: an absorption onset at 500 nm, a shoulder at around 450 nm, and a steep rise below 300 nm.²⁴ As expected, the absorbance edge ($\lambda_e = 478$ nm) of CdS nanoparticles in the polymer brush is blue-shifted relative to that of bulk CdS, indicating the small particle size.

As mentioned before, the core of the polymer brush is reprotonated after the formation of CdS nanoparticles, therefore it is possible to perform further reactions. For example, loading of other metal ions may be used for surface modification of the CdS nanoparticles and core-shell, and onion-type nanoparticles might be obtained.⁴³

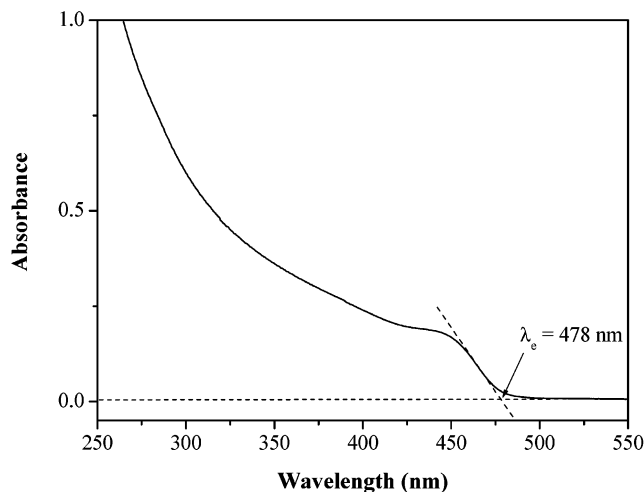


Figure 5. UV/visible spectrum of the hybrid of the polymer brush and CdS nanoparticles.

Additionally, reneutralizing the acrylic acid units with NaOH will increase the stability of the hybrids in organic solution, since the solubility of poly(sodium acrylate) in organic solvents is much lower than that of poly(acrylic acid).

Conclusions

Using the amphiphilic core-shell cylindrical polymer brush with PAA core and P n BA shell as template, wire-like assemblies of CdS nanoparticles were successfully synthesized under mild solution conditions, as confirmed by SFM, TEM, EDX, and UV/visible spectroscopy. The well-defined polymer template provides good control of the formation of CdS nanoparticles and the solubility of the hybrids in organic solvents, which might be very important in some applications. Because of the promising combination of polymeric properties (stability, elasticity, and processability) with those of semiconductor nanoparticles, we might expect some interesting applications based on this hybrid material.

The reaction scheme presented here is not restricted to semiconductor nanoparticles, but can also be used for the preparation of metal or metal oxide particles. The fabrication of magnetic nanoparticles inside the polymer brush is under investigation and the results will be published soon.

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