

A General Solvothermal Route to the Synthesis of CoTe, Ag₂Te/Ag, and CdTe Nanostructures with Varied Morphologies

Ling Jiang^[a] and Ying-Jie Zhu^{*[a]}

Keywords: Cobalt / Silver / Nanostructures / Surfactants / Tellurium

A general and facile surfactant-assisted solvothermal route was developed for the synthesis of CoTe, Ag₂Te/Ag, and CdTe nanostructures using the corresponding metal salt, Na₂TeO₃, ascorbic acid, and polyvinyl pyrrolidone (PVP) or cetyltrimethylammonium bromide (CTAB) in mixed solvents of ethanolamine and water. It was also found that the morphology of the product varied dramatically when using dif-

ferent surfactants such as PVP and CTAB. A formation mechanism of telluride nanostructures was proposed. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), thermogravimetry (TG), and differential scanning calorimetric (DSC) analysis.

Introduction

Recently, considerable attention has been paid to the synthesis of one-dimensional (1D) semiconducting nanostructures such as nanorods, nanowires, and nanotubes because of their unique and interesting properties derived from their dimensionality-dependent anisotropy and potential applications in electronics and optoelectronics.^[1] Metal tellurides are being actively investigated because of their distinctive properties and applications. For example, silver telluride (Ag₂Te) has great technological prospects in magnetic-field measurements, microelectronics, and structural studies.^[2–7] The crystal phase of Ag₂Te undergoes a phase transformation from the low-temperature monoclinic structure (β -Ag₂Te) to a high-temperature face-centered cubic structure (α -Ag₂Te) at about 150 °C.^[8] β -Ag₂Te is known as a narrow band gap semiconductor with high electron mobility and low lattice thermal conductivity, whereas α -Ag₂Te shows superionic conductivity because Ag⁺ cations can move freely, which enhances the conductivity.^[9,10] Recently, it was reported that binary nanocrystal superlattices of PbTe and Ag₂Te enhanced the conductivity of the composite thin films.^[11] Recently, Batabyal et al.^[7] reported a facile route for the synthesis of axial-junction nanowires of Ag₂Te/Ag composite, which was proven to be a potential material for memristors. CoTe, as a typical magnetic semiconductor, has attracted great interest for its distinctive electrical transport properties.^[12] As an important wide band gap II–VI semiconductor, CdTe continues to draw increasing attention in both fundamental studies and for its various promising ap-

plications in the field of photonic crystals, light-emitting diodes (LEDs), solar cells, and bioimaging.^[13–18] The CdTe nanostructured materials exhibit outstanding optical and electrical properties,^[19–27] and reducing the dimensionality and size of CdTe to a nanoscale range may be a successful strategy to gain further enhancements in both optical and electrical properties.

Although many 1D nanostructures of metal tellurides have been synthesized, up to now, studies of cobalt telluride nanostructures have been little reported. Xie et al.^[28] prepared CoTe₂ nanorods by the reaction of CoCl₂·6H₂O and tellurium in ethylenediamine by a solvothermal method. Peng et al.^[12] reported the synthesis of CoTe and NiTe nanowires through a reduction method by using N₂H₄·H₂O as the reducing agent. Fan et al.^[29] synthesized CoTe nanotubes through a Te-templated route. Among these fabricating methods, the two-step Te template-directed synthesis was one of the most popular strategies for the fabrication of 1D telluride nanostructures.^[5,30–32] Furthermore, N₂H₄·H₂O was a common reducing agent for the synthesis of tellurides.^[4–6,12,25,30–33] It is necessary to develop a general and one-step route for the synthesis of nanostructured tellurides.

In this paper, we report a simple one-step solvothermal synthesis of nanostructures of three different kinds of metal tellurides (CoTe, Ag₂Te/Ag, and CdTe) by using only one general method. It is found that the morphology of the products can be adjusted by using different surfactants such as polyvinyl pyrrolidone (PVP) and cetyltrimethylammonium bromide (CTAB).

Results and Discussion

To distinguish the as-prepared samples, the samples with different morphologies are labeled as A1, A2, and A3 for

[a] State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China
Fax: +86-21-52413122
E-mail: y.j.zhu@mail.sic.ac.cn

CoTe; B1 and B2 for Ag₂Te; and C1 and C2 for CdTe, as shown in Figure 1. Figure 2 shows XRD patterns of three as-synthesized CoTe samples A1, A2, and A3 with varied morphologies. Samples A1, A2, and A3 were prepared by using no surfactant, PVP, and CTAB, respectively. The diffraction peaks of the XRD patterns can be indexed to a single phase of CoTe with a hexagonal structure (JCPDS no. 65-8986), thereby indicating that hexagonal CoTe forms independently of the use of the surfactant. TEM micrographs of as-prepared CoTe nanostructures with different morphologies are shown in Figure 3. Figure 3 (a–e) shows TEM micrographs of sample A1 obtained without using any surfactant, from which one can see that sample A1 consists of CoTe nanotubes with lengths of up to several micrometers. Parts c and d of Figure 3 exhibit typical individual nanotubes that clearly present a tubular structure with a diameter of around 60 nm. The selected-area electron diffraction (SAED) pattern (Figure 3, e) indicates that the CoTe nanotube has a polycrystalline structure. To investigate the influence of the surfactant on the morphology of the product, we selected PVP and CTAB as morphology-controlling agents, and the presence of PVP or CTAB has an obvious influence on the morphology, as shown in Figure 3 (f–j) (sample A2, using PVP) and Figure 3 (k–o, sample A3, using CTAB). Part f of Figure 3 displays a typical panoramic TEM image of the CoTe sample synthesized in the presence of PVP, thereby indicating that sample A2 is composed of monodisperse uniform solid nanorods with diameters of about 20 nm and lengths of several hundred nanometers. The magnified TEM image in Figure 3 (h) shows individual CoTe nanorods of about 600 nm in length

and 20 nm in diameter. The SAED pattern (Figure 3, j) shows clear diffraction rings of CoTe crystals, thereby indicating the polycrystalline nature of the nanorod. The morphology of the synthesized product (sample A3) in the presence of CTAB instead of PVP is displayed in Figure 3 (k–o), from which CoTe hierarchical 1D nanostructures can be observed, and each hierarchical 1D nanostructure is composed of a nanotube on which nanorods are grown. The magnified TEM image of a single hierarchical 1D nanostructure (Figure 3, l) shows that the nanotube is about 80 nm in diameter, whereas the nanorods grown on the nanotube show diameters of less than 10 nm. The SAED pattern in Figure 3 (o) shows clear diffraction rings of CoTe crystals, thereby indicating the polycrystalline nature of the hierarchical 1D nanostructure.

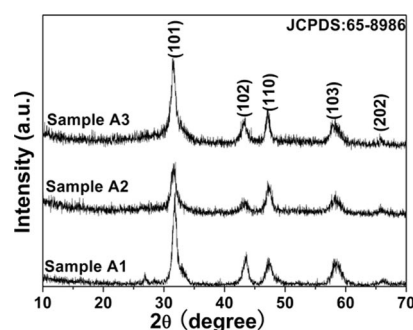


Figure 2. XRD patterns of CoTe 1D nanostructures (samples A1, A2, and A3) prepared under different conditions. Sample A1: without using any surfactant; sample A2: in the presence of PVP; sample A3: in the presence of CTAB.

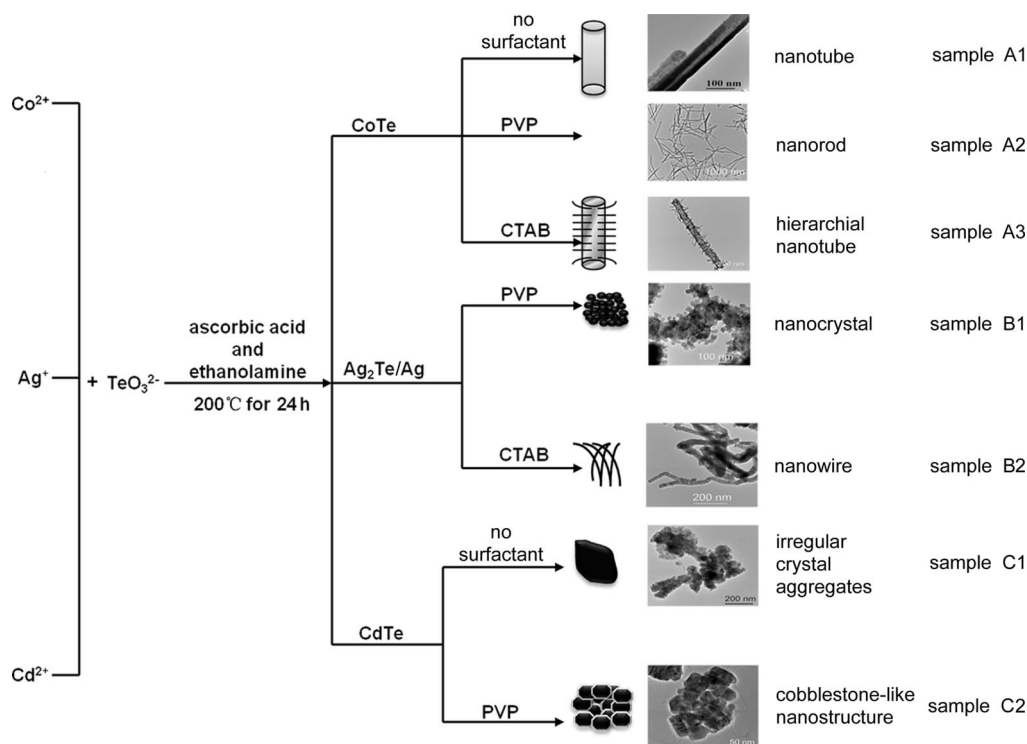


Figure 1. Illustration of the sample preparation and sample numbers of the as-synthesized CoTe, Ag₂Te/Ag, and CdTe nanostructures.

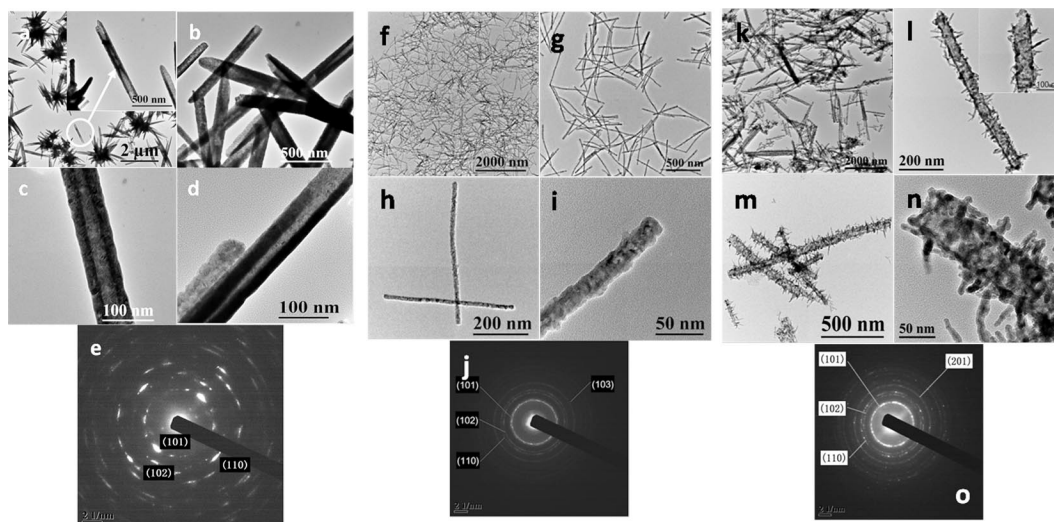


Figure 3. TEM micrographs of as-prepared CoTe 1D nanostructures prepared under different conditions: (a–e) without using any surfactant (sample A1); (f–j) in the presence of PVP (sample A2); (k–o) in the presence of CTAB (sample A3).

In addition to CoTe 1D nanostructures, $\text{Ag}_2\text{Te}/\text{Ag}$ nano-composites as well as CdTe nanostructures with different morphologies have also been successfully synthesized using this method in the presence of PVP or CTAB. Figure 4 shows the XRD patterns of two as-prepared $\text{Ag}_2\text{Te}/\text{Ag}$ samples with different morphologies. The peaks of the XRD patterns can be confidently indexed to monoclinic Ag_2Te (JCPDS no. 34-0142) and cubic Ag (JCPDS no. 04-0783). The TEM images of $\text{Ag}_2\text{Te}/\text{Ag}$ nanostructures are shown in Figure 5. It is found that the morphologies of the $\text{Ag}_2\text{Te}/\text{Ag}$ samples vary dramatically using different surfactant, as shown in Figure 5 (a–d). Sample B1 prepared by using PVP consists of nanocrystals with diameters of about 10 nm, whereas nanowires with diameters around 20 nm are obtained in the presence of CTAB (sample B2).

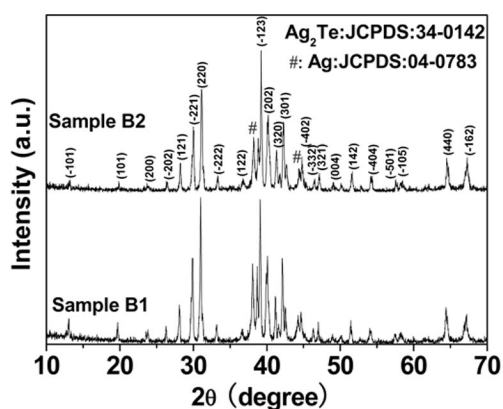


Figure 4. XRD patterns of $\text{Ag}_2\text{Te}/\text{Ag}$ nanostructures synthesized in the presence of PVP (sample B1) and CTAB (sample B2).

To examine the crystal phase transition of the as-prepared Ag_2Te samples from a low-temperature monoclinic structure ($\beta\text{-Ag}_2\text{Te}$) to a high-temperature face-centered cubic structure ($\alpha\text{-Ag}_2\text{Te}$), the DSC and TG measurements of sample B1 were taken, and the results are shown in Figure 6, from which one can see that an endothermic peak

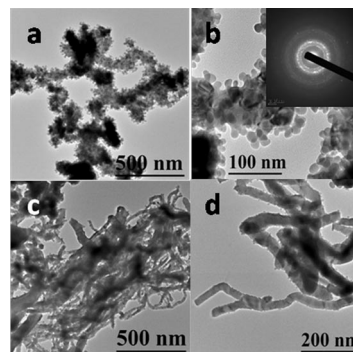


Figure 5. TEM micrographs of as-prepared $\text{Ag}_2\text{Te}/\text{Ag}$ nanostructures synthesized in the presence of (a and b) PVP (sample B1) and (c and d) CTAB (sample B2).

centers at about 150 °C in the DSC curve and the TG curve shows hardly any mass loss in the temperature range investigated, thereby indicating that only a structural phase transition from the monoclinic phase to the cubic phase occurs, and this result is in good agreement with the result reported by Li et al. and Batabyal and Vittal.^[6,7]

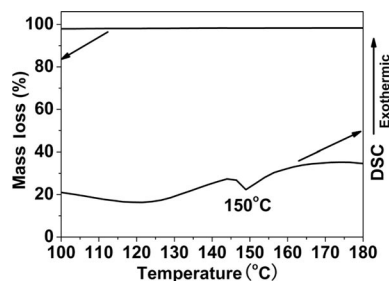


Figure 6. DSC–TG curves of $\text{Ag}_2\text{Te}/\text{Ag}$ nanostructures (sample B1) prepared in the presence of PVP.

The XRD patterns of as-prepared CdTe samples are shown in Figure 7. The diffraction peaks can be indexed to single-phase CdTe with a cubic structure (JCPDS no. 65-

0880). The morphology of the obtained CdTe sample prepared in the absence of any surfactant consists of irregular nanocrystal aggregates (Figure 8, a and b, sample C1), and cobblestone-like structures assembled by small nanocrystals with sizes of around 20 nm are obtained by using PVP as the morphology-controlling agent (Figure 8, c–g, sample C2). The SAED pattern shown in part g of Figure 8 indicates that the cobblestone-like structures are polycrystalline.

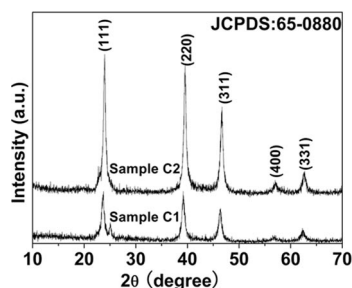


Figure 7. XRD patterns of CdTe nanostructures synthesized without any surfactant (sample C1) and in the presence of PVP (sample C2).

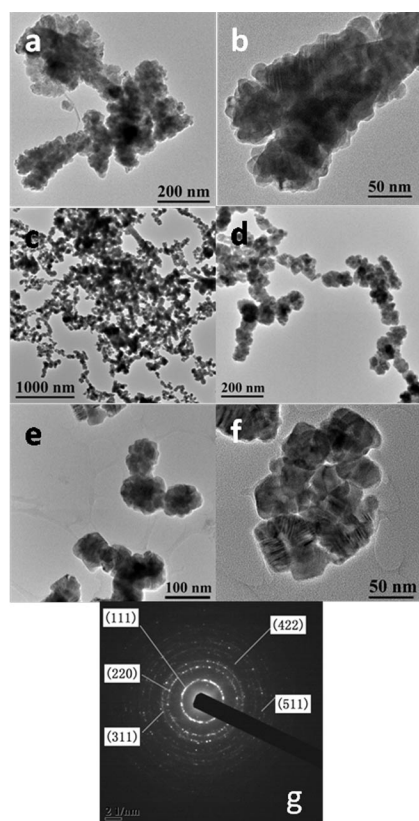
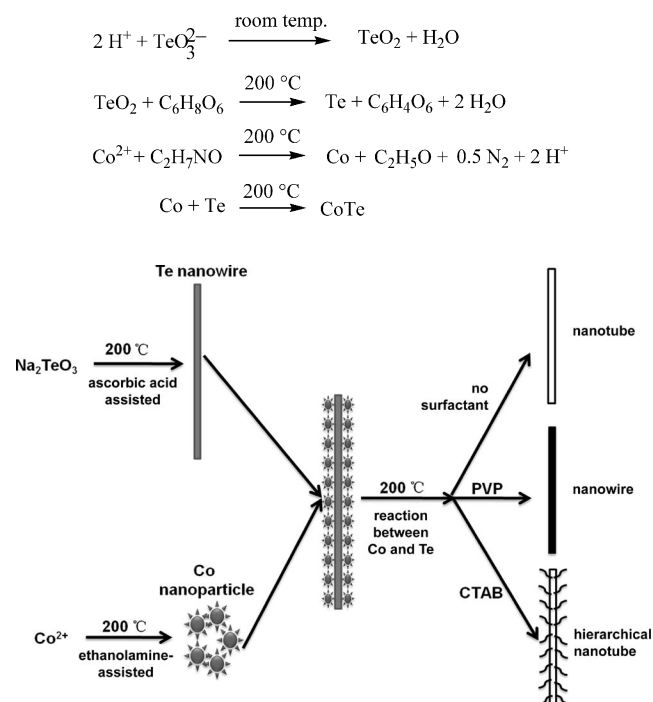


Figure 8. TEM images of as-prepared CdTe nanostructures synthesized without any surfactant (sample C1) (a and b) and in the presence of PVP (sample C2) (c–g).

The solid–solution–solid transformation has been extensively used to explain the formation of 1D nanostructured tellurides in the solution phase.^[5,12,23,30,31,34] On the basis of the experimental results, we propose a possible solid–solution–solid reaction mechanism for the formation of CoTe, Ag₂Te, and CdTe nanostructures. In the early stage,

soluble Na₂TeO₃ dissociated into TeO₃^{2−} and Na⁺ ions in water, and then reacted with Mⁿ⁺ (Mⁿ⁺ = Co²⁺, Ag⁺, or Cd²⁺) to form CoTeO₃, Ag₂TeO₃, or CdTeO₃. When ethanolamine (C₂H₇NO) was added, CoTeO₃, Ag₂TeO₃, or CdTeO₃ was dissolved by the formation of the Mⁿ⁺–C₂H₇NO complex, and simultaneously, the dissociative TeO₃^{2−} formed again. Then, H⁺ ions that resulted from the ionization of ascorbic acid reacted with TeO₃^{2−} to generate TeO₂, which was not dissolved in water at room temperature.^[34] When the reaction mixture was heated to a certain temperature, the previously formed TeO₂ was gradually dissolved in the solution. After the temperature reached 200 °C, TeO₂ had completely dissolved in the solution and subsequent reactions took place in the mixture. It is known that ascorbic acid is a weak reducing agent.^[35–37] The ascorbic acid would slowly reduce Te⁴⁺ to Te in the solution.^[34] At the same time, at such a high temperature, Mⁿ⁺ could also be reduced to M in the presence of ethanolamine. These newly produced atomic Te and M were highly reactive, and they reacted with each other to form CoTe, Ag₂Te, and CdTe. As a result, after 24 h of reaction, nucleation, and crystal growth, the formation of CoTe, Ag₂Te, and CdTe nanostructures finally reached completion. The chemical reactions involved in this process are shown as follows (for example, Co²⁺) and a scheme for the formation of CoTe 1D nanostructures with different morphologies is shown in Scheme 1.



Scheme 1. Illustration of the formation of CoTe 1D nanostructures with different morphologies.

Some reports in the literature have described the effects of the surfactants on the formation of metal tellurides. For example, Gong et al.^[25] reported a CTAB-assisted route for the synthesis of CdTe nanorods; they discussed the role of CTAB and proposed that one possible function of CTAB

was to generate large numbers of rodlike micelles in aqueous solution, which acted as a soft template for the formation of 1D nanostructures as well as stabilized 1D nanostructures. Tai et al.^[31] also discussed the effects of PVP on the morphologies of PbTe nanowires. PVP played an important role in the transformation process from the trigonal tellurium (t-Te) nanowires to the pearl-necklace-shaped PbTe nanowires. Based on both our experimental results and the reports in the literature, we propose that in the formation process of these metal telluride nanostructures, the surfactant functioned as the morphology-controlling agent. PVP or CTAB molecules could generate micelles in solution, which acted as the soft template for the formation of metal telluride nanostructures as well as the stabilizer for these nanostructures.

Conclusion

In summary, we have developed a general and facile surfactant-assisted solvothermal route for the synthesis of CoTe, Ag₂Te/Ag, and CdTe nanostructures by using the corresponding metal salt, Na₂TeO₃, ascorbic acid, and polyvinyl pyrrolidone (PVP) or cetyltrimethylammonium bromide (CTAB) in mixed solvents of ethanolamine and water. The experiments showed that the surfactant, such as PVP and CTAB, had a significant influence on the morphology of the product. A variety of metal telluride nanostructures with various morphologies such as CoTe nanotubes, CoTe nanowires, CoTe hierarchical nanotubes with nanorods grown on them, Ag₂Te/Ag composite nanostructures, and CdTe nanostructures were obtained by using this general method. It is expected that this method may also be extended to the synthesis of other metal telluride nanostructures.

Experimental Section

Synthesis of CoTe, Ag₂Te/Ag, and CdTe Nanostructures: All chemicals were purchased and used as received without any further purification. In a typical procedure for the preparation of CoTe, Ag₂Te/Ag, and CdTe nanostructures, polyvinyl pyrrolidone (PVP; 0.5 g) or cetyltrimethylammonium bromide (CTAB; 0.5 g) was dissolved in deionized water (30 mL). Co(NO₃)₂·6H₂O (0.29 g), AgNO₃ (0.34 g), or CdCl₂·2.5H₂O (0.228 g) was added into the above solution under magnetic stirring at room temperature. Then Na₂TeO₃ (0.22 g) was added while being stirred for about 10 min, and ascorbic acid (2 g) and ethanolamine (40 mL) were added. Next, the mixture was stirred for 20 min to form a well-dispersed suspension and was put into a Teflon-lined stainless steel autoclave of 100 mL capacity. The autoclave was sealed and maintained at 200 °C for 24 h. After the heating process, the autoclave was taken out and cooled to room temperature in air naturally. The black product was collected by centrifugation, washed with deionized water and absolute ethanol several times, and then dried at 60 °C in vacuo.

Characterizations: XRD patterns were recorded with a Rigaku D/MAX 2550V X-ray diffractometer with Cu-K_α radiation ($\lambda = 1.54178 \text{ \AA}$) and a graphite monochromator. The TEM images were taken with a JEOL JEM-2100F field-emission transmission elec-

tron microscope. The TG and DSC curves were taken with a heating rate of 10 °C min⁻¹ in flowing air with a STA 409/PC simultaneous thermal analyzer (Netzsch, Germany).

Acknowledgments

Financial support from the National Natural Science Foundation of China (50772124, 50821004), the Program of Shanghai Subject Chief Scientist (07XD14031), Science and Technology Commission of Shanghai (0852nm05800), and the Opening Project of State Key Laboratory of High Performance Ceramics and Superfine Microstructures (SKL200901SIC) is gratefully acknowledged.

- [1] A. P. Alivisatos, *Science* **1996**, *271*, 933–937.
- [2] B. Q. Liang, X. Chen, Y. J. Wang, Y. J. Tang, *Phys. Rev. B* **2000**, *61*, 3239–3242.
- [3] A. Husmann, J. B. Betts, G. S. Boebinger, A. Migliori, T. F. Rosenbaum, M. L. Saboungi, *Nature* **2002**, *417*, 421–424.
- [4] A. M. Qin, Y. P. Fang, P. F. Tao, J. Y. Zhang, C. Y. Su, *Inorg. Chem.* **2007**, *46*, 7403–7409.
- [5] P. F. Zuo, S. Y. Zhang, B. K. Jin, Y. P. Tian, J. X. Yang, *J. Phys. Chem. C* **2008**, *112*, 14825–14829.
- [6] F. Y. Li, C. G. Hu, Y. F. Xiong, B. Y. Wan, W. Yan, M. C. Zhang, *J. Phys. Chem. C* **2008**, *112*, 16130–16133.
- [7] S. K. Batabyal, J. J. Vittal, *Chem. Mater.* **2008**, *20*, 5845–5850.
- [8] C. R. Martin, *Science* **1994**, *266*, 1961–1966.
- [9] R. Dalven, R. Gill, *J. Appl. Phys.* **1967**, *38*, 753–756.
- [10] R. Z. Chen, D. S. Xu, G. L. Guo, L. L. Gui, *J. Mater. Chem.* **2002**, *12*, 2435–2438.
- [11] J. J. Urban, D. V. Talapin, E. V. Shevchenko, C. R. Kagan, C. B. Murray, *Nat. Mater.* **2007**, *6*, 115–121.
- [12] Q. Peng, Y. J. Dong, Y. D. Li, *Inorg. Chem.* **2003**, *42*, 2174–2175.
- [13] C. B. Murray, D. J. Norris, M. G. Bawendi, *J. Am. Chem. Soc.* **1993**, *115*, 8706–8715.
- [14] Z. Y. Tang, N. A. Kotov, M. Giersig, *Science* **2002**, *297*, 237–240.
- [15] A. Rogach, A. Susa, F. Caruso, G. Sukhorukov, A. Kornowski, S. Kershaw, H. Mohwald, A. Eychmuller, H. Weller, *Adv. Mater.* **2000**, *12*, 333–337.
- [16] I. Gur, N. A. Fromer, M. L. Geier, A. P. Alivisatos, *Science* **2005**, *310*, 462–465.
- [17] N. N. Mamedova, N. A. Kotov, A. L. Rogach, J. Studer, *Nano Lett.* **2001**, *1*, 281–286.
- [18] J. Lee, P. Hernandez, A. O. Govorov, N. A. Kotov, *Nat. Mater.* **2007**, *6*, 291–295.
- [19] P. T. K. Chin, J. W. Stouwdam, S. S. van Bavel, R. A. J. Janssen, *Nanotechnology* **2008**, *19*, 205602.
- [20] Y. Liu, Q. Shen, D. Yu, W. Shi, J. Li, J. Zhou, X. Liu, *Nanotechnology* **2008**, *19*, 245601.
- [21] J. W. Cho, H. S. Kim, Y. J. Kim, S. Y. Jang, J. Park, J. G. Kim, E. H. Cha, *Chem. Mater.* **2008**, *20*, 5600–5609.
- [22] J. Sun, L. W. Wang, W. E. Buhro, *J. Am. Chem. Soc.* **2008**, *130*, 7997–8005.
- [23] M. C. Kum, B. Y. Yoo, Y. Rheem, K. N. Bozhilov, W. Chen, A. Mulchandani, N. V. Myung, *Nanotechnology* **2008**, *19*, 325711.
- [24] J. W. Sun, W. E. Buhro, L. W. Wang, J. Schrier, *Nano Lett.* **2008**, *8*, 2913–2919.
- [25] H. Gong, X. P. Hao, C. Gao, Y. Z. Wu, J. Du, X. G. Xu, M. H. Jiang, *Nanotechnology* **2008**, *19*, 445603.
- [26] Y. P. Rakovich, Y. Volkov, S. Sapra, A. S. Susa, M. Doblinger, J. F. Donegan, A. L. Rogach, *J. Phys. Chem. C* **2007**, *111*, 18927–18931.
- [27] S. S. Ho, K. Critchley, G. D. Lilly, B. Shim, N. A. Kotov, *J. Mater. Chem.* **2009**, *19*, 1390–1394.
- [28] Y. Xie, B. Li, H. L. Su, X. M. Liu, Y. T. Qian, *Nanostruct. Mater.* **1999**, *11*, 539–544.

- [29] H. Fan, Y. G. Zhang, M. F. Zhang, X. Y. Wang, Y. T. Qian, *Cryst. Growth Des.* **2008**, *8*, 2838–2841.
- [30] H. W. Liang, S. Liu, Q. S. Wu, S. H. Yu, *Inorg. Chem.* **2009**, *48*, 4927–4933.
- [31] G. A. Tai, W. L. Guo, Z. H. Zhang, *Cryst. Growth Des.* **2008**, *8*, 2906–2911.
- [32] G. Tai, B. Zhou, W. L. Guo, *J. Phys. Chem. C* **2008**, *112*, 11314–11318.
- [33] P. Kumar, K. Singh, *Cryst. Growth Des.* **2009**, *9*, 3089–3094.
- [34] G. C. Xi, Y. K. Liu, X. Q. Wang, X. Y. Liu, Y. Y. Peng, Y. T. Qian, *Cryst. Growth Des.* **2006**, *6*, 2567–2570.
- [35] N. R. Jana, L. Gearheart, C. J. Murphy, *Chem. Commun.* **2001**, 617–618.
- [36] N. R. Jana, L. Gearheart, C. J. Murphy, *J. Phys. Chem. B* **2001**, *105*, 4065–4067.
- [37] N. R. Jana, L. Gearheart, C. J. Murphy, *Adv. Mater.* **2001**, *13*, 1389–1393.

Received: September 27, 2009

Published Online: February 2, 2010