Preparation of Nanoscale PbSe Particles with Different Morphologies in

Diethylene Glycol

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Synthesis of PbSe nanoparticles: All chemicals were used as received. A similar synthetic method to the preparation of nanostructured PbS was adopted here.¹ Briefly, in a typical procedure for synthesizing nanostructured cubic PbSe, a 6.0 ml solution of poly-(vinyl pyrrolidone) (PVP-K30, 1.0 mol L⁻¹ in terms of repeating unit, Mw \approx 50 000, Shanghai Lite Chemical Technology Co., Ltd) dissolved in anhydrous diethylene glycol (DEG, Shanghai Chemical Reagents Company) was added into a 50.0 ml three-neck flask containing a Teflon-coated magnetic stirring bar. The flask was connected with a reflux condenser and placed on a heating plate. The temperature of the solution was increased to 240°C under constant stirring and maintained at the same temperature until a clear solution was formed. Then 0.076 g lead (II) acetate trihydrate (or same mole of Pb(NO₃)₂) and 0.021 g selenius acid (H₂SeO₃, all these three chemicals were purchased from Shanghai Chemical Reagents Company) dissolved into 2.0 ml DEG separately were transferred into the PVP-K30 solution using a two-channel peristaltic pump (HL-2D, Qingpu Huxi Instrument Factory, Shanghai) at a rate of 10.0 ml h⁻¹. After finishing the introduction of these two chemicals, the reaction system was kept at the same

temperature for another 13.0 min. The flask was then removed from the heating mantle and allowed to cool down to room temperature naturally. In order to collect the product from viscous DEG solution, 20.0 ml DDI water was added to the flask. The as-synthesized black product could precipitate to the bottom of the flask after sonication. After decanting the supernatant, the precipitates were transferred to a 100.0 ml beaker and washed by ethanol and DDI water for three times, respectively.

Other morphologies of nanostructured PbSe could be obtained under similar conditions by varying the concentration of capping agent, the category and concentration of source chemicals (especially for lead salts) or molar ratio of selenius acid to Pb²⁺.

Characterization: X-Ray Diffraction (XRD) of the samples was recorded with a Rigaku-Dmax2500 diffractometer using Cu K α radiation (40.0 kV, 200 mA) at a step width of 8.0°/min. The field emission scanning electron microscopy (FESEM) images were taken using a XL30-ESEM-FEG operated at an acceleration voltage of 15 kV and Hitachi S-4800 operated under deceleration mode with acceleration voltage of 500 V. Energy dispersive X-ray analysis (EDX) was obtained on Bruker Quantax 200 attached to S-4800.

Reference:

1. Z. Peng, Y. Jiang, Y. Song, C. Wang and H. Zhang, Chem. Mater. 2008. 20, 3153.

PbSe Morphology	Peak area ratio (200/111)
Tetradecahedral	1.38
Octahedral	1.75
Cube	2.76

Table S1. Peak area ratio (200/111) of PbSe nanoparticle

Table S2. Effect of $R_{Se/Pb}$ on the morphology and particle size of PbSe using $Pb(NO_3)_2$ as lead precursor.

R _{Se/Pb}	Morphology	Average Size (nm)
0.1	Cube	90
0.2	Cube	200
0.5	Cube	290
0.8	Cuboid	210×500



Fig. S1 The XRD pattern of the products obtained in EG. Concentration of $Pb(Ac)_2$ in 2.0 ml EG: 0.1 mol L⁻¹, $R_{Se/Pb} = 0.8$, concentration of PVP-K30 in 6.0 ml EG: 1.0 mol L⁻¹, reaction temperature: 190 °C, duration time: 8 h.



Fig. S2 EDX analysis result of cube-like PbSe obtained in DEG. Concentration of $Pb(Ac)_2$ in 2.0 ml DEG: 0.1 mol L⁻¹, $R_{Se/Pb}$: 0.5, concentration of PVP-K30 in 6.0 ml DEG:1.0 mol L⁻¹, reaction temperature: 240 °C, duration time: 13 min.



Fig. S3 FE-SEM images and XRD patterns of Pb (A), Pb@PbSe (B,C) and PbSe (D) nanoparticles. Pb (A), Pb@PbSe (B,C): $R_{Se/Pb} = 0.8$, PbSe (D) : $R_{Se/Pb} = 1.0$, concentration of Pb(Ac)₂: 0.1 mol L⁻¹, reaction temperature: 240 °C, duration time: 1.0 h.



Fig. S4 FESEM images of PbSe obtained with different concentration of PVP -K30: (A) 0 mol L^{-1} , (B) 0.2 mol L^{-1} and (C) 2.0 mol L^{-1} . Concentration of Pb(Ac)₂: 0.1 mol L^{-1} , R_{Se/Pb}: 0.5, reaction temperature: 240 °C, duration time: 13 min.



Fig. S5 FE-SEM images of PbSe with 50% octahedral and 50% tetradecahedral shapes.Concentration of PVP-K30: 2.0 mol L⁻¹, concentration of Pb(Ac)₂: 0.2 mmol L⁻¹ in mixed solvent (0.4 ml EG + 1.6 ml DEG), $R_{Se/Pb}$: 0.6, reaction temperature: 240 °C, duration time: 13 min.