

Shape-Controlled Solution-Synthesis of Single Crystalline ZnTe 1D Nanocrystals

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ABSTRACT

Precursor-reduction method is employed to synthesize nanostructures of ZnTe. The shape of zinc blende ZnTe nanocrystals could be influenced by reaction temperature, concentration of the precursors as well as the use of stabilizing agent. By controlling the synthetic conditions, three types of nanoscaled ZnTe, quasi-spherical ZnTe nanocrystals, ZnTe nanobelts and ZnTe nanorods have been observed. Their crystalline structures are also discussed.

INTRODUCTION

Compared with the size-control [1], maintenance of the particle shape is hard and there still have been plenty of targets to challenge [2-5]. ZnTe is an attractive semiconductor with a direct band gap of 2.1 - 2.26 eV [6,7] and a Bohr exciton radius of 6.2 nm [8]. Its broad range of potential applications in optoelectronic devices operating in the blue-green region of the spectrum and thermoelectric devices has attracted increasing attention recently [5,9,10]. In addition, the crystal structure of ZnTe is very similar to that of CdSe, a commonly studied semiconductor [2,11,12]. Compared with other semiconductor NCs, however, studies on the preparation of colloidal ZnTe NCs are still limited. Previous studies indicated that a direct reaction between metal zinc (or zinc salts) and tellurium could result in very little ZnTe leaving most reactant unreacted¹⁰. Yadong Li [13] etc. suggested that this might be due to the fact that tellurium was not easily to be reduced to anions. We therefore design a reaction approach in which the Te precursor reduction and NC growth could be “separated” by altering the reducing rate. The feature of this strategy is that the NC shape could be controlled through various parameters, such as reaction temperature, concentration of precursors, and use of crystallographic-plane-selective stabilizing agent.

EXPERIMENT

Chemicals: Metal tellurium (99.99%), zinc acetate dehydrate (98+%), trioctylphosphine (TOP, 90%), oleylamine (70%), oleic acid (90%), benzyl ether (99%), dioctyl ether (99%) and super-hydride (LiBH(CH₂CH₃)₃) solution in THF (1M) are Aldrich products and were used as received. tetradecylphosphonic acid (TDPA, 98%) and phenyl ether (99%) were purchased from Alfa Aesar. Anhydrous ZnCl₂ was dried in an oven at 130 °C for one week before use. Super-hydride solution in dioctyl ether (1M) was freshly prepared before use according to literature [14,15].

Synthesis of ZnTe Quasi-spheres: In a typical experiment, zinc acetate dihydrate (1 mmol), benzyl ether (15 mL), oleic acid (1 mL) were mixed and heated to 150 °C for 30 min under vacuum to

remove moisture. The temperature was then raised to 250 °C. A mixture of Te-TOP solution (1 mL) and 1 M superhydride solution in dioctal ether (1 mL) was then rapidly injected into this hot solution. The colloidal system was kept at 250 °C for 10 min before being cooled down. Resultant NCs were collected in different periods of time for analyses. The products were separated by adding excessive amount of ethanol followed by centrifugation. The isolated NCs were re-dispersed in hexane, producing ZnTe colloidal suspensions.

Synthesis of ZnTe Nanobelts: 5ml of benzyl ether containing 1mmol of zinc acetate dihydrate and 1 ml of oleic acid was heated up to 150 °C under vacuum in a 100 mL three-neck round-bottom flask, kept at the same temperature for 10 minutes, and then cooled down to room temperature. A mixture of Te-TOP solution (1 mL) and 1 M superhydride solution in dioctal ether (1 mL) was added into the system, forming a transparent solution. The precursor was then injected into 10 ml of hot phenyl ether containing 0.2 g of TDPA which was preheated to 250 °C under argon protection. The reaction was terminated by removal of heating source after 15 min. The products were collected by centrifugation and washed with acetone, ethyl alcohol, hexane and toluene in sequence, and re-dispersed in toluene.

Synthesis of ZnTe Nanorods: 0.272g of ZnCl₂ (2 mmol,) was added to the mixture of benzyl ether (10 mL) and oleylamine (2.0 mL) at room temperature and the resultant solution was heated to 150 °C under vacuum. The homogeneous and clear mixture was then naturally cooled to room temperature. 2 mL of Te-TOP solution (1 M) and superhydride solution in dioctal ether (2 mL) were then introduced into this system. Such resultant precursor (5 mL) was aged for 24 h and then added into 10 mL of benzyl ether, gradually heated up to 150 °C, and kept at this temperature for a certain period of growth time, up to 3h. The separation procedure was as same as that mentioned in the synthesis of quasi-spheres.

Characterization: Powder XRD was carried out on a PANalytical X'pert diffractometer (CuK α 1 radiation). TEM images were obtained using a JEOL 2010 FEG TEM operating at 200 kV.

DISCUSSION

We propose that there are at least three equilibriums which exist in this synthesis, i.e. a conversion of metallic Te to intermediate state [Te²⁻]^{*} [16], a fast inorganic formation to ZnTe clusters, and a ZnTe NC growth. When the superhydride, a very strong reducing agent, was introduced into the system, the conversion rate of the first step should be tremendously increased. Under this condition, the rate-controlling step should be the step 3, crystal growth, since the inorganic nucleation (the second step) is usually fast [17] and could not be a rate-determining step. It is generally believed that, for a primarily formed single-phase crystal with ultra-small size, their surfaces must be polyhedral containing high-index crystallographic planes, which have a tendency of growing for increasing the surface area of those crystallographic planes that possess low total surface energy. Thus, the shape development of the NCs is actually dependent on the growth-rate-competition on different surface facets dominated by their surface energies. Relatively enriched amount of [Te²⁻]^{*}, kinetically generated by a strong reducing agent (superhydride), can efficiently minimize the growing-rate-difference among all the surface facets, resulting in a tendency of spherical NC formation. As revealed in Fig. 1a, transmission

electron microscopy (TEM) images show that the resulting NCs present in shape of quasi-sphere and in average size of ~ 5 nm when growing for 5 min at 250 °C. High-resolution TEM (HRTEM) image presented in Fig. 1d exposes the high crystallinity in these NCs. The X-ray diffraction (XRD) pattern of corresponding sample given in Fig. 2a verifies the single-phase of zinc blende (or sphalerite) structure. All of the detected peaks are indexed as those from the standard ICDD PDF card (No. 15-0746).

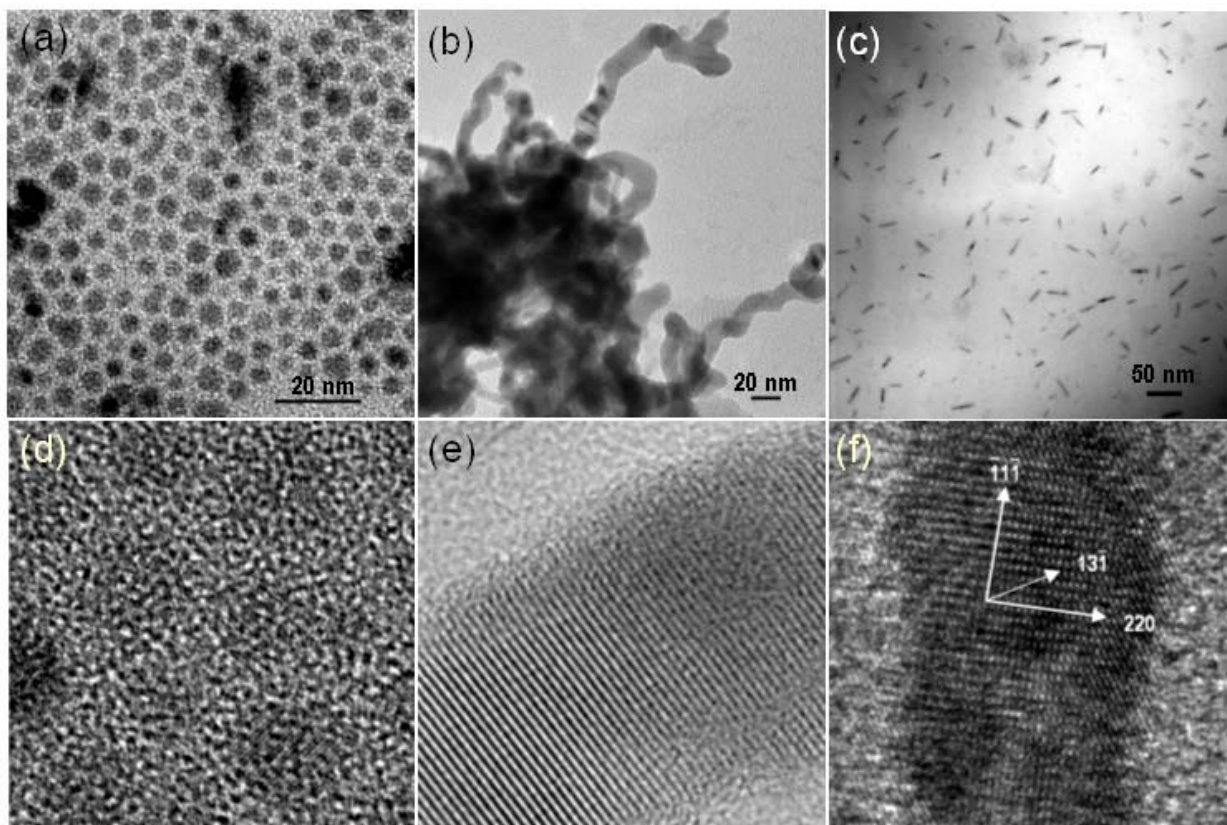


Figure 1. Transmission electron microscopy images of nanoscaled ZnTe produced from three reaction pathways. (a) quasi-spherical ZnTe NCs; (b) ZnTe nanobelts, and (c) ZnTe nanorods. (d), (e) and (f) are their high-resolution TEM images, respectively.

As reported before, however, such competitive but “isotropic” growth could be altered if certain crystalline face(s) is capped with special organic ligand [18,19]. Tetradecylphosphonic acid (TDPA) is a crystallographic-plane-selective capping ligand used for “aligning” the crystal growth direction [12,20], and has been used in anisotropic growth of several semiconductors, in which the presence of two surfactants with significantly different binding abilities to NC faces is essential. For example, nanowires of PbSe grown along $\langle 100 \rangle$ axis could be observe when oleic acid and TDPA were utilized as stabilizing agents [21]. We accordingly adopted the use of TDPA and applied this stabilizing agent together with oleic acid to above system, successfully observing a formation of ZnTe nanobelts. Fig. 1b is a low-magnification TEM image, displaying that the as-prepared products consist of a large quantity of ribbon-like nano-constituents with the lengths in the range of several hundred nanometers to 10 microns and the widths of straight belts are in range of 10-30 nm. The phase purity of the products was examined by XRD, exhibiting a cubic zinc blende phase of ZnTe (Fig. 2b). These ZnTe nanobelts (or nanoribbons) are very uniform in width along the entire length, and no discrete particle was detected among the nanobelts. As shown in Fig. 1e, HRTEM

image further provides insight into the microstructural details of the belt-like nanostructures, revealing that they are single-crystalline with interplanar spacing of about 0.36 nm, which corresponds to the (111) crystalline plane. This indicates that the growth direction for these nanobelts is along $\langle 111 \rangle$.

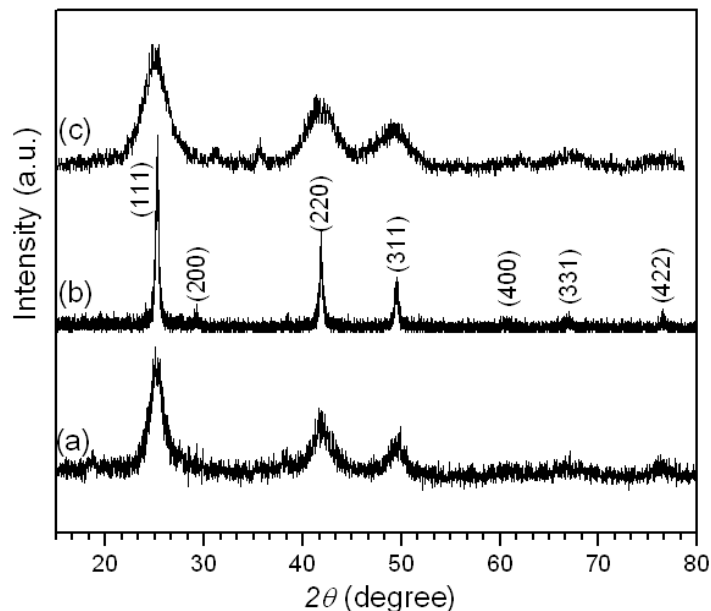


Figure 2. XRD patterns obtained from samples produced from three types of reactions. (a), quasi-spherical ZnTe NCs; (b), ZnTe nanobelts; (c), ZnTe nanorods. The broadened peaks were caused by the co-existing tiny particle, the minor peaks centered at 31.77, 34.40 and 36.25 degrees could be indexed to those from pattern of ZnO (ICDD PDF Card No. 36-1451).

The reaction temperature and precursor concentration are two of the critical parameters to control the final shape of a NC. As reported before [4], the competition of growth regime between thermodynamic and nonequilibrium kinetic growth can be tuned by varying the growth temperature [11,20,22-24] and by altering the concentration of monomers [4]. At high growth temperature (in our current circumstance, 250 °C), zero-dimensional structures such as nanospheres which are thermodynamically most stable shapes are normally anticipated to form. At low temperature and sufficient amount of $[\text{Te}^{2-}]^*$, however, the third step might be the rate-controlling growth step and the reaction favors 1D growth. As an example, ZnTe nanorods were observed at 150 °C, indicating an anisotropic crystal growth. Fig. 1c is a TEM image, showing that the ZnTe NCs are rod-like and well dispersed, with an average size of ~5 nm by ~30 nm. The average diameter of these nanorods is smaller than the Bohr diameter of (bulk) ZnTe (6.2 nm [8]) and much less than those ZnTe nanorods reported previously [9,10]. Based on the analysis of the HRTEM image (Fig. 1f), it can be concluded that the nanorods grow along a $\langle 111 \rangle$ direction. We therefore suggest that ZnTe nanorods might be resulted from the higher growth rate in $\langle 111 \rangle$ direction of the preliminary ZnTe nuclei, which is the *c*-direction of a rod structure. It is worth mentioning that the presence of oleylamine is also essential to yield ZnTe nanorods under the low-temperature condition, implying that oleylamine probably acts as a weak template [25] to assist the formation of ZnTe nanorods at low temperature. Meanwhile, we also realize that these nanorods is always in company with some tiny ZnTe particles. These extremely small particles could be most likely oxidized if the

sample being exposed in air for long time. In the XRD pattern presented in Fig. 2c, the minor peaks centered at 31.77, 34.40 and 36.25 degrees could be indexed to those from ZnO (ICDD PDF Card No. 36-1451), further confirming the presence of such tiny particles.

CONCLUSIONS

Syntheses of three-type nanostructures of ZnTe have been discussed. At high reaction temperature and high concentration of precursors, the crystal growth should be the rate-controlling step and normally spherical ZnTe NCs are expected to form; whereas at low reaction temperature and in the presence of oleylamine as a weak capping ligand, ZnTe nanorods were observed. However, use of TDPA, a crystallographic-plane-selective, may alter the shape of product. At 250 °C, injection the same constituents into TDPA solution results in a formation and ZnTe nanobelts. In all three cases, only cubic phase of ZnTe was determined.

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REFERENCES

1. C. B. Murray, S. Sun, W. Gaschler, H. Doyle, T. A. Betley and C. R. Kagan, *IBM J. Res. Dev.* **45**, 47 (2001).
2. X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich and A. P. Alivisatos, *Nature* **404**, 59 (2000).
3. Y.-w. Jun, J.-w. Seo, S. J. Oh and J. Cheon, *Coordin. Chem. Rev.* **249**, 1766–1775 (2005).
4. L. Manna, E. C. Scher and A. P. Alivisatos, *J. Clust. Sci.* **13**, 521 (2002).
5. S. H. Lee, Y. J. Kim and J. Park, *Chem. Mater.* **19**, 4670 (2007).
6. X. Huang, J. Li and H. Fu, *J. Am. Chem. Soc.* **122**, 8789 (2000).
7. T. Mahalingam, V. S. John, S. Rajendran and P. J. Sebastian, *Semicond. Sci. Technol.* **17**, 465 (2002).
8. L. Li, Y. Yang, X. Huang, G. Li and L. Zhang, *J. Phys. Chem. B* **109**, 12394 (2005).
9. K.-T. Yong, Y. Sahoo, H. Zeng, M. T. Swihart, J. R. Minter and P. N. Prasad, *Chem. Mater.* **19**, 4108 (2007).
10. J. Du, L. Xu, G. Zou, L. Chai and Y. Qian, *J. Cryst. Growth* **291**, 183–186 (2006).
11. Z. A. Peng and X. Peng, *J. Am. Chem. Soc.* **123**, 1389 (2001).
12. F. Shieh, A. E. Saunders and B. A. Korgel, *J. Phys. Chem. B* **109**, 8538 (2005).
13. Y. Li, Y. Ding and Z. Wang, *Adv. Mater.* **11**, 847 (1999).
14. J. Fang, K. L. Stokes, W. L. Zhou, W. Wang and J. Lin, *Chem. Commun.*, 1872–1873 (2001).
15. S. Sun and C. B. Murray, *J. Appl. Phys.* **85**, 4325 (1999).
16. W. Lu, Y. Ding, Y. Chen, Z. L. Wang and J. Fang, *J. Am. Chem. Soc.* **127**, 10112 (2005).
17. C. B. Murray, C. R. Kagan and M. G. Bawendi, *Annu. Rev. Mater. Sci.* **30**, 545–610 (2000).

18. S.-M. Lee, S.-N. Cho and J. Cheon, *Adv. Mater.* **15**, 441 (2003).
19. Y.-w. Jun, J.-H. Lee, J.-s. Choi and J. Cheon, *J. Phys. Chem. B* **109**, 14795 (2005).
20. L. Manna, E. C. Scher and A. P. Alivisatos, *J. Am. Chem. Soc.* **122**, 12700 (2000).
21. K.-S. Cho, D. V. Talapin, W. Gaschler and C. B. Murray, *J. Am. Chem. Soc.* **127**, 7140 (2005).
22. W. Lu, J. Fang, K. L. Stokes and J. Lin, *J. Am. Chem. Soc.* **126**, 11798 (2004).
23. S.-M. Lee, Y.-w. Jun, S.-N. Cho and J. Cheon, *J. Am. Chem. Soc.* **124**, 11244 (2002).
24. Y.-w. Jun, Y.-y. Jung and J. Cheon, *J. Am. Chem. Soc.* **124**, 615 (2002).
25. Y. Hou, Z. Xu and S. Sun, *Angew. Chem. Int. Ed.* **46**, 6329 (2007).