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Direct Synthesis of Water-Soluble Ultrathin CdS Nanorods and Reversible Tuning of the Solubility by Alkalinity

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Semiconductor nanocrystals have attracted much attention this decade.[1] The traditional solution-phase organometallic approach provides an effective way to synthesize high quality hydrophobic semiconductor nanocrystals.[2] However, in many cases, such as biological labeling and drug delivery, the hydrophobic nanocrystals are limited and water-soluble nanocrystals are desired.[3] The traditional methods employ an extra step to replace the ligands by hydrophilic ones or *in situ* grow a hydrophilic shell on a presynthesized nanocrystal.[4] By contrast, direct synthesis is more convenient and effective to produce water-soluble nanocrystals. Some methods have been developed, for example, by using small molecules with polar groups as ligands, such as thioglycolic acid,[5] or using water-soluble polymers, such as polyvinylpyrrolidone (PVP).[6] However, directly synthesizing water-soluble ultrathin quantum rods[7] remains a challenging task. It is difficult to find a suitable water-soluble ligand which can bind to the nanocrystal firmly, so that it can protect the nanocrystal well and further induce the anisotropic growth.

Previous studies have shown that ethylenediamine (*en*) induces the formation of CdS nanorods based on a solvent coordination molecular template (SCMT) mechanism.[8] It suggests that the polymerized *en* (polyethyleneimine, PEI; its structure is shown in Figure S1) may have a similar effect in the controlled synthesis of CdS nanorods. PEI is also known as a kind of polyelectrolyte, which can be well dissolved in water. Compared to *en*, PEI has multiple amino groups on each polymer chain. These amino groups can bind to nanocrystals more firmly and strongly confine the nanocrystals all through the growth period, further resulting in ultrathin nanorods. There are also uncoordinated amino groups of PEI remaining on the surface of the protected nanocrystals, which causes the nanocrystals to obtain some special functions and enable them to be further modified, such as coupling to bioactive molecules.

CdS is a semiconductor which has extensive applications in biological labels.[9] Several groups have reported the synthesis of hydrophobic CdS nanorods.[10] In this paper, we report a solution-phase method to directly synthesize water-soluble CdS nanorods by employing PEI as ligands. Ethylene glycol was chosen as the solvent; thus the reaction could be carried out at a relatively high temperature for the sake of good crystallinity. The as-obtained nanorods are ultrathin (only ~2 nm in diameter) and show quantum effected fluorescent properties compared to the nanorods obtained with the assistance of *en*.[8] The capping PEI molecules enable the as-obtained nanorods to be stably dispersed in water, which makes them quite suitable for application in biological labeling. However, it would aggregate and precipitate out under ultrahigh alkalinity (3 M NaOH). The precipitates could be redispersed when the alkalinity decreases. Thus it is a smart material that can respond to alkalinity of the solution, which is important in biological separations and sensors.

A hot-injection technology was employed to start the reaction by injecting thioacetamide into the ethylene glycol solution containing Cd^{2+} and PEI at 120 to 180 °C (see Supporting Information for details). Simple cadmium salt, such as cadmium nitrate, can be adopted because of its high solubility in ethylene glycol. Thioacetamide was chosen as the sulfur source, because it can release S^{2-} at a certain temperature, which reacts with Cd^{2+} to generate CdS under the protection of PEI. PEI plays a critical role in the synthesis, and nanorods cannot be obtained by using other polyelectrolytes, such as polystyrenesulfonate (PSS) and poly(acrylic acid) (PAA).

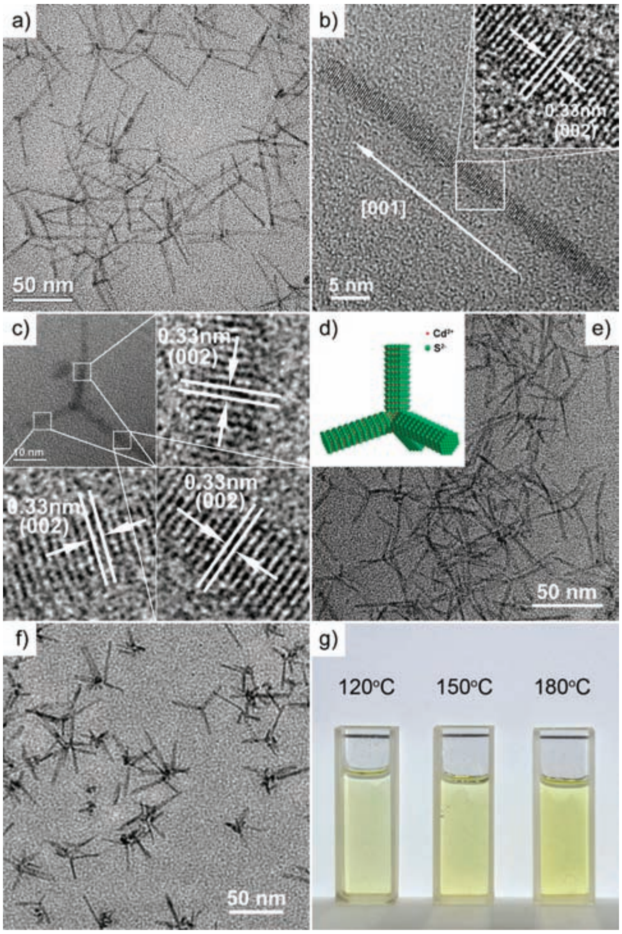

Figure 1. (a) TEM image of the CdS nanorods obtained at 120 °C. (b) HRTEM image of an individual rod; the inset is magnified image of the lattice fringe. (c) HRTEM image of an individual tetrapod and magnified images of the lattice fringe of the three arms, respectively. (d) Scheme of the structure of tetrapod. (e) TEM image of the CdS nanorods obtained at 150 °C. (f) TEM image of the CdS nanorods obtained at 180 °C. (g) Photograph of the samples dispersed in water.

Figure 1a shows the TEM image of the products obtained at 120 °C. They are rod-like nanocrystals with a diameter of ~2 nm and length of more than 50 nm. They are thinner than twice the

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exciton Bohr radius of CdS (2.9 nm), which indicates that they may show a quantum size effect. The HRTEM image (Figure 1b) image shows the good crystallinity of the nanorod. The lattice fringe with an interplanar spacing of 0.33 nm is ascribed to the (002) plane of wurtzite CdS. It indicates that the nanorods grow along the [001] direction. Some tetrapods are also found in the TEM image, and Figure 1c shows the HRTEM image of an individual tetrapod. The tetrapod can be recognized as the assembly of four nanorods,[10,11] and the scheme of the structure is given in Figure 1d. Because one of the arms is vertical to the sample plane, only three arms can be observed in the TEM image. The detailed structure of tetrapod is discussed in Figure S2. The lattice fringes (Figure 1c) indicate all the arms grow along [001] directions. When the reaction temperature increased, similar but thicker and shorter nanorods were obtained (Figure 1e and 1f). When the reaction temperature is 180 °C, the diameter of the nanorods increased to ~4 nm and the length reduced to ~35 nm. A photograph (Figure 1g) shows all of them can be well dispersed in water and form homogeneous, transparent suspensions.

Figure S3 shows the XRD patterns of the as-obtained nanorods. They are in agreement with the wurtzite phase CdS (JCPDS Card No. 41-1049). The EDS pattern (Figure S4) shows the signals of Cd and S, which also confirms the composition of CdS. It is notable that the (002) diffraction peak is rather strong and sharp in the XRD pattern, which is consistent with the preferred [002] growth direction of CdS nanorods. The XRD patterns also show that the diffraction peaks of the nanorods obtained at higher temperatures are stronger, which indicates that the sample has better crystallinity. When the reaction temperature is lower than 100 °C, amorphous products are obtained. Only poor products can be obtained by using water as the solvent because of its low boiling point. Thus ethylene glycol is important for the good crystallinity of the products.

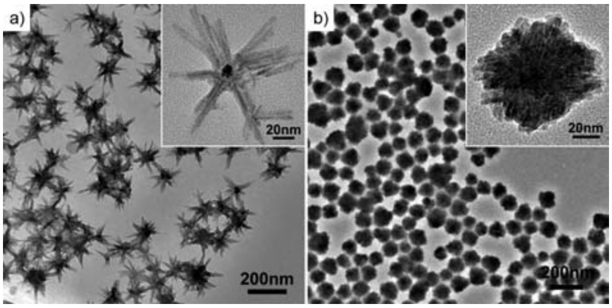

Figure 2. TEM images of (a) hyperbranched CdS nanostructures obtained by dropwise addition of thioacetamide and (b) CdS nanospheres obtained by introducing acetic acid (200 μL).

In our experiment, it was found that the rate of the reaction is critical for the shape control of the nanocrystals. By employing hot-injection technology, a burst nucleation occurs at the beginning of the reaction, and a separated growth period arises subsequently. Thus high quality nanorods could be obtained. Instead of by injection, dropwise addition of the reactant produced hyperbranched nanostructures (Figure 2a). It can be recognized as a multi-injection process, and a secondary nucleation occurred, resulting in a hyperbranched shape.[12] The reaction can be also adjusted by pH. By using acetic acid (200 μL) to lower the pH of the reaction system, nanospheres with diameters of ~100 nm were obtained (Figure 2b). A magnified TEM image (inset of Figure 2b) shows that the spheres are not in single crystal form but are an aggregation of small particles. Acid is of benefit to decompose thioacetamide and release S^{2-}, which accelerates the reaction. Also, the amino groups of the PEI are protonized and the coordinate abilities are reduced in an acidic environment. Thus PEI does not protect the nuclei as well as the condition without acid. In this case, a lot of nuclei are generated at the beginning of the reaction. They are unstable and aggregated to spheres. Figure S5 shows the TEM images along with the increase of the amount of the acetic acid. The products deviate from the rod shape gradually, indicating the acidic environment hinders the generation of nanorods.

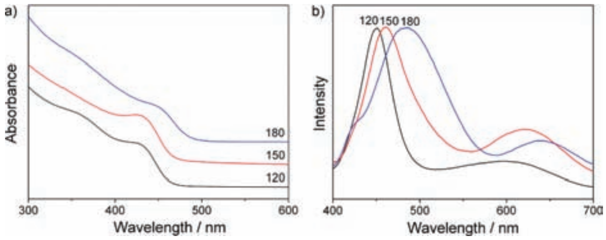

Figure 3. (a) UV−vis spectra of the CdS nanorod obtained at 120, 150, and 180 °C, respectively. (b) PL spectra of the as-obtained CdS nanorods under irradiation at 365 nm.

The typical band gap of bulky CdS is 2.5 eV, which is according to an absorption wavelength of 490 nm. The as-obtained nanorods are ultrathin, and thus the quantum effect happens, driving the absorption and emission peaks to blue-shift. The UV−vis spectra (Figure 3a) show a dominating absorption edge at ~430 nm for the nanorods obtained at 120 °C that shifts to 460 nm for the nanorods obtained at 180 °C. This shift is consistent with the increased diameters of the nanorods when growth is at a higher temperature. Compared with the nanorods obtained with the assistance of *en*,[8] these CdS nanorods show tunable fluorescence, which is important in applications such as biological labeling. The PL spectra (Figure 3b) show a narrow typical direct electron−hole recombination (i.e., band-edge emission) at 450 nm for the nanorods obtained at 120 °C. A broad and weak emission is observed at ~600 nm, which corresponds to the trap-related electron−hole recombination and comes from the surface state emission of the material.[10,13] The peaks are red-shifted correspondingly when the nanorods are obtained at a higher temperature. They become broader, which may stem from the wider size distributions of the nanorods.

These nanorods obtained in our experiment are all highly water-soluble and can be stably dispersed in water for more than 1 month. This high water solubility comes from the PEI molecules binding on the surface of the CdS nanorods. PEI is a polyelectrolyte with amino groups, which can be easily protonized in an aqueous solution. FTIR spectra were employed to demonstrate the presence of the NH_3^+ of PEI. The FTIR spectra of the nanorods (Figure S6b) show a strong peak located at 1643 cm^{-1} for the NH_3^+ deformation mode and a weak band located at 1472 cm^{-1} which is assigned to the CH_2 deformation mode of the polymer chain.[14] By comparing the FTIR spectra of the PEI aqueous solution (Figure S6a), it is clear that a large amount of amino groups remain on the surface of nanocrystals even after extensive washing, the reason of which is that there are multiple anchor points for every single polymer chain. Moreover, it was found that the nanorods could be stably dispersed in water in a wide range of pH, up to 14. This wide pH window may be useful in biological labeling.

Alkalinity is a critical factor to the ionizability of the PEI; thus it can be used for controlling the aggregation and dispersion of the nanorods. If these charges of the NH_3^+ groups on PEI molecules are neutralized, the solubility of the polymer reduced. Figure 4 shows the absorption spectra of the nanorod solution was dependent on the concentration of NaOH in the solution. The concentrations

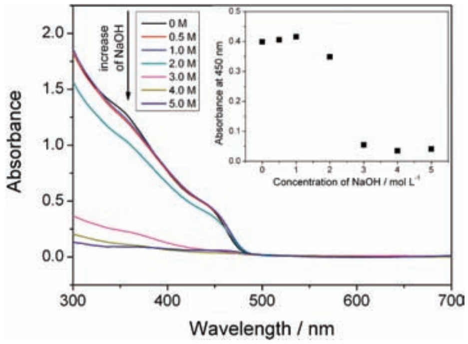

Figure 4. UV−vis spectra of the CdS nanorods dispersion in various concentrations of NaOH. The inset is the absorbance at 450 nm versus NaOH concentration.

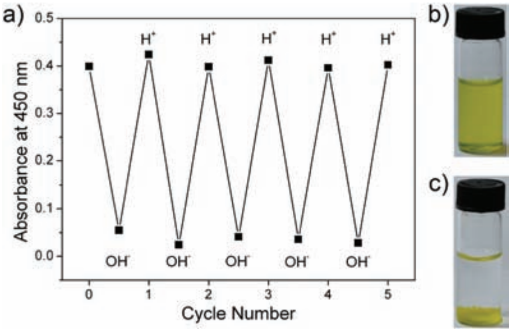

Figure 5. (a) Optical monitoring of alkalinity switched reversible cycling between aggregated and dispersed states of CdS nanorods. (b) Photograph of the CdS nanorods disperse in neutral aqueous solution, which forms a homogeneous, transparent suspension. (c) Photograph of the CdS nanorods precipitate from the ultrahigh alkaline solution (4 M NaOH).

of CdS nanorods dispersed in solution are monitored by the absorbance at 450 nm (inset of Figure 4). The CdS nanorods can be stably dispersed in water when the concentration of NaOH is less than 1.0 M but become almost insoluble in water when the concentration of NaOH is greater than 3.0 M. FTIR spectra of the precipitate (Figure S6c) show the strength of the peak located at 1643 cm^{-1} (NH_3^+ deformation mode) decreased clearly. A new peak located at 1560 cm^{-1} appears, which is attributed to the NH_2 deformation mode.[14] It indicates that most of the NH_3^+ groups have been neutralized. The neutralized molecule has low solubility in water; thus the CdS nanorods aggregate and precipitate. The precipitate can be redispersed in water by adding H^+. The absorbance returns to its initial intensity and indicates that the nanorods can redisperse in water in a neutral aqueous solution. This process can be repeated several times (Figure 5a), corresponding to the reversible aggregation and dispersion of the CdS nanorods. Figure 5b and 5c show two photographs of the CdS nanorods in dispersion and aggregation forms, respectively. It shows the potential in the design of a smart material that can respond to the alkalinity of the system, which may be used in separation or detection applications.

In conclusion, highly water-soluble ultrathin CdS nanorods were directly synthesized with the assistance of PEI. PEI acts as the passivator to control and induce the growth of the CdS nanorods and also makes the as-obtained nanorods dispersible in water. By adjusting the alkalinity of the solution, CdS nanorods can be controlled to precipitate or redisperse in water, which is believed to stem from the variation of the charges of the capping PEI molecules. The as-obtained CdS nanorods also show the fluorescent property and the wavelength of the emission are tunable. These results provide an efficient and convenient way to directly synthesize water-soluble and fluorescent nanocrystals, which has potential application in biological labeling and detection.

Acknowledgment. This work was supported by NSFC (90606006, 20771064) and the State Key Project of Fundamental Research for Nanoscience and Nanotechnology (2006CB932303, 2006CB932608).

Supporting Information Available: Experimental details; scheme of the detailed structure of tetrapod; additional TEM, XRD, EDS, and FTIR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Alivisatos, A. P. *Science* **1996**, *271*, 933. (b) Burda, C.; Chen, X. B.; Narayanan, R.; El-Sayed, M. A. *Chem. Rev.* **2005**, *105*, 1025.

(2) (a) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706. (b) Yin, Y. D.; Alivisatos, A. P. *Nature* **2005**, *437*, 664. (c) Park, J.; Joo, J.; Kwon, S. G.; Jang, Y.; Hyeon, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 4630. (d) Jun, Y. W.; Choi, J. S.; Cheon, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 3414.

(3) (a) Chan, W. C. W.; Nie, S. M. *Science* **1998**, *281*, 2016. (b) Larson, D. R.; Zipfel, W. R.; Williams, R. M.; Clark, S. W.; Bruchez, M. P.; Wise, F. W.; Webb, W. W. *Science* **2003**, *300*, 1434. (c) Bagalkot, V.; Zhang, L. F.; Levy-Nissenbaum, E.; Jon, S.; Kantoff, P. W.; Langer, R.; Farokhzad, O. C. *Nano Lett.* **2007**, *7*, 3065.

(4) (a) Pellegrino, T.; Manna, L.; Kudera, S.; Liedl, T.; Koktysh, D.; Rogach, A. L.; Keller, S.; Radler, J.; Natile, G.; Parak, W. J. *Nano Lett.* **2004**, *4*, 703. (b) Pradhan, N.; Battaglia, D. M.; Liu, Y. C.; Peng, X. G. *Nano Lett.* **2007**, *7*, 312. (c) Zhang, T. R.; Ge, J. P.; Hu, Y. X.; Yin, Y. D. *Nano Lett.* **2007**, *7*, 3203.

(5) (a) Nosaka, Y.; Ohta, N.; Fukuyama, T.; Fujii, N. *J. Colloid Interface Sci.* **1993**, *155*, 23. (b) Bao, H. B.; Gong, Y. J.; Li, Z.; Gao, M. Y. *Chem. Mater.* **2004**, *16*, 3853. (c) Chen, C. C.; Chao, C. Y.; Lang, Z. H. *Chem. Mater.* **2000**, *12*, 1516. (d) Sapra, S.; Nanda, J.; Sarma, D. D.; El-Al, F. A.; Hodes, G. *Chem. Commun.* **2001**, 2188.

(6) (a) Schill, A. W.; El-Sayed, M. A. *J. Phys. Chem. B* **2004**, *108*, 13619. (b) Qi, L. M.; Colfen, H.; Antonietti, M. *Nano Lett.* **2001**, *1*, 61. (c) Duxin, N.; Liu, F. T.; Vali, H.; Eisenberg, A. *J. Am. Chem. Soc.* **2005**, *127*, 10063.

(7) (a) Cademartiri, L.; Ozin, G. A. *Adv. Mater.* **2009**, *21*, 1013. (b) Panda, A. B.; Glaspell, G.; El-Shall, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 2790. (c) Pradhan, N.; Xu, H. F.; Peng, X. G. *Nano Lett.* **2006**, *6*, 720. (d) Sun, J. W.; Buhro, W. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 3215.

(8) (a) Li, Y. D.; Liao, H. W.; Ding, Y.; Qian, Y. T.; Yang, L.; Zhou, G. E. *Chem. Mater.* **1998**, *10*, 2301. (b) Yu, S. H.; Wu, Y. S.; Yang, J.; Han, Z. H.; Xie, Y.; Qian, Y. T.; Liu, X. M. *Chem. Mater.* **1998**, *10*, 2309. (c) Deng, Z. X.; Li, L. B.; Li, Y. D. *Inorg. Chem.* **2003**, *42*, 2331. (d) Yang, J.; Zeng, J. H.; Yu, S. H.; Yang, L.; Zhou, G. E.; Qian, Y. T. *Chem. Mater.* **2000**, *12*, 3259.

(9) (a) Winter, J. O.; Liu, T. Y.; Korgel, B. A.; Schmidt, C. E. *Adv. Mater.* **2001**, *13*, 1673. (b) Santra, S.; Yang, H.; Stanley, J. T.; Holloway, P. H.; Moudgil, B. M.; Walter, G.; Mericle, R. A. *Chem. Commun.* **2005**, *25*, 3144. (c) Deka, S.; Quarta, A.; Lupo, M. G.; Falqui, A.; Boninelli, S.; Giannini, C.; Morello, G.; De Giorgi, M.; Lanzani, G.; Spinella, C.; Cingolani, R.; Pellegrino, T.; Manna, L. *J. Am. Chem. Soc.* **2009**, *131*, 2948.

(10) (a) Peng, Z. A.; Peng, X. G. *J. Am. Chem. Soc.* **2001**, *123*, 183. (b) Jun, Y. W.; Lee, S. M.; Kang, N. J.; Cheon, J. *J. Am. Chem. Soc.* **2001**, *123*, 5150. (c) Gao, F.; Lu, Q. Y.; Xie, S. H.; Zhao, D. Y. *Adv. Mater.* **2002**, *14*, 1537. (d) Chen, M.; Xie, Y.; Lu, J.; Xiong, Y. J.; Zhang, S. Y.; Qian, Y. T.; Liu, X. M. *J. Mater. Chem.* **2002**, *12*, 748. (e) Bunge, S. D.; Krueger, K. M.; Boyle, T. J.; Rodriguez, M. A.; Headley, T. J.; Colvin, V. L. *J. Mater. Chem.* **2003**, *13*, 1705. (f) Li, Y. C.; Li, X. H.; Yang, C. H.; Li, Y. F. *J. Mater. Chem.* **2003**, *13*, 2641.

(11) Manna, L.; Milliron, D. J.; Meisel, A.; Scher, E. C.; Alivisatos, A. P. *Nat. Mater.* **2003**, *2*, 382.

(12) (a) Milliron, D. J.; Hughes, S. M.; Cui, Y.; Manna, L.; Li, J. B.; Wang, L. W.; Alivisatos, A. P. *Nature* **2004**, *430*, 190. (b) Shieh, F.; Saunders, A. E.; Korgel, B. A. *J. Phys. Chem. B* **2005**, *109*, 8538. (c) Carbone, L.; Kudera, S.; Carlino, E.; Parak, W. J.; Giannini, C.; Cingolani, R.; Manna, L. *J. Am. Chem. Soc.* **2006**, *126*, 748.

(13) Saunders, A. E.; Ghezelbash, A.; Sood, P.; Korgel, B. A. *Langmuir* **2008**, *24*, 9043.

(14) Okabayashi, H.; Shimizu, I.; Nishio, E.; O'Connor, C. J. *Colloid Polym. Sci.* **1997**, *275*, 744.

JA909776G