

# Surfactant-Assisted Synthesis of Lead Telluride Nanoparticles: Shape, Size, and Assembly

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**Abstract.** Colloidal suspensions of PbTe nanoparticles coated with oleic acid (OA) were obtained using a high-temperature solution phase (HTSP) method. Diphenyl ether was used as a high-boiling heat-transfer agent. Nanoparticle size was tuned during the synthesis by means of reaction temperature. The reaction temperature was varied between 140 °C and 200 °C, and the trioctylphosphine -Te/lead oleate molar ratio was selected as 2 : 1. High-resolution transmission electron microscopy (HRTEM) and powder X-ray diffraction (XRD) were used to characterize the size, shape, structure, and composition of the PbTe nanocrystals. Ordering of nanocrystals into a close-packed structure indicates that the PbTe nanoparticles have a well-defined shape and a narrow size distribution.

## I. INTRODUCTION

The study of synthesis methods for nanoscale lead chalcogenides is focused on control of the dimensions and shape of nanoparticles in the process of their nucleation and growth. Colloidal chemistry makes it possible to make the nanoparticle size less than the excitonic Bohr radii, resulting in the size dependence on a number of nanoparticle properties [1]. Surfactant-assisted synthesis allows for adequate control of the size and shape of the particles during nucleation, growth, and self-assembly; it is found to be advantageous in producing important semiconductor nanomaterials of the  $A^{IV}B^{VI}$  class [2, 3]. Nanocrystalline PbTe is a remarkable  $A^{IV}B^{VI}$  semiconductor illustrated by the following reasons. It is a suitable and compliant material for nanoengineering due to the tunability of the size of nanocrystals, with the excitonic Bohr radius being one order of magnitude larger. An extensive investigation of the various chemical routes has also revealed other strategies for shape tuning, such as varying the precursor molar ratios, the type of surfactant, growth time, and other synthesis parameters.

In the present work, main attention is paid to the influence of synthesis temperature on the size and shape of the PbTe nanocrystals.

## II. METHODS

Tri-*n*-octylphosphine (Aldrich, 90%), amorphous tellurium shot (Aldrich, 99.999%), squalane (Aldrich, 99%), diphenyl ether (DPE) (Fluka, 98%), lead acetate trihydrate (Aldrich, 99.99%), and oleic acid (cis-9-octadecenoic acid, Aldrich, 90%) were used as purchased without further purification. Anhydrous ethanol, hexane,

chloroform, acetone, tetrachloroethylene, and trichloroethylene were purchased from different companies and used without further purification. Trioctylphosphine telluride (0.75 M, TOP-Te) was prepared by completely dissolving the necessary amount of tellurium in 50 ml of TOP at 60–70 °C with moderate stirring.

High-resolution transmission electron microscopy (HRTEM) and powder X-ray diffraction (XRD) were used to characterize the size, shape, structure, and composition of the PbTe nanocrystals. The powder XRD data were recorded with  $\text{CuK}\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ) on a Scintag diffractometer, operating in the Bragg–Brentano geometry. Samples for the XRD measurements were prepared by the deposition of concentrated PbTe colloidal solutions in chloroform or trichloroethylene onto a glass substrate. A Philips CM 30 transmission electron microscope (TEM) equipped with a Super-Twin lens and  $\text{LaB}_6$  emitter was used for HRTEM measurements. All the images were taken at 300 kV accelerating voltage and recorded with a megapixel CCD camera. The EDX spectra were collected on a Tecnai F30 TEM, operating at an accelerated voltage of 300 kV and equipped with a Schottky field emission electron source and a Super-Twin lens. Samples for the TEM were prepared by the deposition of a drop of dilute colloidal solution in chloroform, hexane, or trichloroethylene on a carbon-coated copper grid (200 mesh), allowing slow evaporation at room temperature. For the investigation of the obtained nanomaterial, products of the following synthesis parameters were selected: TOPTe/lead oleate molar ratio  $r = 2.0$  for each synthesis, and  $T = 140, 160, 180, \text{ and } 200 \text{ }^\circ\text{C}$  during 10 min. As mentioned above, the samples were prepared for X-ray powder diffraction by

depositing the colloidal solution onto a glass substrate dropwise.

The HTSP method was used as the basis for preparing lead telluride nanoparticles. A detailed description of the PbTe synthesis has been previously published [4–7]. Diphenyl ether was selected as a solvent for the precursor mixture in the synthesis. A standard synthesis of PbTe semiconductor nanoparticles was performed in a round-bottom three-neck flask equipped with a magnetic stirrer, a thermocouple, and a temperature control unit. Lead oleate was prepared by heating a mixture of 0.758 g (2 mmol) lead acetate, 1.27 ml (4 mmol) of oleic acid, and 11.2 ml (20 mmol) of squalane or 20–25 ml of diphenyl ether. Oleic acid was employed both for group IV precursor formation and nanoparticle stabilization during the synthesis intended for nucleation and reaction rate control. This solution was heated under vacuum at 75–80 °C for 5–6 h in order to form lead oleate and remove already formed acetic acid. The subsequent synthesis of lead telluride nanoparticles was carried out by rapid injection of trioctylphosphine telluride (TOP-Te) solution, maintained at room-temperature, into a vigorously stirred mixture containing lead oleate heated from 140°C to 200°C under N<sub>2</sub> atmosphere.

### III. RESULTS

Our previous investigations of the influence of precursor molar ratios on final synthesis products show that values of TOP-Te/lead oleate molar ratio within 1.5–2.5 yield high-quality PbTe nanoparticles and prevent precipitation of unreacted components. Synthesis routes based on TOP-Te/lead oleate molar ratio values ranging within 2.5–4.5 both with synthesis temperature and the time manipulations allowed the secondary precipitation of Te, together with PbTe nanoparticles. Thus, two parallel synthesis procedures, available through slightly adjusting synthesis temperature and precursor molar ratios, can produce qualitative modifications of the end product. As was mentioned above, synthesis procedures were based on diphenyl ether as a high-boiling organic solvent. The optimum amount of this solvent was determined for group VI precursor solutions, namely 3–3.5 mmol of Te solution per 10 ml of organic solvent. The reaction temperature was varied between 140°C and 200°C, and the TOP-Te/lead oleate molar ratio was selected as 2 : 1. The reaction mixture was maintained at the fixed temperature for 10 min and then promptly cooled to room temperature using an ice-water bath. The solution quickly turned dark during the synthesis due to the formation of PbTe colloidal solution.

A solvent containing two parts of hexane, one part of anhydrous ethanol, and five parts of acetone was prepared to purify the nanoparticles from unreacted precursor, excess surfactant and high-boiling point solvents. A size-selective precipitation was carried out by centrifugation, using a polar/nonpolar solvent combination, consisting of acetone and either hexane or chloroform. After precipitation, the PbTe nanoparticles were isolated and re-suspended in chloroform, hexane, and trichloroethylene, followed by ultrasonic treatment to form stable colloidal solutions, used for further preparation and characterization. The chemical analysis and atomic

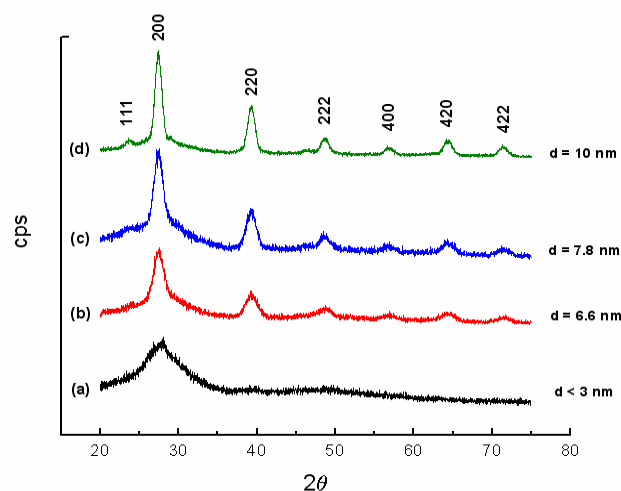


Fig.1. X-ray powder diffraction patterns of PbTe nanopowders synthesized in the presence of DPE at (a) T = 140 °C; (b) T = 160 °C; (c) T = 180 °C; (d) T = 200 °C

absorption spectroscopy confirmed the PbTe composition of the nanomaterial deposited after multiple purifying and re-suspension of the original solution.

The typical powder diffraction patterns of the PbTe nanolayers obtained at different temperatures in the presence of diphenyl ether are shown in Fig.1. The nanomaterial exists in a single-phase and has a cubic close-packed structure. The peak positions correspond to polycrystalline PbTe. The average dimensions of the PbTe nanoparticles were estimated using the Scherrer equation [8] for the (200) peak:  $L = K \cdot \lambda / \beta \cos \theta$ . The estimated average size is 10 nm for nanoparticles obtained at 200°C, 7.2 nm for nanoparticles obtained at 180°C, ~6.6 nm for nanoparticles obtained at 160°C, and less than 3 nm for nanoparticles synthesized at 140°C. The correspondence between the particle sizes estimated from XRD and observed in TEM is quite good for the larger nanocrystals.

Thus, nanoparticle size was tuned during the synthesis by means of reaction temperature.

It is known that the shape of fcc nanoparticles is determined basically by the growth rate in the <100> and <111> directions. Growth rates of the {100} and {111} facets with different surface energies vary during the nucleation and nanoparticle growth, and depend on the synthesis duration [5]. It should be noted that the presence of surfactants also influences the nanocrystal shape [9].

The size, shape, and crystallinity of nanoparticles were examined using TEM methods. Self-assembled PbTe nanopowders were brought from various solvents onto copper grids. TEM images represented in Figs. 2a-2d show well-separated nanoparticles with an average size in agreement with the values calculated from the Scherrer equation. The EDX measurements (inset of Fig. 2d) confirmed the Pb:Te ratio of ~1. Figure 2a shows the TEM image of the assembly of PbTe cubic nanoparticles with an average size of 10 nm, synthesized at 200°C during 10 min. A HRTEM image shown in the inset of Fig. 2a confirms the high crystallinity of the single cubic nanoparticle. Local ordering of the cubic nanocrystals (Fig. 2c) into a close-packed structure indicates that the PbTe cubic nanoparticles have a well-defined shape and a

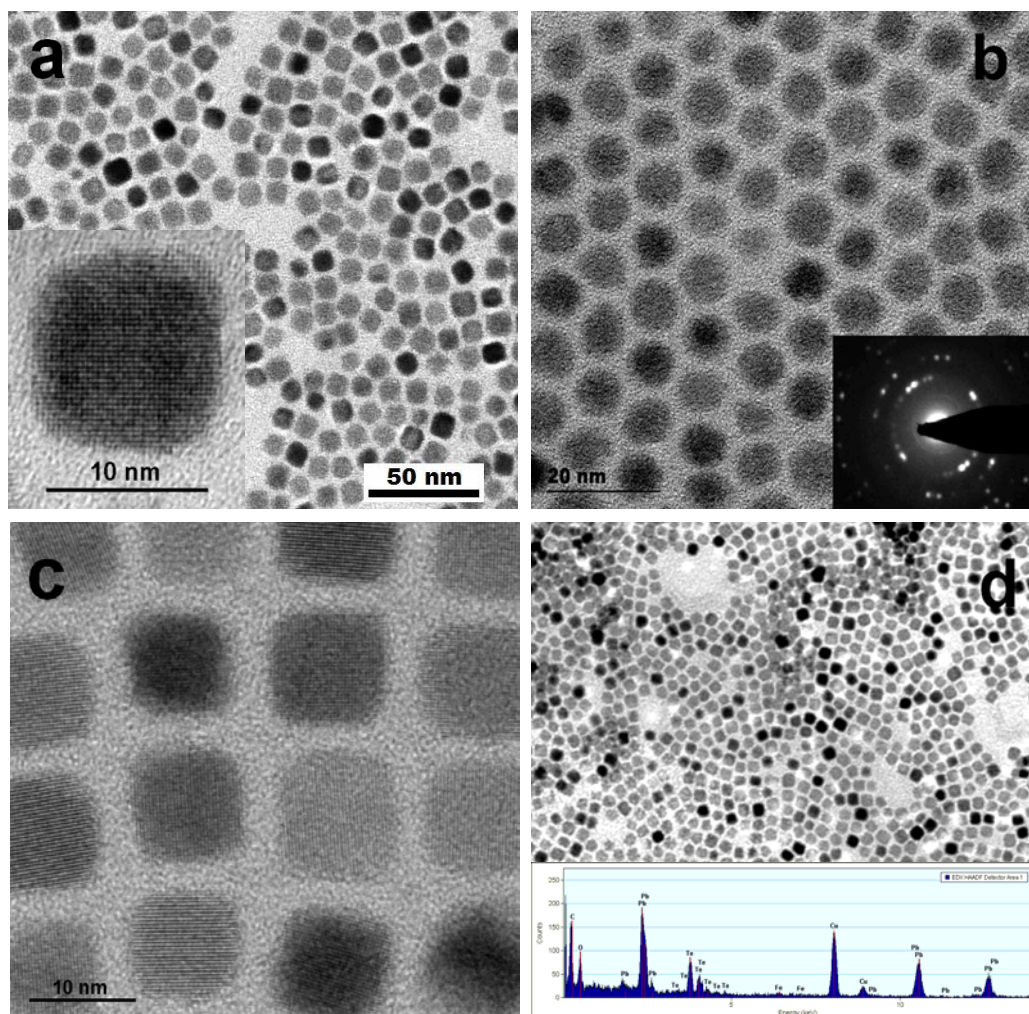


Fig. 2. Transmission electron micrographs of (a) PbTe nanoparticles obtained under typical synthesis based on DPE and reaction temperature 200°C, the inset shows representative HRTEM image of individual cubic nanocrystal; (b) spherical PbTe nanoparticles obtained at 180°C, the inset shows SAED pattern, demonstrating the crystallinity; (c), (d) local ordered cubic nanocrystals (inset represents EDX spectrum).

narrow size distribution. As can be seen, the interparticle spacing of these close-packed structures is  $\sim 2$  nm. We can assume that each separated nanoparticle is surrounded by a surfactant monolayer.

The PbTe nanoparticles synthesized at lower temperatures (150–180°C) with the same precursor molar ratio and time of synthesis have a spherical shape and a size of 7–8 nm in diameter (Fig. 2b) and could be assembled into a hexagonal long-range ordered array. The “spherical” nanoparticles have, in fact, cuboctahedral geometry with  $\{100\}$  and  $\{111\}$  growth facets. The faster growth rate of  $\langle 111 \rangle$  facets eliminates them and results in the formation of cubic-shaped nanoparticles. As was mentioned in Ref. 20 and 21, the growth rate in the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  directions could be simultaneously tuned by balancing the choice of surfactant, precursor molar ratio, and time of synthesis, leading to cubic, cuboctahedral, or octahedral shapes.

Under the synthesis conditions described above, the shape and size of the PbTe nanoparticles is determined by the reaction temperature.

#### IV. CONCLUSIONS

Lead telluride nanocrystals were obtained by means of high-temperature solution phase synthesis route based on DPE. High-resolution transmission electron microscopy both with powder X-ray diffraction demonstrated high crystallinity and narrow size distribution of PbTe nanoparticles. Nanoparticle size and shape was tuned during the synthesis by means of reaction temperature. Cuboctahedral and cubic shaped nanoparticles could be assembled into ordered arrays with interparticle spacing reduced to surfactant coating dimensions. Reaction temperature represents a suitable facility for size and shape tuning as well as precursor molar ratio, growth time, and type of surfactant.

#### ACKNOWLEDGMENTS

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