Facile Synthesis of a Hierarchical PbTe Flower-like Nanostructure and Its Shape Evolution Process Guided by a Kinetically Controlled Regime

Genqiang Zhang, Xiaoli Lu, Wei Wang, and
Xiaoguang Li*

*Hefei National Laboratory for Physical Sciences at
Microscale, Department of Physics, University of Science
and Technology of China, Hefei, 230026, P.R. China*

*Received April 27, 2007
Revised Manuscript Received September 3, 2007*

The architectural manipulation of nanobuilding blocks with well-defined shapes and accurately tunable sizes remains the focus in modern colloids and materials chemistry and is a key for the success of "bottom-up" approaches toward future nanodevice fabrication.[1] Thus, considerable efforts have been devoted to exploit powerful synthetic schemes which allow kinetically or thermodynamically controlling the fabrication of various nanocrystals, and remarkable progress has been achieved.[2,3] Recently, the formation of complex three-dimensional (3D) nanostructures has attracted more and more attention in the synthetic chemistry and materials area,[4] which is relatively undeveloped, especially in mild and low-cost synthetic routes.

It was reported that PbTe and PbTe based compounds are superior materials for thermoelectric cooling and electric power generation devices.[5] Thus, their synthesis has been greatly stimulated. For example, PbTe nanospheres/cubes, nanorods, and nanotubes have been synthesized using high-temperature solution-phase synthesis (HTSPS) methods based on trioctylphosphine telluride (TOP−Te) precursor,[6] sonoelectrochemistry,[7] and a hydrothermal driven approach,[8] respectively. Recently, Yu et al. and Wang et al. reported two kinds of interesting PbTe architectures, micro-hopper crystals and nanoboxes using the hydro/solvothermal process,[9] which greatly stimulated the study of complex PbTe nanostructures. Therefore, to exploit PbTe new nanostructures under simple and mild conditions is of great interest.

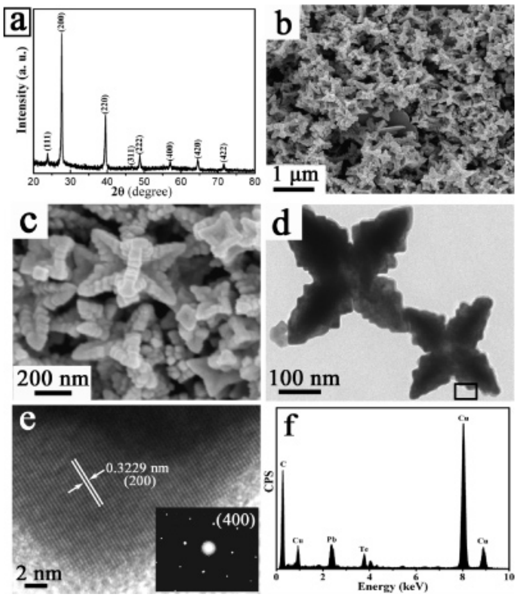

Figure 1. Integrated characterization of PbTe flower-like crystals obtained at 170 °C using PVP as surfactant. (a) Typical XRD pattern; (b and c) SEM images; (d) TEM image; (e) HRTEM image (the inset is the corresponding SAED pattern); and (f) EDS spectrum.

Here, we report the synthesis of PbTe hierarchical flower-like crystals with eight tower-like horns through a simple refluxing process using nontoxic ethylene glycol (EG) as solvent and convenient inorganic salts as precursors. In addition, by kinetically controlling the surface energy of the crystal nuclei, the morphology can be selectively evolved to one-dimensional (1D) nanowires and well-defined nanocubes with tunable sizes by simply adjusting surfactant or pH value of the medium.

In a typical synthesis, 2 mmol of $Pb(Ac)_2 \cdot 3H_2O$ and 2 mmol of TeO_2 were dissolved in 50 mL of hot EG containing 0.5 g of poly(vinyl pyrrolidone) (PVP, K-30, Ms $\approx$ 40 000). Afterward, 1.5 mL of $N_2H_4 \cdot H_2O$ was injected at 170 °C, and the products were collected by centrifugation after 30 min of reaction. They were washed with distilled water and ethanol several times and then dried in vacuum at 60 °C for further characterization.

The X-ray diffraction (XRD) pattern of the as-prepared products (see Figure 1a) matches well with the face-centered cubic (fcc) PbTe structure with the *Fm*3*m* space group

---

* Corresponding author. E-mail: lixg@ustc.edu.cn. Fax: 86-551-3603408.

(1) (a) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226. (b) Hu, J.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435. (c) Markovich, G.; Collier, C. P.; Henrichs, S. E.; Remacle, F.; Levine, R. D.; Heath, J. R. *Acc. Chem. Res.* **1999**, *32*, 415.

(2) (a) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545. (b) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706. (c) Puntes, V. F.; Krishnan, K. M.; Alivisatos, A. P. *Science* **2001**, *291*, 2115.

(3) (a) Peng, X. G.; Manna, L.; Yang, W. D.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59. (b) Peng, Z. A.; Peng, X. G. *J. Am. Chem. Soc.* **2001**, *123*, 1389. (c) Kuno, M.; Ahmad, O.; Protasenko, V.; Bacinello, D.; Kosel, T. H. *Chem. Mater.* **2006**, *18*, 5722. (d) Wang, Q. B.; Seo, D. K. *Chem. Mater.* **2006**, *18*, 5764. (e) Tang, B.; Yang, F.; Lin, Y.; Zhuo, L. H.; Ge, J. C.; Cao, L. H. *Chem. Mater.* **2007**, *19*, 1212. (f) Wang, W.; Lu, X. L.; Zhang, T.; Zhang, G. Q.; Jiang, W. J.; Li, X. G. *J. Am. Chem. Soc.* **2007**, *129*, 6702.

(4) (a) Narayanaswamy, A.; Xu, H. F.; Pradhan, N.; Kim, M.; Peng, X. G. *J. Am. Chem. Soc.* **2006**, *128*, 10310. (b) Narayanaswamy, A.; Xu, H. F.; Pradhan, N.; Peng, X. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 5361.

(5) (a) Shchennikov, V. V.; Ovsyannikov, S. V. *Solid State Commun.* **2003**, *126*, 373. (b) Harman, T. C.; Taylor, P. J.; Walsh, M. P.; LaForge, B. E. *Science* **2002**, *297*, 2229. (c) Hsu, K. F.; Loo, S.; Guo, F.; Chen, W.; Dyck, J. S.; Uher, C.; Hogan, T.; Polychroniadis, E. K.; Kanatzidis, M. G. *Science* **2004**, *303*, 818.

(6) (a) Lu, W. G.; Fang, J. Y.; Stokes, K. L.; Lin, J. *J. Am. Chem. Soc.* **2004**, *126*, 11798. (b) Murphy, J. E.; Beard, M. C.; Norman, A. G.; Phillip Ahrenkiel, S.; Johnson, J. C.; Yu, P. R.; Micic, O. I.; Ellingson, R. J.; Nozik, A. J. *J. Am. Chem. Soc.* **2006**, *128*, 3241.

(7) Qiu, X. F.; Lou, Y. B.; Samia, A. C. S.; Devadoss, A.; Burgess, J. D.; Dayal, S.; Bruda, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 5855.

(8) Zhang, L. Z.; Yu, J. C.; Mo, M. S.; Wu, L.; Kwong, K. W.; Li, Q. *Small* **2005**, *1*, 349.

(9) (a) Zhu, J. P.; Yu, S. H.; He, Z. B.; Jiang, J.; Chen, K.; Zhou, X. Y. *Chem. Commun.* **2005**, *46*, 5802. (b) Wang, W. Z.; Poudel, B.; Wang, D. Z.; Ren, Z. F. *Adv. Mater.* **2005**, *17*, 2110.

10.1021/cm071144g CCC: $37.00

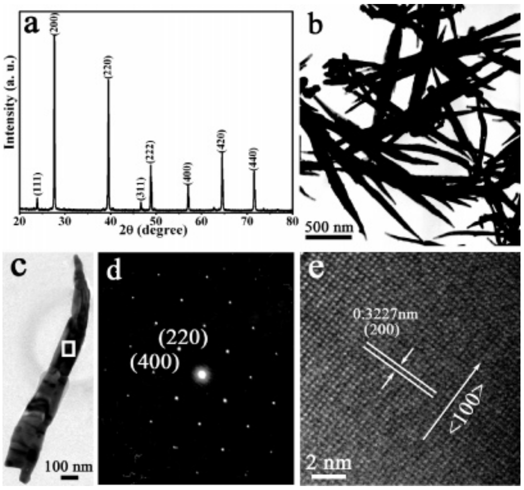

Figure 2. Intergrated characterization of PbTe nanowires obtained by completely replacing PVP with mass equivalent CTAB. (a) XRD pattern; (b and c) TEM images of the as-prepared products; (d) SAED pattern; and (e) HRTEM image taken from the marked area of the individual nanowire in part c.

(JCPDS, 38-1435). Typical scanning electron microscopy (SEM) images in Figure 1b,c show that the majority of the products are composed of hierarchical flower-like crystals with eight identical tower-like horns which present fascinating cubic symmetric structure. The size of these hierarchical crystals ranges from 300 to 400 nm. In addition, it can be seen from the transmission electron microscopy (TEM) image shown in Figure 1d that each horn exhibits dendritic character with short branches perpendicular to the trunk. High-resolution TEM (HRTEM) analysis (Figure 1e) taken from the marked area in Figure 1d gives the single crystalline nature of the products, and the lattice spacing of ∼0.3229 nm corresponds to the interplanar distance of {200} planes. The composition of the as-prepared products is confirmed by energy dispersive X-ray spectroscopy (EDS) analysis, as shown in Figure 1f, where, besides the Cu, C, and Cr signals from the copper grid used during the HRTEM analysis, only Pb and Te signals are detected with an atomic ratio of ∼1:1, which is consistent with the nominal composition.

To shed light on the formation of the hierarchical flower-like nanostructure, several comparison samples are prepared by adjusting the surfactant or pH value of the medium. Typical SEM images of the samples obtained with different amounts of PVP (see Supporting Information, Figure S1) indicate the shape evolution of the products from irregular particles to well-defined flower-like crystals along with the increased PVP molecules in the solution. The result clearly illustrated the importance of the PVP for the formation of PbTe flower-like crystals. To study the possible shape evolution of the products under the kinetically controlled regime, the morphology of the products obtained by completely replacing PVP with mass equivalent hexadecyltrimethylammonium bromide (CTAB) was analyzed in detail, as shown in Figure 2. Interestingly, pure nanowires with sharp tails are obtained.

It is well-known that, to kinetically control the morphology of nanocrystals, it is necessary to find an effective strategy which can change the surface energy of different facets of the crystal nuclei and induce the subsequent anisotropic growth.[6,9−11] To the best of our knowledge, the fabrication of 1D PbTe nanostructures using simple refluxing methods remains a challenge, although it has been carried out on the basis of a CTAB assisted hydrothermally driven rolling up process[7] and sonoelectrochemistry method.[8] Herein, a simple refluxing process combined with a common surfactant, CTAB, was found to be feasible for obtaining a 1D PbTe nanostructure.

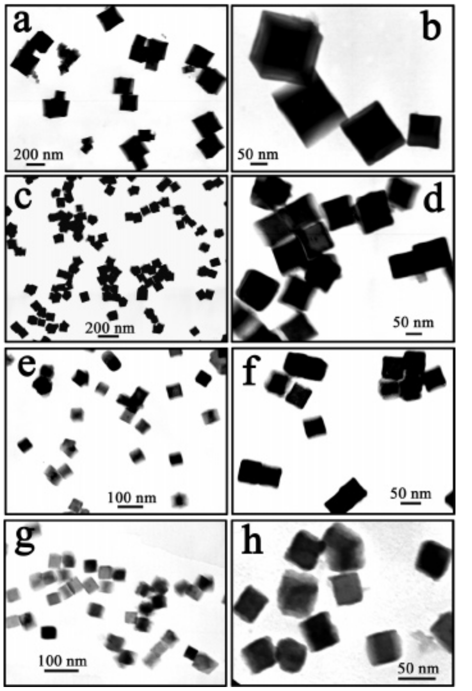

Figure 3. Typical TEM images of the PbTe nanocubes obtained with 0.5 g of PVP and 5 mL of NaOH solution with different concentrations: (a and b) 2; (c and d) 4; (e and f) 6; and (g and h) 10 mol/L. The corresponding pH values of the medium are 12.39, 13.08, 13.49, and 14, respectively.

The phase purity of the as-synthesized nanowires was examined by XRD analysis (Figure 2a), presenting no difference from that of the flower-like crystals. Typical TEM images (Figure 2b,c) indicate that each nanowire has sharp tails at both ends. The diameters at the middle of the nanowires are 100−130 nm, and the lengths are up to several micrometers. The growth direction of the nanowires is confirmed by the HRTEM analysis. Figure 2d,e shows the selected area electron diffraction (SAED) pattern and HRTEM image taken from the marked area of the individual nanowire shown in Figure 2c. The lattice spacing of ∼0.3227 nm corresponds to the {200} planes, indicating the 〈100〉 growth direction of the nanowires, which is consistent with the SAED pattern. The EDS spectrum (see Supporting Information, Figure S2) confirms the formation of PbTe crystals with an atomic ratio of about 1:1.

The effect of pH value on the morphology of PbTe nanostructure is also investigated by adding 5 mL of NaOH solution with different concentrations into the medium while keeping the other conditions constant. Figure 3 gives typical TEM images of the nanocubes obtained by adding 5 mL of

---

(10) (a) Murphy, C. J. *Science* **2002**, *298*, 2139. (b) Sun, Y. G.; Xia, Y. N. *Science* **2002**, *298*, 2176. (c) Wang, Z. L. *J. Phys. Chem. B* **2000**, *104*, 1153.

(11) Lee, S. M.; Cho, S. N.; Cheon, J. *Adv. Mater.* **2003**, *15*, 441.

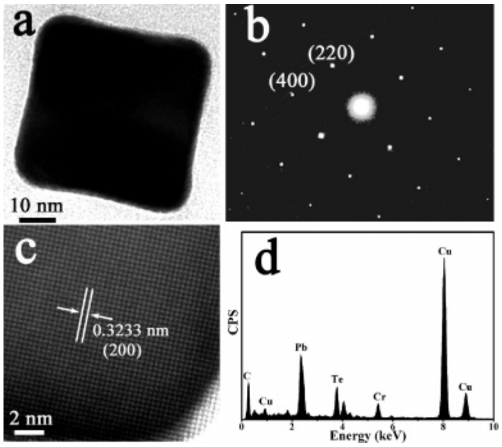

Figure 4. Microstructure and composition analysis of the PbTe nanocubes obtained using PVP as the stabilizing agent with 5 mL of 6 mol/L NaOH solution. (a) A typical TEM image of a randomly selected nanocube; (b) SAED pattern; (c) the corresponding HRTEM image; and (d) the EDS spectrum taken from the individual nanocube shown in part a.

NaOH solution with different concentrations: 2 (Figure 3a,b), 4 (Figure 3c,d), 6 (Figure 3e,f), and 10 mol/L (Figure 3g,h), respectively. All the products are well-defined cubes with controllable sizes, and the edge lengths of the as-synthesized nanocubes are about 120−160, 65−72, 40−45, and 30−35 nm, corresponding to Figure 3a,c,e,g, respectively. The microstructure and composition analyses of a randomly selected PbTe nanocube obtained with 5 mL of 6 mol/L NaOH solution are presented in Figure 4. The SAED pattern (Figure 4b) and the HRTEM image (Figure 4c) taken from the cube shown in Figure 4a indicate the single crystalline nature of the product. The spacing of the adjacent fringes is about 0.3233 nm, corresponding to the {200} planes. The EDS spectrum shown in Figure 4d gives that the approximate atomic ratio of Pb/Te is 1:1.

The shape evolution of the PbTe nanostructures in this solution process may involve several shape guiding parameters, and it is therefore significant to understand the possible growth mechanism of different morphologies. It is well-known that for the rock salt structure, the {111} surface intrinsically possesses a higher surface energy than those of the {100} or {110} faces. Generally, the ratio of the growth rate in the ⟨100⟩ direction to that in the ⟨111⟩ direction determines the shape of the fcc nanocrystal and faster growth on the {111} faces could favor the formation of cubic-shaped crystals.[10,11] To obtain complex nanostructures, the growth rate of different faces of the crystal nuclei should be controlled or adjusted in a delicate balance by using effective surfactants. In our work, the PVP should act as the capping agent, which is responsible for the formation of flower-like PbTe crystals.

As a result of the existence of the PVP, the adsorption and desorption of the surfactant molecules on different faces of PbTe nuclei may kinetically control the crystal growth direction.[10,11] First, the prevailing growth rate for {111} faces will diminish these faces and lead to the formation of cubic symmetry structure, and the subsequently preferential growth on the {100} faces should be responsible for the dendritic character of each horn. It can be concluded that the growth process of the flower-like crystal made of eight horns could be the delicate balance between growth velocity of the {111} and that of the {100} faces. Thus, these new flower-like PbTe crystals could be formed under a kinetic growth regime and strongly depend on the involved surfactant.

When PVP was completely replaced by mass equivalent CTAB, the related mechanism may have been drastically changed. The polar face of the PbTe nuclei could be terminated with CTAB molecules,[7,8] which may prevent the growth along these faces and induces the subsequently anisotropic growth guided by the soft template formed by the CTAB.

Introducing a certain amount of NaOH could intrinsically change the growth mechanism, and a fast growth process dominated by pH value could be appropriate for the formation of PbTe nanocubes. During this process, the interaction between PVP molecules and PbTe nuclei was weakened because of the role of OH^-, and this will induce the surface energy rearrangement of each face of the PbTe nuclei. The PVP could act as the stabilizing agent for the formation of PbTe nanocubes, and this is further supported by examining the products obtained with 5 mL of 4 mol/L NaOH only and 0.5 g of CTAB together with 5 mL of 4 mol/L NaOH (see Supporting Information, Figure S3).

In conclusion, a facile and low-cost solution-phase synthetic method was developed for fabricating PbTe hierarchical flower-like crystals composed of eight identical tower-like horns using an appropriate capping agent. In addition, guided by the kinetically controlled regime, the morphology can be controllably evolved into 1D nanowires and size-tunable nanocubes by adjusting the involved surfactant or pH value. This method provides an additional strategy for kinetically controlling the nanostructures on the basis of the simple solution-phase method and can be extended to synthesizing other alloy nanostructures.

Acknowledgment. This work was supported by the National Natural Science Foundation (No. 50421201) and the National Basic Research Program of China (No. 2006CB922005).

Supporting Information Available: The detailed experimental procedures of the reaction, the SEM images of the products with different amounts of PVP (Figure S1), TEM images of the products obtained with NaOH only and NaOH together with CTAB (Figure S2), and the EDS spectrum of the as-prepared nanowires (Figure S3) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM071144G