Communication

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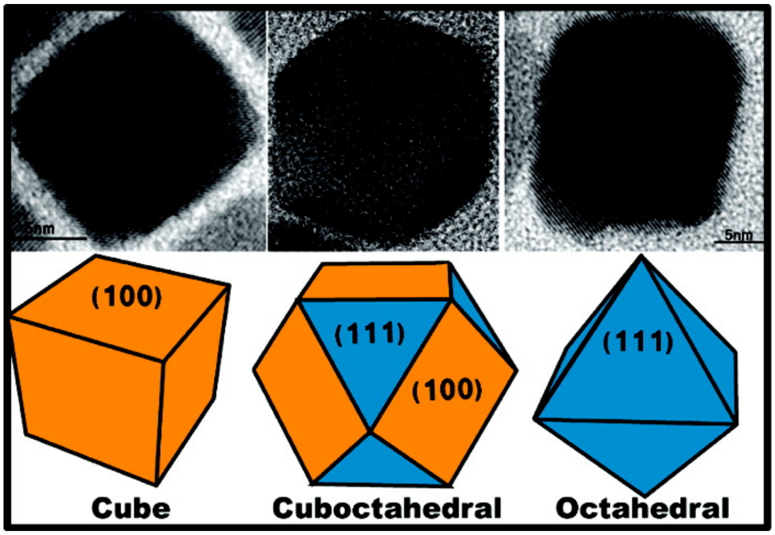

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Shape, Size, and Assembly Control of PbTe Nanocrystals

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The small band gap and the large Bohr radius[1] of the Pb-chalcogenide enable unique optical, electrical, and chemical properties, presenting this family of materials as a good candidate for potential application in solar cells,[2−4] thermoelectric (TE)[5] devices, telecommunication,[6] field effect transistors (FET),[7] and biological imaging. Integrating Pb-chalcogenide nanostructures in these devices requires precise control of their properties by manipulating size and morphology of the nanocrystals.

Tremendous efforts have been put toward controlling the properties of the nanocrystals by controlling their size due to quantum confinement phenomena.[8,9] Recently, more focus has been directed toward shape control as a means of tailoring chemical, physical, and optical properties of nanocrystals. Metals, insulators, and semiconductors have been well studied in the past decade as this strategy is particularly relevant for colloidal synthesis. Different routes to achieve shape control, including surfactants,[10−12] seeded growth,[13−15] and the use of different template materials,[16,17] were used to obtain shape control. In this paper, we focus on controlling PbTe nanocrystal growth by surfactant mediation and changing the ratio between the precursors. This mechanism for shape control is based on controlling the kinetics of the growth process by binding surfactants to different crystal facets and allowing a decrease or increase of crystal growth rate in different directions.

Several groups have reported controlled synthesis of PbTe nanocrystals,[18] all obtaining cube-shape structures with sizes ranging from 15 to 20 nm.[19,20] They showed that particle size is dependent on reaction time: for long growth times (∼20 min), the size of the particles is around 200−500 nm. These larger particles show cube-shaped morphologies even if they are initially cuboctahedral at earlier stages of the reaction.

Herein, we demonstrate the synthesis of PbTe nanocrystals with controllable shape and size. We establish a new method for controlling the shape of Pb-chalcogenide materials by controlling the reaction kinetic, using proper surfactant, the right temperature, and changing the molar ratio between Pb and Te. The reaction was carried out using trioctylphosphine (TOP) or diphenyl ether (DPE) as the growth solvent and phosphonic acid or amines (hexadecylamine, HDA, and dodecylamine, DDA) as the stabilizer surfactant. Two separate precursor solutions were prepared for Pb and Te. The Pb solution contained Pb-acetate trihydrate and oleic acid in TOP or DPE, and the Te solution was prepared by dissolving Te powder in TOP (see Supporting Information). The precursor was first injected at 250 °C followed by a constant growth temperature of 170−180 °C for 3−4 min. Figure 1 shows three different shapes that were obtained by changing the mole ratio between the Pb and the Te precursors. The rock salt structure of the PbTe materials, which possess different surface energies in different directions, allow controlling the shape of the nanoparticles by increasing and/or decreasing the growth rate in different directions. The ratio was changed from 5:1 (Pb:Te) to 1:5, and all the other parameters were kept the same (see Supporting Information). High Te ratio (1:5 Pb:Te) leads to the formation of cube-shape morphology, as shown in Figure 1A. However, changing the ratio to 5:1 of Pb:Te leads to an octahedral shape morphology with 20 nm particle size (Figure 1C). The intermediate ratio (1:1) forms the cuboctahedral shape with 22 nm size, and this shape was also observed with Pb:Te ratios of 1:2 and 2:1.

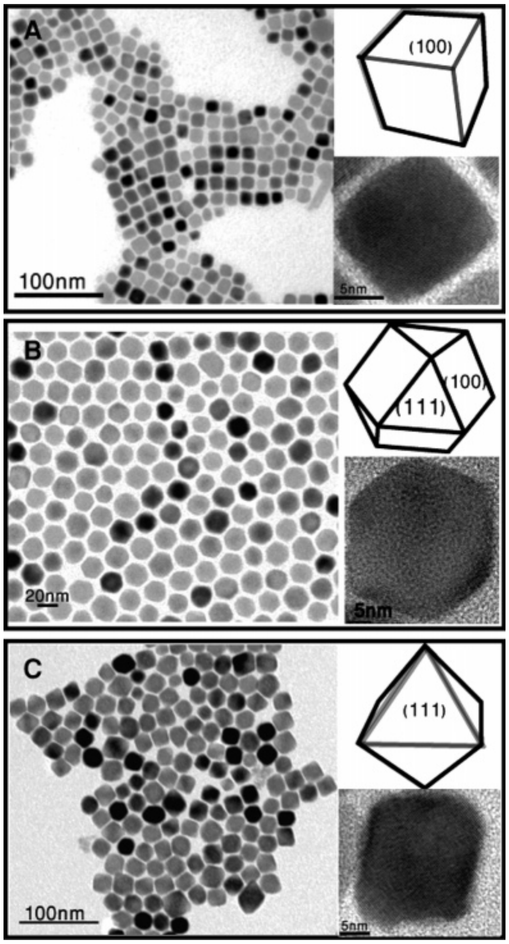

Figure 1. Three different shapes of PbTe nanocrystals are shown: (A) cubes (13 nm), (B) cuboctahedral (20 nm), and (C) octahedral particles (22 nm). Enlarged HRTEM images of the three shapes are shown in Figure S1.

The PbTe nanoparticle structures were studied by high-resolution transmission electron microscopy (HRTEM) and are shown to be single-crystalline as presented in Figures 1 and S1. Another evidence for the particles' crystallinity was provided by the powder X-ray diffraction (XRD) measurement; the obtained pattern (Figure S2)

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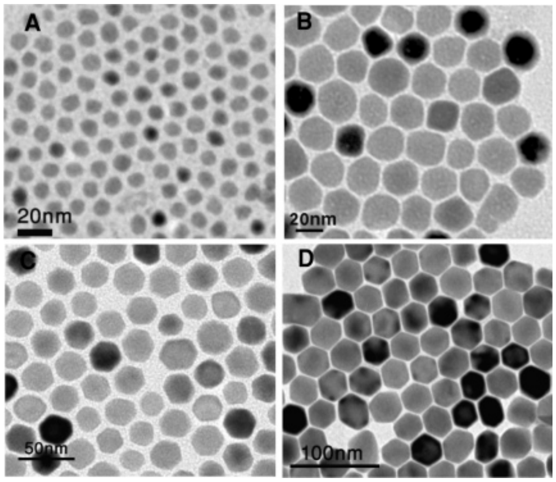

Figure 2. TEM images of PbTe cuboctahedral particles with different sizes: (A) 8 nm, (B) 22 nm, (C) 28 nm, and (D) 40 nm particles.

agrees well with PbTe bulk with cubic crystal structure. The selected area energy-dispersive X-ray spectroscopy (SA-EDS, Figure S3) spectrum of the single PbTe nanoparticle also confirms their composition.

Achieving shape control using surfactant becomes one of the most studied effects in the nanoparticle shape control field.[21] Here, we use HDA and DDA as stabilizers for obtaining the three different shapes. When the ratio between the Pb:Te is 1:5, the cube structures were obtained, and this is due to the saturation of the facets with Te. The effect of the amine is minimized since the amine has a high binding energy to the Pb atoms on the surface. On the other hand, saturation of the facets with Pb atoms (Pb:Te 5:1) leads to faster growth of the {100} facets compared to {111}, while the {111} facets are passivated by amines. The cuboctahedral nanocrystals have a more-or-less isotropic facet with either Pb or Se atom dominated (111) planes and equally distributed Pb and Se atoms on (100) planes. They represent an intermediate stage of (100) versus (111) shape regulation.

To study the effect of the surfactant, we have also tested tetradecylphosphonic acid (TDPA) or one of its derivatives (octadecyl- and hexylphosphonic acids), instead of the amines. The phosphonic acid leads to a slow growth rate; it takes $\sim$10 s for the nucleation to take place after the precursors' injection (change in the color of growth solution from colorless to black) compared to an immediate nucleation when the amine is used. This is due to the strong binding of the phosphonic acid to the nanoparticles' surface. The ratio between the precursors (Pb:Te) was also examined for this surfactant, and it was changed from 5:1 to 1:5. Cube particles were obtained when the ratio between the Pb:Te precursors is 1:5. However, the cuboctahedra were produced when the ratio for Pb:Te is 5:1 to 1:3. Octahedral particles were not achieved by using the phosphonic acid surfactant, and again this could be related to the fact that growing octahedra nanocrystals required a fast growth rate of the (100) direction compared to the (111) facet, and this is not achievable using phosphonic acid surfactant since the growth rate is slower using phosphonic acid.

Size uniformity of the cubic, cuboctahedral, and octahedral nanoparticles prepared using TOP and phosphonic acid can be controlled by the proper choice of surfactants and the reaction time (cuboctahedra shown in Figure 2 as an example). We used hexylphosphonic acid (HPA) and tetradecylphosphonic acid (TDPA) as two different surfactant systems (see Supporting Information) with a fixed time. When the HPA ligand is used, larger particles ($\sim$22 nm, Figure 2B) were obtained compared to the TDPA ($\sim$8 nm, Figure 2A). This can be attributed to faster growth kinetics in the HPA case (both of the reactions were stopped 3 min after the precursors' injection). We also examined octadecylphosphonic acid (ODPA) as a surfactant and observed smaller particles (3−5 nm) with a spherical shape (where it did not begin to form the facets). Typically, surfactants with a longer hydrocarbon chain generate smaller particles due to the slower nucleation and growth rate.[22] Additional size control of the cuboctahedral nanoparticles could be obtained by changing the reaction time and a fixed surfactant type. For example, we succeeded in producing solutions of monodisperse nanoparticles with different sizes ranging from 5 to 50 nm, as can be seen in Figure 2C,D. The 28 and 40 nm nanoparticles were obtained 5 and 7 min, respectively, after the injection of the precursors, where, in both reactions, the TDPA was used as surfactant. We show for the first time that cuboctahedral PbTe nanocrystals larger than 8 nm can be obtained, and this is in contrast to earlier reports, where it is shown that particles larger than 8 nm tend to be cubes.

The cubic, octahedral, and cuboctahedral shape PbTe particles could have a special interest for thermoelectric and photovoltaic application once they are processed into thin film form. We have so far already established an approach for assembling the PbTe nanocrystals and succeeded in preparing a large area close-packed film using the Langmuir−Blodgett technique, as shown in Figure S4, with cube and cuboctahedral nanocrystals.

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Supporting Information Available: Experimental details of the synthesis, enlarged HRTEM images of the three shapes and XRD, EDS of the cuboctahedral particles. This material is available free of charge via the Internet at http://pubs.acs.org.

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