

Synthesis of PbSeTe Single Ternary Alloy and Core/Shell Heterostructured Nanocubes

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Chemicals:

Diphenyl ether (99%), oleic acid (90%), Se pellets (99.99%), Te shots (99.999%), trioctylphosphine (TOP, 90%), were purchased from Sigma-Aldrich. Lead oxide (PbO, 99.99%) was an Alfa Aesar product. All these chemicals were used as received. Stock solutions of trioctylphosphine selenide (Se-TOP, 1 M for Se) and trioctylphosphine telluride (Te-TOP, 1 M for Te) were pre-prepared by loading 0.1 mol of Se pellets (or Te shots) into 100 mL of TOP in a glovebox and they were stirred at 150 °C for overnight, respectively.

Preparation of Pb-oleate Solution:

In a typical experiment, 3 mmol of PbO, 14.0 mL of diphenyl ether, and 6.0 mL of oleic acid were loaded into a 100 mL three-neck flask. The mixture was heated to 150 °C and maintained at this temperature for 1 h with vigorous stirring, and then naturally cooled to room temperature, forming a lead stock solution (Pb-oleate).

Self-Assembly of PbSeTe Single Ternary Alloy Nanocubes:

The concentration of PbSeTe nanocubes in hexane was first adjusted to ~3 mg/mL for the use of a self-assembly. 5.0 mL of PbSeTe nanocube suspensions was transferred into a 10 mL vial, in which a piece of surface-polished silicon (Si) wafer was horizontally pre-placed on the bottom as a face-up substrate, and the vial was then sealed using a parafilm with a small hole to control the solvent evaporation rate. The vial was subsequently placed on a lab bench with a stable air flow until all of the solvent was evaporated, leaving the assembled nanocubes onto the substrate.

Characterization Details:

X-ray diffraction (XRD) patterns were recorded using a PANalytical X'Pert X-ray powder diffractometer equipped with a Cu $K_{\alpha 1}$ radiation source ($\lambda = 0.15406$ nm). A Hitachi 7000 transmission electron microscope (TEM) operated at 75 kV was used for low-magnification TEM imaging. A FEI Tecnai G² F20 ST operated at 200 kV was adopted to obtain high-resolution TEM (HR-TEM) image, as well as the high-angle annular dark field imaging in the scanning TEM mode (HAADF-STEM), energy dispersive X-ray spectroscopy (EDS) in HAADF-STEM line scan using the smallest electron beam (diameter is about 0.8 nm), weak-beam dark-field (WBDF) imaging, and electron energy loss spectroscopy (EELS) elemental mapping. The EELS mapping was made using a standard three-window procedure by selecting the elemental edges of Pb M₅ (2484 eV), Se L₃ (1436 eV), and Te M_{4,5} (572 eV), respectively, with the exposure time of 80 s. Since these edges are well separated, there was no overlapping problem. To avoid the sample drift and beam damage during the acquisition, the samples were pre-pumped in the microscope overnight, and an additional anti-contamination device was used. The final mapping results were generated by the Gatan Digital Micrograph program automatically using cross correlation for the drift measurement, without any manual inputs to affect its computation. Scanning electron micrographs (SEM) were taken on a field emission scanning electron microscope (Carl Zeiss Supra 55 VP). Inductively coupled plasma optical

emission spectrometric (ICP-OES) analyses were conducted at Perkin-Elmer ICP-OES Optima 7000 DV.

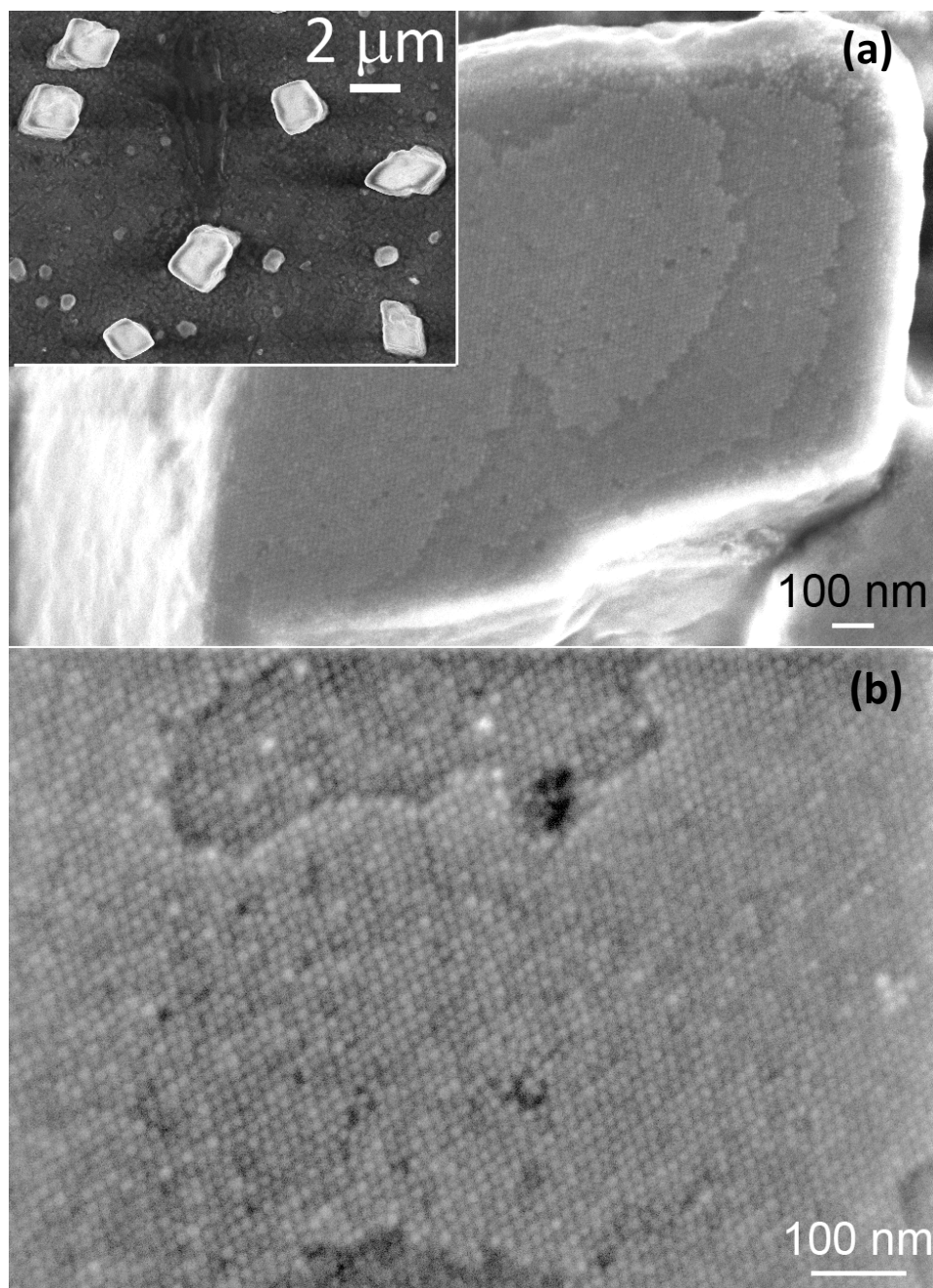


Figure S1. SEM images of self-assembled supercrystals consisting of PbSeTe single ternary alloy nanocubes at different magnifications.

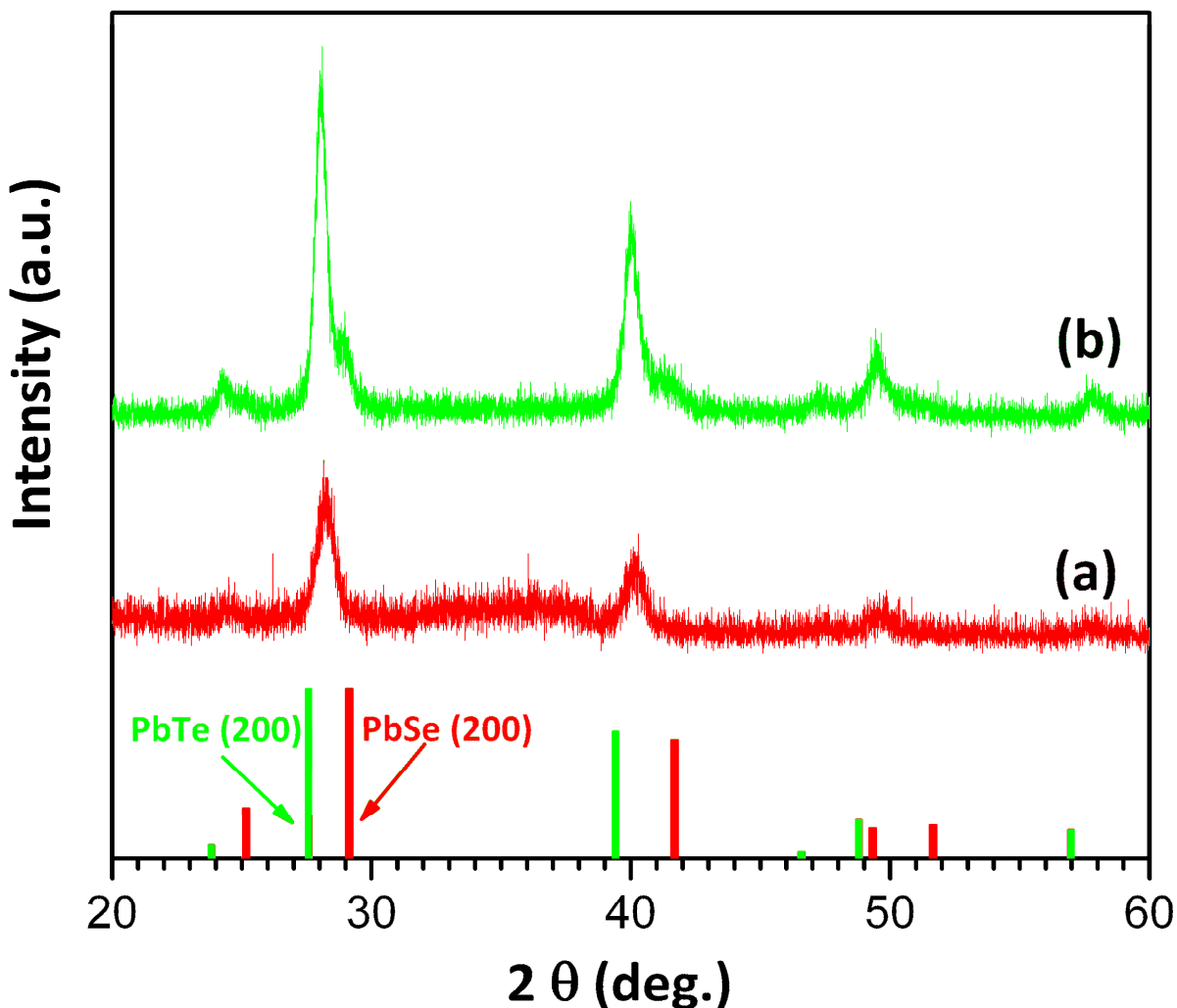


Figure S2. Typical XRD traces of (a) $\text{Pb}_3\text{Se}_{2.8}\text{Te}_{0.2}$ single ternary alloy and (b) PbSeTe core-shell heterostructured nanocubes, as well as the standard patterns from ICDD PDF cards (card 06-0354 for PbSe in red color, card 38-1435 for PbTe in green color). Samples were randomly deposited on a PANalytical zero-background Si sample holder without assembly.

Table S1. ICP-OES analysis results of samples prepared with different precursor ratios.

Sample denotation	Se/(Se+Te) ratio in precursors	Se/(Se+Te) ratio in products
$\text{Pb}_3\text{Se}_{1.5}\text{Te}_{1.5}$	0.50	0.0052
$\text{Pb}_3\text{Se}_{2.5}\text{Te}_{0.5}$	0.83	0.0258
$\text{Pb}_3\text{Se}_{2.6}\text{Te}_{0.4}$	0.87	0.0510
$\text{Pb}_3\text{Se}_{2.7}\text{Te}_{0.3}$	0.90	0.0828
$\text{Pb}_3\text{Se}_{2.8}\text{Te}_{0.2}$	0.93	0.1216
$\text{Pb}_3\text{Se}_{2.9}\text{Te}_{0.1}$	0.97	0.9952

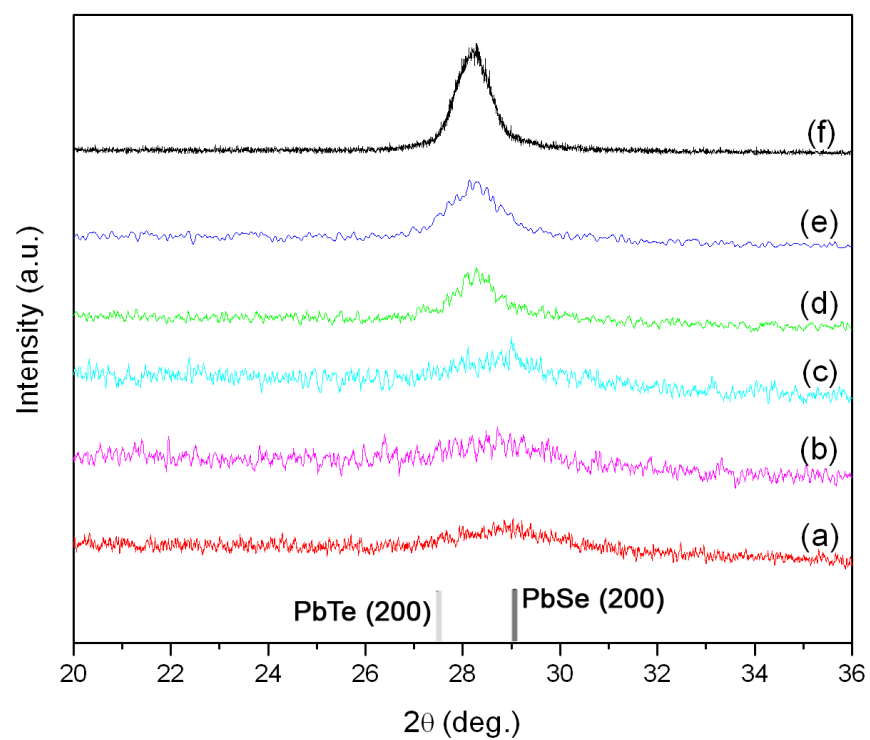
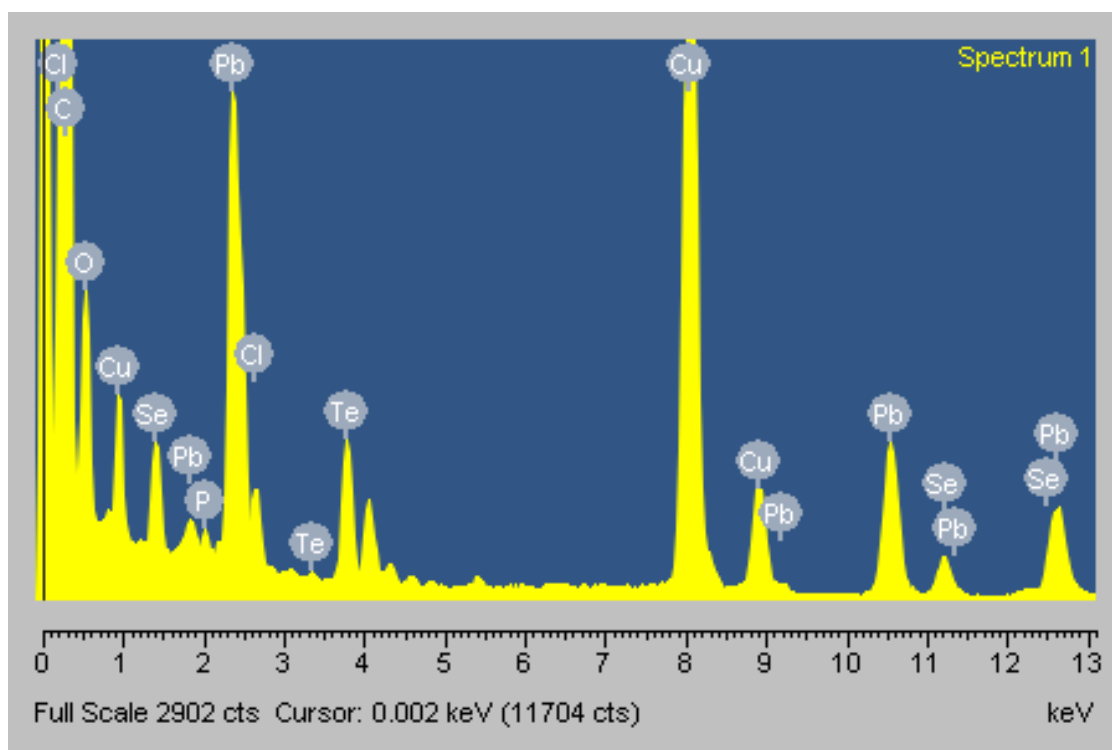


Figure S3. XRD patterns of intermediates of PbSeTe ternary alloy nanocubes with different reaction times, that is, (a) 0 min, (b) 1 min, (c) 2 min, (d) 3 min, (e) 4 min, and (f) 6 min.



	Se (at%)	Te (at%)	Pb (at%)
Spot 1	18.11	33.54	48.34
Spot 2	17.96	33.44	48.60
Spot 3	18.31	33.36	48.33
Spot 4	19.74	32.89	47.37
Spot 5	19.65	34.59	45.76
mean	18.75	33.57	47.68

Figure S4. A typical EDS spectrum (top) and quantification results obtained from five different spots (bottom) on PbSeTe core-shell nanocubes.

Composition Discussion:

Suppose the core composition is $\text{Pb}_{0.5}\text{Se}_x\text{Te}_{0.5-x}$, and shell $\text{Pb}_{0.5}\text{Se}_y\text{Te}_{0.5-y}$. As the volume fraction of the core is 0.548, and the shell, 0.452, according to the measured Se/Te ratio $C_{\text{Se}}/C_{\text{Te}}=0.561$ from EDS, we have

$$\frac{C_{\text{Se}}}{C_{\text{Te}}} = \frac{0.548x + 0.452y}{0.548(0.5 - x) + 0.452(0.5 - y)} = 0.561, \quad (1)$$

thus

$$x = 0.328 - 0.825y, \text{ or } y = 0.398 - 1.212x. \quad (2)$$

In order to keep $x \geq 0$ and $y \geq 0$, we obtain the x and y range as

$$0 \leq x \leq 0.328, \text{ and } 0 \leq y \leq 0.398. \quad (3)$$

According to the EELS mapping (Figure 4), Se is mainly in the core, and thus

$$x \gg y. \quad (4)$$

Let's take an example for $x = 0.3$, thus $y = 0.034$ according to eq. (2). The core is $\text{Pb}_{0.5}\text{Se}_{0.3}\text{Te}_{0.2}$, and the shell is $\text{Pb}_{0.5}\text{Se}_{0.034}\text{Te}_{0.466}$. Along the electron beam direction, the shell is 11 nm, while the core area is 9 nm but also summed with 2 nm shell on the top and bottom, respectively. Thus, the effective Se contribution in the core is $0.3 \times 9 + 0.034 \times 2 = 2.768$, which is largely greater than the shell Se $0.034 \times 11 = 0.374$. Therefore, only Se in the core is imaged. In a similar way, the Te in the core is $0.2 \times 9 + 0.466 \times 2 = 2.732$, while in the shell is $0.466 \times 11 = 5.126$, so Te can be imaged in both core and shell, but the latter one has higher content. All those compositions are consistent with the experimental observations in Figure 4.