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Simple Route to Dots and Rods of PbTe Nanocrystals

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Lead chalcogenides in various forms with critical dimensions on the order of nanometers have attracted considerable interest because of their unique physical and chemical properties; they have potential in many applications.[1] The routes to such materials have included: sputtering,[2] ultrasonic,[3] hydrothermal, and solvothermal methods.[4] The injection of a solution of a lead salt and trioctylphosphine chalcogenide (TOPE, E = S, Se, Te) into a hot solvent[5] or thermolysis of single-source precursors are other examples of methods.[6]

PbTe is an important narrow band gap semiconductor material with a large excitonic Bohr radius (~46 nm).[7] It can or could be used in optical switches,[8] solar cells,[9] photodetectors,[10] thermoelectrical applications, and electroluminescent devices.[11] Nanodimensional crystals of PbTe have been reported, as dendrites,[12] sponge like structures,[13] spheres,[14] and boxes.[4] Many groups report that nanodimensional lead chalcogenide crystals undergo shape evolution from spherical to polyhedral, cubic, or tetragonal structures with increasing size/reaction time.[15] Dependence of the form of the final product on reaction temperature and the choice of capping ligand has also been noted.[5] The synthesis of 1D PbTe nanostructures is challenging.[16] Rods can also show good thermoelectric figures of merit (ZT) as compared to isotropic structures.[17] There are only a few reports of synthesis of PbTe nanorods or nanotubes, which include hydrothermal, sonoelectrochemical, and template-assisted synthesis.[16−18] However, these methods have limited success in the control overall shape and size. Herein, we report a completely new simple two-step colloidal method to synthesize single-crystal PbTe nano-spheres and -rods with control of size and shape.

Lead telluride was synthesized by the addition of an aqueous solution or suspension of a lead salt (chloride, nitrate, or carbonate), to a freshly prepared NaHTe solution. The solid product of this reaction was isolated by centrifugation, dispersed into TOP and injected into hot hexadecylamine (HDA) at temperatures of 190, 230, or or 270 °C and held at the same temperature for 2 or 4 h. After being cooled to 50 °C, the PbTe nanoparticles were isolated by the addition of methanol to the reaction mixture. The sequence of reactions is shown in eqs 1 and 2

$$4NaBH_4 + 2Te + 7H_2O \rightarrow 2NaHTe + Na_2B_4O_7 + 14H_2 \quad (1)$$

$$NaHTe + PbCO_3 \rightarrow PbTe + NaHCO_3 \quad (2)$$

In experiments using the carbonate, the type of PbTe nanocrystal obtained at different temperatures and reaction times varied as illustrated in Figure 1. This lead source gave distinct and interesting results as with the other soluble

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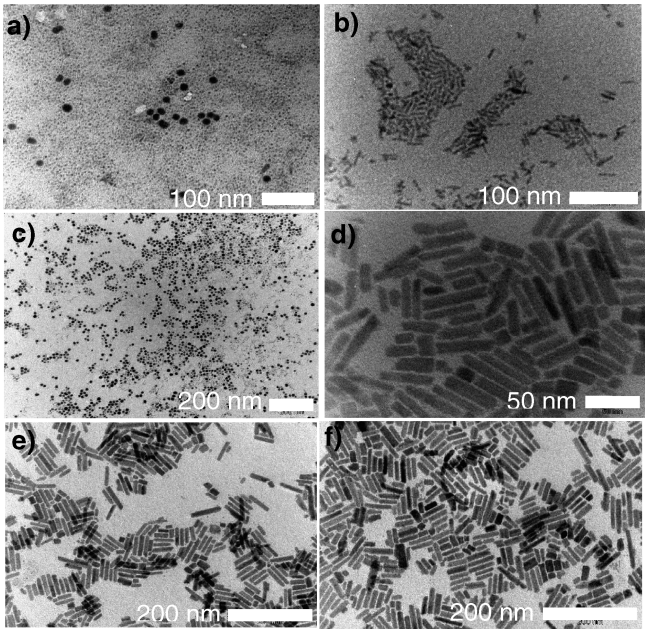

Figure 1. TEM images of PbTe nanocrystals prepared from $PbCO_3$ at (a, b) 190, (c, d) 230, and (e, f) 270 °C after (a, c, e) 2 and (b, d, f) 4 h, respectively.

salts only spherical particles were obtained (see the Supporting Information). With the soluble salts, it seems likely that nanoparticles are formed in aqueous suspension and are subsequently annealed in the HDA. For $PbCO_3$ at 190 °C spherical dots are seen after 2 h which after 4 h have changed to small rods (Figure 1a,b). Similar results were observed at 230 °C (Figure 1c,d), whereas at the highest temperature, 270 °C, only rods were formed (Figure 1e,f).

The intermediate material in the case of carbonate contains not only PbTe but also lead carbonate and tellurium, as confirmed by FT-IR and PXRD (see the Supporting Information). This composition allows for further kinetically controlled decomposition and the growth of particles in HDA in a "feed-limited" system. In the halite-structured lead chalcogenides, the formation of rods in which cubic symmetry is broken is really quite a common phenomenon. Close to spherical nanoparticles are minimum surface energy structures with no obvious facets. The growth rates on different facets in the system are dominated by surface energy. For halite type crystals the {111} face with high surface energy grows faster than the lower-surface-energy {100} face.

This favors {100} facets leading to cubes or rods.[19] Once an anisotropic structue has started to form, it is easy for this to propagate into a rod. The nature of the milieu of precursors produced by the carbonate system allows for this possibility.

The crystallinity of the spheres and rods prepared has been confirmed by powder X-ray diffraction (PXRD) indicating all are halite (fcc, space group *Fm*3*m*), Figure 2. The major diffraction peaks are indexed as (200), (220), (222), (420), and (422) of cubic PbTe (ICDD no. 08−0028). The X-ray photoelectron spectra from the PbTe nanorod

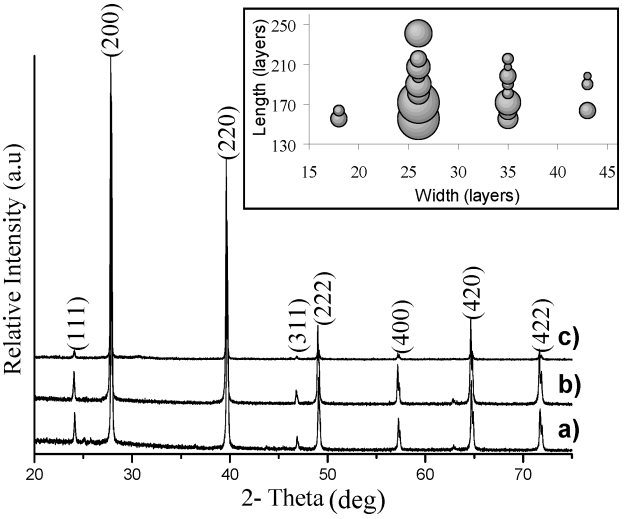

Figure 2. PXRD pattern of PbTe prepared from lead carbonate 4 h at (a) 190, (b) 230, and (c) 270 °C. The inset shows distribution of rods prepared at 270 °C (width and length are measured in units of $a/2$ as a buble graph); total number of rods measured 152 the area of the each circle is proportional to number of the rods whose size is given by position of center of the circle.

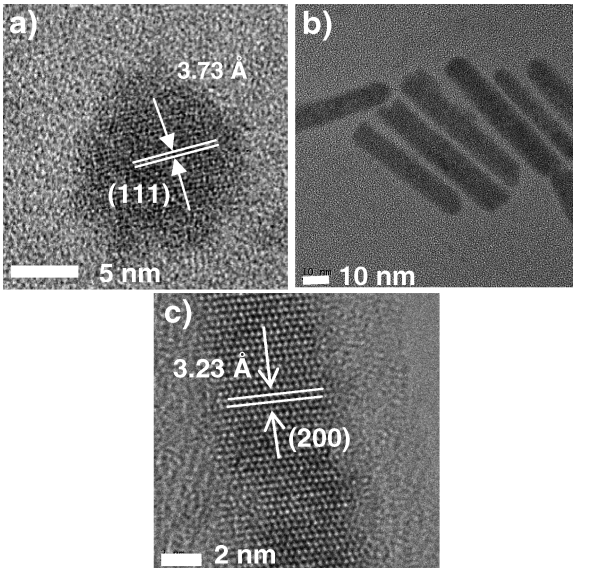

Figure 3. HRTEM images of PbTe prepared from lead carbonate: (a) nanospheres at 190 °C after 2 h, (b, c) nanorods at 270 °C after 4 h.

samples show evidence for PbTe and the oxides of Pb and Te (see the Supporting Information). The Pb 4f 7/2 sub-band at 136.9 eV and the dual Te 3d sub-bands at 571.6 and 582.1 eV correspond to unoxidized PbTe.[20] The high-energy Pb 4f sub-bands at 138.4 eV and Te 3d chemical states at 575.5 and 585.8 eV are from oxides of Pb and Te. The presence of oxides of Pb and Te is expected, as no especial precautions to exclude oxygen were taken. The predominance of PbTe (as also by PXRD) suggests that any oxide is likely to be only on the surface and with a thickness less than the Pb 4f and Te 3d electron escape depths (< 2 nm).

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At 190 °C, spherical particles with diameter 10.8 ± 1 nm were obtained after 2 h, 4 h gave rods of PbTe with length 15 ± 2 nm, width 5 ± 1 nm. At 230 °C, spherical particle diameters of 15.2 ± 1 nm were seen at 2 h, with rod lengths and widths of 35 ± 3 and 8 ± 1 nm after 4 h. Only rods were obtained at 270 °C, with a length of 45 ± 5 nm and width of 7.3 ± 1 nm after 2 h and length of 51.7 ± 10 nm and width of 9.1 ± 1.5 nm after 4 h. HRTEM (Figure 3a) images of the spherical particle showed with the expected lattice spacings of 3.7 Å corresponding to the (111) reflection. The rods show lattice fringes with a spacing 3.23 Å, the (200) reflection of cubic PbTe. Selected area electron diffraction patterns (SAED) show the single-crystalline nature of both the dots and rods of PbTe.

In summary, high-quality PbTe nanocrystals have been prepared by a simple route using telluride produced from tellurium powder reduced with $NaBH_4$ and lead as the carbonate. The shape of the final product is relatively easy to control and provides a more reliable route to such rods than some earlier approaches. Similar results also obtained in the synthesis of PbSe.

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Supporting Information Available: Synthesis of PbTe nanocrystals, TEM images of PbTe spherical particles, additional TEM images of PbSe and PbTe rods, XPS, IR spectra, table explaining particles obtained from different lead sources at different temperatures and time, and XRD pattern of product obtained using $PbCO_3$ before heating process. This material is available free of charge via the Internet at http://pubs.acs.org.