Amphiphilic ABC Triblock Copolymer-Assisted Synthesis of Core/Shell Structured CdTe Nanowires

Haijun Niu,[†] Liwei Zhang,[‡] Mingyuan Gao,[*,†] and Yongming Chen[*,‡]

Key Laboratory of Colloid, Interface Science and Chemical Thermodynamics, and
State Key Laboratory of Polymer Physics and Chemistry, Joint Laboratory of Polymer Science
and Materials, Institute of Chemistry, The Chinese Academy of Sciences, Zhong Guan Cun,
Bei Yi Jie 2, Beijing 100080, China

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A new type of amphiphilic ABC triblock copolymer, poly(acrylic acid)$_{33}$−poly(styrene)$_{47}$−poly(ethylene oxide)$_{113}$ (PAA$_{33}$−PS$_{47}$−PEO$_{113}$), was designed to assist the synthesis of core/shell structured CdTe nanowires via a one-step synthetic route. The PAA block was adopted to capture cadmium ions as the precursor of CdTe. Due to the bivalent coordination of Cd^{2+}, the copolymer in dioxane/H_2O formed micelles with Cd^{2+}−polychelate cores. Then CdTe nanocrystals were obtained within the micelles after introduction of NaHTe into the micelle solution. Transmission electron microscopy experiments revealed that the CdTe nanocrystals obtained simultaneously formed "pearl-necklace" aggregates in solution possibly driven by dipole interactions between neighboring particles, and then single crystalline CdTe nanowires upon reflux. Accompanying this morphology change, a phase transition from cubic zinc blende to wurtzite structure was observed by selected-area electron diffraction. The aggregation of the PS block in dioxane with a certain amount of H_2O enabled the PS blocks to form a densely packed shell on the CdTe nanowires whose typical size is 700−800 nm in length and 15−20 nm in width. The third block of PEO was employed to render the finally formed CdTe nanowires dispersibility.

Introduction

One-dimensional (1D) nanomaterials such as nanorods and nanowires have attracted increasing attention because they are not only fundamentally interesting but also potentially useful.[1−3] Over past years, different synthetic approaches for 1D nanomaterials have been developed, such as template-directed method,[4] vapor-phase approach,[5] vapor−liquid−solid (VLS) growth,[6] solution−liquid−solid (SLS) technique,[7] solvothermal synthesis,[8] solution-phase growth based on capping reagents,[9] self-assembly,[10] and size reduction.[11] Nevertheless, each method has its own merits and inevitable limitation.[12] Therefore, to develop different methodologies remains an important subject of synthetic chemistry for 1D nanomaterials.

Up to now, in the family of II−VI semiconductor nanomaterials, although the preparation of CdTe rods and terapods has been extensively studied,[13,14] there are relatively limited reports on the preparation of 1D CdTe nanowires. For example, Guo and co-workers[15] reported the preparation of CdTe nanowire arrays by dc electrochemical deposition using porous aluminum oxide as template. Although this hard-template approach is very effective in controlling the final shape of CdTe nanowires, the resultant nanowires are hardly dispersible. Apart from the hard-template method, a solvothermal route was also successfully used in the preparation of CdTe nanowires by employing adequate coordinating solvents, such as ethylenediamine.[16,17] However, the products obtained were characterized by low purity, low yield, and poor uniformity in morphology. Moreover, the solvothermal process is inherently complex, and the growing process of 1D materials in autoclaves is difficult to monitor. Recently Kotov and co-workers found out that uniformly sized CdTe nanocrystals can also form nanowire structures via dipole−dipole interaction after the surface-capping thiols are partly removed.[18] They also succeeded in coating CdTe nanowires with SiO_2.[19] Additionally, Rogach et al. have obtained CdTe nanowires by the growth of luminescent CdTe nanocrystals in a phosphate buffer solution.[20] Generally speaking, to coat nanomaterials with inert materials may favor their chemical and mechanical

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[*] To whom correspondence should be addressed. E-mail: gaomy@iccas.ac.cn. FAX: 0086 10 8261 3214.

[†] Key Laboratory of Colloid, Interface Science and Chemical Thermodynamics.

[‡] State Key Laboratory of Polymer Physics and Chemistry.

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stability and enable 1D nanomaterials to be dispersible in media and thus provide the possibility to manipulate the nanowires in single wire levels. Up to now, many candidate materials, such as silica[19] and polymers,[21] have been used to coat nanowires by various methods. But most processes are carried out after the formation of nanowires. Therefore, developing a one-step synthetic route for coating nanowires during their formation remains a very interesting subject.

It is well-known that amphiphilic block copolymers can simultaneously form self-assembled nanostructures, such as rod, wire, lamella, sphere, vesicle, and LCM (large compound micelle);[22−24] therefore they are potentially useful as soft templates for regulating nanometer-sized inorganic materials.[12] For example, cylindrical polymer brushes with different structures were used to induce the formation of Au and CdS nanowires and nanochains by Schmidt[25] and Müller,[26] respectively. But the 1D nanomaterials obtained are generally characterized by polycrystalline structures. Apart from the cylindrical copolymers, linear diblock and triblock copolymers of AB and ABA types also showed potentials in controlling the formation of 1D structures of semiconductor and metal nanomaterials.[27,28] However, there is no example of using ABC type triblock copolymers as templates to obtain 1D nanomaterials with core/shell structure so far.

In this paper, we report our investigations on the preparation of CdTe nanowires coated with an amphiphilic triblock copolymer of poly(acrylic acid)$_{33}$−poly(styrene)$_{47}$−poly(ethylene oxide)$_{113}$. This copolymer was designed according to the different properties of each block. The PAA block was used to combine with Cd^{2+} ions. Since bivalent cadmium ions could coordinate with carboxylic groups from different polymers, they cross-linked the copolymers to form micelles with Cd^{2+}-rich cores. The reaction with NaHTe in dioxane/H_2O turned the Cd^{2+} ions into CdTe nanoparticles in micelles. Upon reflux, core/shell structured CdTe nanowires were obtained on which the PS block finally formed a densely packed shell. The PEO block provided the eventually formed CdTe nanowires with aqueous dispersibility.

Experimental Section

Chemicals. *N*,*N*,*N*′,*N*′,*N*″-Pentamethyldiethylenetriamine (PMDETA, 99%) was purchased from Aldrich. Anhydrous styrene (St) and *tert*-butyl acrylate (*t*BA) were dried by CaH_2 and distilled under reduced pressure before use. Similarly, anhydrous anisole was washed with 10% NaOH solution and then dried by $CaCl_2$ before distillation. Trifluoroacetic acid (TFA, 99%) from Fluka was used as received.

Al_2Te_3 (99.5%) was purchased from CERAC Inc. $CdCl_2{\cdot}2.5H_2O$ (99+%), $NaBH_4$ (99%), H_2SO_4 (+98%), and NaOH (96+%) were commercially available products and used without further purification. 1,4-Dioxane (Beijing Chemical Co., A.R.) was refluxed in the presence of $NaBH_4$ for 3 h to eliminate peroxides and then distilled before use.

Preparation of PAA$_{33}$−PS$_{47}$−PEO$_{113}$ Triblock Coplymer. The triblock copolymer of poly(ethylene oxide)−poly(styrene)−poly(acrylic acid), specifically PEO$_{113}$−PS$_{47}$−PAA$_{33}$, was synthesized with sequential atom transfer radical polymerization (ATRP) of styrene and *t*BA using PEO$_{133}$−Br as initiator. PEO$_{133}$−Br was prepared according to a previous report by the reaction of poly(ethylene oxide) methyl ethers (M_n ca. 5000, Alfa) with 2-bromoisobutyryl bromide (Aldrich) in the presence of triethylamine.[29]

Synthesis of PEO$_{113}$−PS$_{47}$−Br. A 25 mL Schlenk flask containing PEO$_{113}$−Br (1.2 mmol) and CuBr (0.6 mmol) was purged thoroughly with N_2 and then sealed with a rubber stopper. After the mixture was bubbled with N_2 for 30 min, a mixture solution of PMDETA (1.2 mmol), St (0.12 mol), and anisole (13.9 mL) was transferred into the Schlenk flask with a syringe. Then the flask was placed in an oil bath of 100 °C to allow the polymerization to take place. Three hours later, the reaction mixture was cooled to room temperature. The polymerization was terminated by exposing the reaction mixture to air. The catalyst was removed by filtration through alkaline alumina using anisole as eluent. The polymer was obtained by precipitation using ether. After being dried at 40 °C under vacuum, it was characterized by GPC (gel permeation chromatography) and then used for the next step in polymerization.

Synthesis of PEO$_{113}$−PS$_{47}$−PtBA$_{33}$. All procedures are generally the same as those mentioned for the preparation of *PEO$_{113}$−PS$_{47}$−Br*. The typical ingredients are 0.5 mmol of PEO−PS−Br (M_n(GPC) = 10000, M_w/M_n = 1.12), 0.5 mmol of CuBr, 0.5 mmol of PMDETA, and 0.05 mmol of *t*BA.

Preparation of PEO$_{113}$−PS$_{47}$−PAA$_{33}$. PEO$_{113}$−PS$_{47}$−PAA$_{33}$ was obtained by hydrolysis of PtBA block in the PEO−PS−P*t*BA. Typically, PEO−PS−P*t*BA was first dissolved in methylene chloride at 0.08 g/mL. Then TFA was introduced at 5-fold of *t*BA concentration. After reaction at room temperature for 24 h, a precipitate was obtained upon addition of ether into the concentrated solution. The polymer of PEO$_{113}$−PS$_{47}$−PAA$_{33}$ was finally obtained after drying under vacuum at 40 °C for 48 h. NMR results demonstrated that the PtBA block was successfully converted to PAA. The GPC measurements revealed the distribution of molecular weights of the final block copolymers is 1.14 (M_w/M_n). More details on the synthesis and characterizations of PEO$_{113}$−PS$_{47}$−PAA$_{33}$ will be published elsewhere.

Synthesis of CdTe Nanowires. The preparation of CdTe nanowires assisted by triblock copolymer was performed as follows. First, 40 mg of PAA$_{33}$−PS$_{47}$−PEO$_{113}$ (containing 0.11 mmol of acrylic acid) was dissolved in 40 mL of purified dioxane to give a stock solution of about 0.1% (w/w). Then 172 μL of 0.5 M NaOH aqueous solution was added to convert 80% of −COOH groups to −COONa. A 174 μL portion of $CdCl_2$ aqueous solution was added 6 h after the neutralization reaction. The molar ratio between Cd^{2+} and the initial concentration of −COOH was set to 0.3:1. Since bivalent Cd^{2+} ions can coordinate with two monovalent carboxylate groups, they can act as both inter- and intramolecular cross-linking agents. Therefore, after the reaction mixture was stirred overnight, a turbid dispersion of micelles stemming from the Cd^{2+}-cross-linked PAA blocks was obtained and denoted as Micelle-I. The resultant dispersion was then divided into two equal parts. One part was used for turbidity measurements (see Turbidity Measurements). Into the second part of the dispersion, 1.2 mL of deionized water was added dropwise under stirring to precipitate the PS blocks, which further increased the turbidity of the dispersion. The resultant micelle (denoted as Micelle-II) dispersion was degassed for 1 h with N_2 gas before the injection of 323 μL of 0.05 M NaHTe aqueous solution which was prepared according to a previous report.[30] The reaction between NaHTe and Cd^{2+} ions located in the center of the micelles changed the dispersion color to orange and then deep brown 0.5 h later, indicating the formation of CdTe nanocrystals. Then the solution was refluxed for 5 h. During reflux, a certain volume of the refluxed solution was extracted at different time points to monitor the morphology change in resultant CdTe nanomaterials. The finally obtained nanowires

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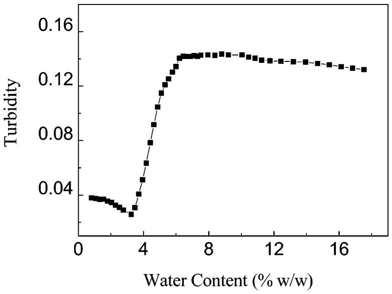

Figure 1. Turbidity diagram of Micelle-I in dioxane against water content.

turned out to be very stable in aqueous dispersion. No structural changes were observed under transmission electron microscopy (TEM) for several months after they were prepared. Nonetheless, different from the thinner nanowires reported by Kotov[18] and Rogach,[20] they do not show photoluminescence.

Turbidity Measurements. The turbidity of the micelle dispersion was monitored by UV−vis absorption spectrometer at $\lambda = 650$ nm upon further addition of water into Micelle-I. In an experiment, the turbidity of 20 mL of micelle solution was measured each time after 50 μL of deionized water was introduced until the turbidity remained nearly constant. The final weight percentage of water in the mixture was 17.5%.

Characterizations. UV−vis absorption spectra were recorded at room temperature with a Cary 50 UV−vis spectrophotometer. The TEM images and selected-area electron diffraction (SAED) patterns were captured on a JEM-100CXII electron microscope operating at an acceleration voltage of 100 kV. High-resolution TEM (HRTEM) images and SAED patterns were performed on a JEM-2010 electron microscope at an acceleration voltage of 200 kV. The energy-dispersive X-ray analysis was measured by EDAX phoenix.

Results

The PAA block from the triblock copolymer was designed to capture Cd^{2+} ions. Due to the cross-linking effect of Cd^{2+} ions, micelles with Cd^{2+}−polychelate[31] cores will be formed. The final size of the micelles should be related to the amount of Cd^{2+} ions loaded, the length of PAA blocks, as well as the water content in the reaction system since water was present during the preparation of the final nanowires. The PS block will aggregate with increasing water content since it is not soluble in water and form a polymer shell structure on the nanometer-sized CdTe obtained. Therefore, further aggregation behavior of the triblock copolymer was studied after the Cd^{2+}−polychelate core was initially formed. The turbidity of Micelle-I as a function of water content was recorded on a UV−vis spectrometer and is shown in Figure 1. The turbidity of Micelle-I decreases slightly before the water content reaches 3.3% and then increases abruptly when the water content is raised to 6.2% (w/w). Thereafter, the turbidity remains nearly constant upon further increase of water content in the whole investigated range. This indicates that in the Micelle-I system the PS blocks completely aggregated when the water content was higher than 6.2% (w/w). According to this result, the water content was controlled above 6.2% for all preparations of CdTe nanoparticles described in this paper.

The aggregation of PS blocks with increasing water content was also demonstrated by TEM measurements. In Figure 2, the TEM images of both Micelle-I and Micelle-II obtained according to that described in the Experimental Section are presented. The weight percentages of water in dispersions of Micelle-I and Micelle-II were 0.83% and 6.4%, respectively. The Micelle-I appears as spherical particles with an average diameter of about 3.1 nm, while Micelle-II is about 4.9 nm as shown in Figure 2. The increase in micelle size with increasing water content can be attributed to the aggregation of PS blocks since the aggregated PS blocks become visible under TEM.[22−24] However, the contrast between the Cd^{2+}−polychelate core and PS shell may not be high enough. Therefore, the PS shell cannot be distinguished from the Cd^{2+}−polychelate core under TEM.

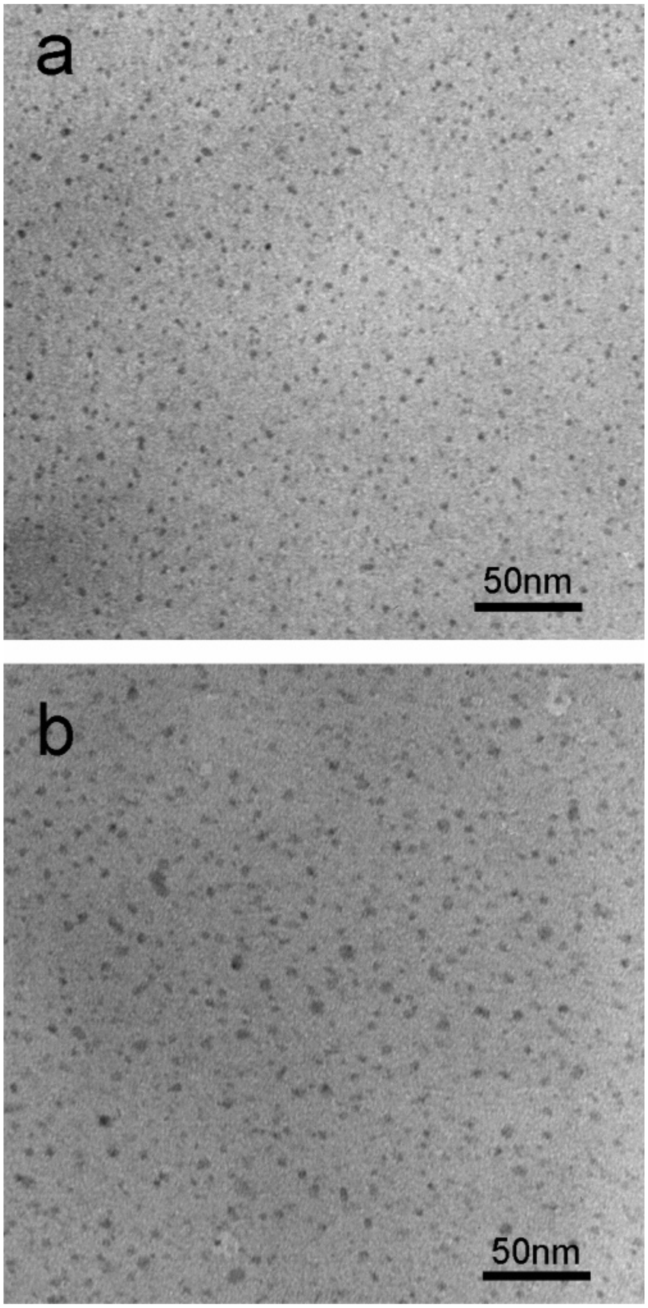

Figure 2. TEM micrographs of Micelle-I (a) and Micelle-II (b) prepared at water content of 0.86% and 6.4% (w/w), respectively.

After the injection of NaHTe aqueous solution into Micelle-II, the total water content reached 7.8%. Half an hour later, the solution of Micelle-II became deep brown and “pearl-necklace” agglomerates with zigzag morphology in great abundance were observed by TEM, as shown in Figure 3a. In general, the “pearl-necklace” structures with an irregular boundary are characterized by indistinct edges under higher magnification as shown in Figure 3b. The diameter of the “pearl-necklace” agglomerates is about

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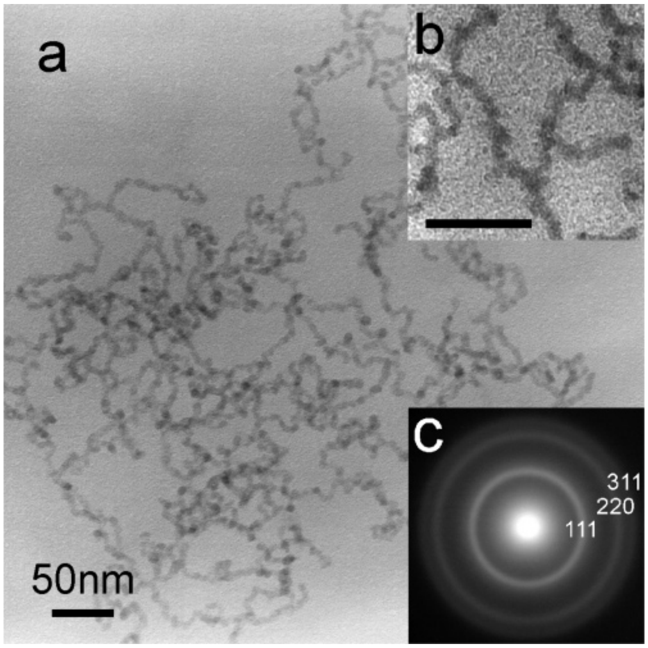

Figure 3. (a) TEM image of the CdTe aggregates formed after introduction of NaHTe into the Micelle-II solution. (b) TEM image of the CdTe aggregates by higher magnification. (c) Selected-area electron diffraction pattern.

4−7 nm, which is very close to the size of Micelle-II, revealing that the formation of CdTe quantum dots did not change the overall dimensions of the micelles significantly. The selected-area electron diffraction patterns of the CdTe agglomerates shown in Figure 3c support a crystalline structure for CdTe. The *d* spacings calculated from the diffraction rings are 3.733, 2.280, and 1.954 Å, corresponding to the reported *d* spacings for lattice planes (111), (220), and (311) for cubic (zinc blende) CdTe.

The "pearl-necklace" CdTe nanochains were completely converted to straight nanowires after they were refluxed for 5 h as shown in Figure 4a. The typical aspect ratio of the nanowires obtained is about 50:1. Under high-resolution TEM (Figure 4b), the nanowires exhibit a single-crystal structure covered by a layer of amorphous materials which might be the copolymers. The lattice plane spacings, calculated from the electron diffraction patterns inserted in Figure 4b, are 3.974 Å *hkl* (100), 2.298 Å *hkl* (110), and 2.005 Å *hkl* (200) and are typical for hexagonal wurtzite CdTe structures. In addition, the spacings of lattice planes, as indicated in Figure 4b are 0.39 and 0.34 nm, are consistent with that for (100) and (101) planes of hexagonal wurtzite CdTe, respectively. These results indicate that the growth direction of the single crystal CdTe nanowires is along the (001) axis. It is known that the presence of crystal defects, such as twins and stacking faults, can dramatically affect contrasts between different parts of single-crystal nanowires,[32] which explains the nonuniform contrast along single nanowires shown in Figure 4a.

On-line elemental analysis of the CdTe nanowires was carried out using the energy-dispersive X-ray (EDX) spectroscopy. The results given in Figure 4c not only confirm the presence of both cadmium and tellurium but also reveal that the atomic ratio of Cd/Te over the selected area is 1:1.02, which is quite close to the feed ratio of Cd/Te.

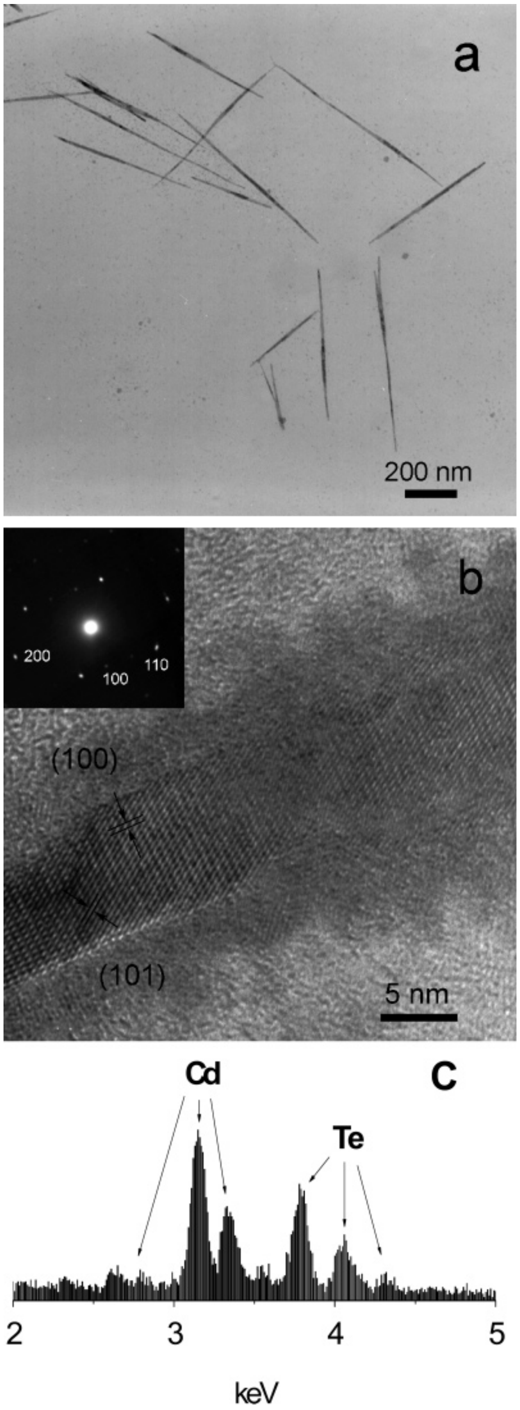

Figure 4. (a) TEM image of the CdTe nanowires obtained after the dispersion of CdTe nanochains was refluxed for 5 h. (b) High-resolution TEM image of single CdTe nanowires shown in image (a). The insert is the corresponding electron diffraction pattern. (c) EDX spectrum of the CdTe nanowires.

Discussions

Formation of the "Pearl-Necklace" Nanochains before Reflux. Kotov and co-workers reported the preparation of CdTe nanowires using the strong dipole interactions between neighboring CdTe nanoparticles which were partly capped with thioglycolic acid. Before the formation of CdTe nanowires, they also observed "pearl-necklace" structures formed by nanoparticles. However, the "pearl-necklace" nanochains shown in Figure 3 are different from what they observed. The main difference is that in the current system there is not clear boundary between the "pearls". This may be because the

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PS blocks existing between the CdTe "pearls" smear out the boundary between the CdTe nanoparticles. For the current system, the driving force for the formation of nanochains is also believed to be the dipole interactions similar to the former case. Since the binding energy between carboxylate and Cd^{2+} is weaker than that between thiols and Cd^{2+}, the surfaces of CdTe nanoparticles covered by the copolymers are more easily charged in the presence of water than that stabilized by thiol molecules, which makes the dipole interactions main driving force for the "pearl-necklace" formation.

To support that the dipole interactions were the main driving force for the formation of CdTe nanochains, the following experiments were carried out. The morphology change with respect to micelles containing Cd^{2+}−polychelate cores was followed by TEM with increasing water content. It was proven that there were no "pearl-necklace" structures formed after water content was raised to 7.8% (w/w). However, addition of water into the dispersion of micelles containing CdTe cores prepared at low water content of 2.4% (w/w) could induce the formation of "pearl-necklace" structures. Quite similar "pearl-necklace" structures appeared again when the water content reached 7.8% (w/w). This further supports the dipole interactions as the driving force for the formation of "pearl-necklace" structures since increasing the water content can enhance the dipole interactions between the CdTe nanoparticles by charging the particle surface.

Formation of CdTe Nanowires during Reflux. Since the single crystal CdTe wires were formed during reflux, TEM was employed to track the transformation from CdTe "pearl-necklace" structures to single crystal CdTe nanowires. It was observed that the color of the CdTe dispersions gradually become darker and darker as the reflux was prolonged. Along with the color change, short rods with a typical length of 100−150 nm and diameter of 10−15 nm wrapped by "pearl-necklace" CdTe nanochains were observed 30 min after reflux, as shown in Figure 5a. Two hours of reflux further increases the length of the CdTe nanrods to 300−500 nm. The diameter of the nanorods slightly increased to 15−20 nm (Figure 5b). After approximately 5 h of reflux, the length of the nanowires becomes 700−800 nm, while the diameter remains nearly unchanged as shown in Figure 5c. In the meantime, the "pearl-necklace" CdTe nanochains disappeared completely. This indicates that the CdTe nanochains were converted to the single crystal CdTe nanowires during reflux. From the detailed structures of some intermediate nanorods whose ends were linked with short nanochains, more clearly shown in Figure 5d, it can be deduced that the single crystal CdTe nanowires were growing longer by gradually merging CdTe nanparticles from the nanochains. This growth mechanism can be explained by the following two reasons. First, the wurtzite structure of CdTe is highly anisotropic and the growth of CdTe nanostrystals along the (001) axis of the nanowires is favorable.[9,18] On the other hand, from the symmetry point of view, both ends of the CdTe nanowires growing along the (001) axis should possess the strongest dipoles, which drives the growth of the CdTe nanowires from both ends by merging the CdTe "pearls".

The electron diffraction patterns inserted in Figure 4b show that the CdTe nanowires obtained exhibits hexagonal wurtzite structure, which indicates that the transformation from nanochains to nanowires was accompanied by a phase transition. It has been reported that II−VI semiconductor nanoparticles such as CdS present a size-dependent structural transformation. The nucleation and growth of nanocrystals are primarily governed by the competition between the surface and volume free energies. During the nucleation, symmetry favors the cubic crystal structure for spherical nucleus over hexagonal structure by adopting low-energy (111) facets on the nanocrystal surface.[33] However, when the particle size grows to a certain level, the cubic structure becomes unstable in energy and transforms to the bulk stable hexagonal structure. This explains the phase transition observed in the current investigation.

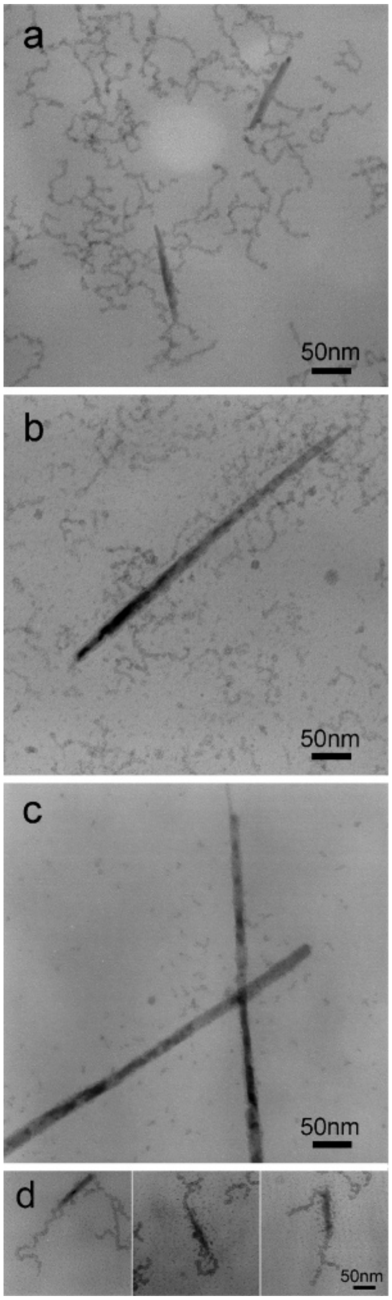

Figure 5. TEM micrographs of CdTe nanowires obtained after the dispersion of CdTe nanochaines was refluxed for 0.5 h (a), 2 h (b), and 5 h (c), respectively. TEM images of CdTe chains/rods composite structures formed at earlier stage of reflux are shown in (d).

Furthermore, it was also demonstrated that the reflux process only accelerated the formation of CdTe nanowires since similar but shorter nanowire structures were also observed after the original dispersion of nanochains was

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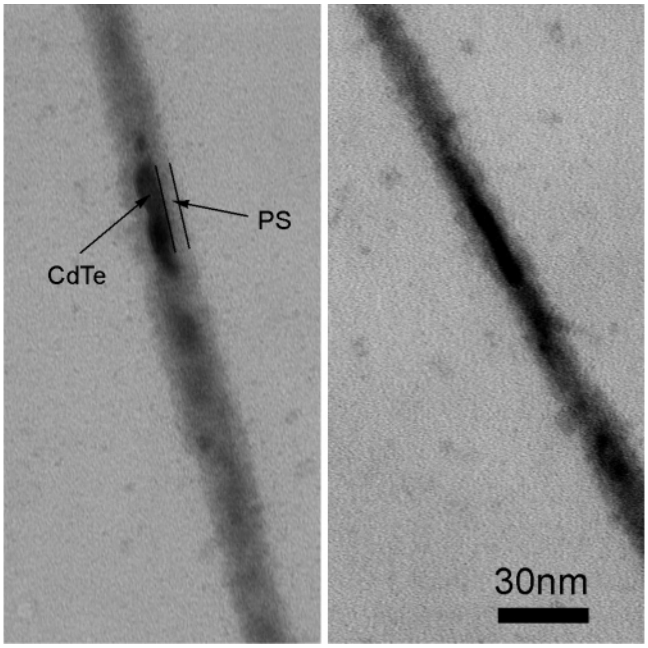

Figure 6. TEM images of single CdTe nanowires with core/shell structure.

aged for ~24 h in darkness. Similar nanochain to nanowire transformation was also observed in a previous report by Kotov.[18] It is well-known that the stacking fault energy (SFE) is closely related to the low activation energy of phase transition between the two types of crystalline structures. The refluxing process will decrease the SFEs of semiconductors and facilitate such transition.[34] Furthermore, in the current case, refluxing will also activate the PS layer and increase the mobility of the triblock copolymer. Hence, the hindrance effect of the block copolymer is reduced, which favors the transformation from nanochains to nanowires. As the coordinating ability of carboxlate group with CdTe is relatively weak, the equilibrium diameter of CdTe nanowires finally obtained is generally larger than the size of the CdTe particle in the nanochain structure but still rather uniform.

CdTe Nanowire−Polymer Core/Shell Structure. The relatively high contrast in the vicinity of crystal defects allows clear observations on the nanostructures of the finally obtained composites. The shell structure as indicated by arrows in Figure 6 can be assigned to PS blocks from the ABC triblock copolymer since amorphous PEO and PAA are invisible under TEM. The thickness of the shell is about 4−5 nm and thicker than that covering the CdTe nanoparticles in nanochains whose total width is 4−7 nm. This may be due to the fact that the surface-to-volume ratio of CdTe nanoparticles in the nanochain structures is greater than that for nanowires, the rearrangement of the copolymer during the formation of CdTe nanowires leading to higher shell thickness. Such a densely packed PS layer may favor the photochemical stability of the nanowires obtained. The average diameter of the CdTe core within the PS shell is about 6−8 nm, leading to an aspect ratio of 100:1 for CdTe wires. It was also demonstrated, as we designed, the outside PEO blocks offered the eventually formed CdTe nanowires aqueous dispersibility. This will offer the opportunity to manipulate the CdTe nanowires at single wire level.

Summary

To explore the novel applications of ABC type triblock copolymers in the preparation of inorganic nanomaterials, a new type of amphiphilic triblock copolymer, PEO−PS−PAA, was designed and synthesized by the ATRP method to assist the synthesis of CdTe nanowires. Upon addition of the aqueous solution of Cd^{2+} ions into the dioxane solution of the copolymer, roughly spherical micelles with Cd^{2+}−polychelate cores were formed. Since water is the bad solvent of the PS block, the water content in the system was controlled to favor the formation of micelles. After reacting with NaHTe, Cd^{2+} ions were converted to CdTe nanocrystals within the micelles that simultaneously formed "pearl-necklace" nanochains driven by dipole interactions between neighboring CdTe nanoparticles. Such "pearl-necklaces" can further be converted to single crystal CdTe nanowires by either reflux for hours or aging at room temperature for tens of hours. Meanwhile, on the surface of the finally obtained CdTe nanowires, the ABC copolymer constructed a shell structure on the CdTe nanowires with the middle block of PS forming a densely packed inert shell and the outmost block of PEO rendering the nanowires dispersibility. We believe the current investigations have demonstrated that by designing differently structured block copolymers with various functional blocks, ABC type copolymers may find new applications in regulating inorganic nanomaterials with multifarious morphologies.

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