Electronic Supplementary Information

Controllable Synthesis of PbSe Nanocubes in Aqueous Phase Using a Quasi-Biosystem

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Experimental Section

Materials: Ultrapure water (purified using a Synergy ultrapure water system (Millipore)) was used as solvent in all experiments. Sodium selenite (97%) and lead acetate trihydrate (99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Yeast glutathione reductase (GR) was purchased from Calbiochem with specific activity no less than 100 units/mg protein. Reduced glutathione (GSH) and oxidized glutathione (GSSG) were purchased from Amresco. NADPH was purchased from Biomol. Amicon centrifugal filter units were purchased from Millipore.

Synthesis of PbSe nanocubes: 2.2 micromoles of $Pb(Ac)_2$, 5.5 micromoles of GSH and 11mL of NaOH (pH 13) solution were mixed in a flask and vigorously stirred at 90 °C to obtain $[Pb\text{-}GSH]^{2+}$ precursors. 8.8 micromoles of GSH, 2.2 micromoles of Na_2SeO_3, 8.8 micromoles of NADPH and 5 units of GR were mixed in 3 mL of BR buffer (pH7.2) at room temperature to obtain fresh Se precursors. To synthesize PbSe nanocubes, 3mL of the fresh Se precursors were injected into the flask of $[Pb\text{-}GSH]^{2+}$ precursor solution, and the mixture was stirred at 90 °C for 10 min. The whole process was operated under N_2 atmosphere.

Characterization: Inductively coupled plasma-optical emission spectroscopy (ICP-OES) data of PbSe nanocube content were obtained on a Spectro Genesis EOP ICP spectrometer. X-ray diffraction (XRD) data were recorded on a Bruker AXS D8 advance X-ray diffractometer, using a single-crystal silicon wafer as sample holder.

Transmission electron microscopy (TEM) images were taken on a JEOL JEM-2100 transmission electron microscope at 200 kV. High resolution transmission electron microscopy (HRTEM) images were taken on a JEOL JEM-2010FEF transmission microscope at 200 kV. Samples for TEM and HRTEM observation were prepared through dropped 5 μL of the solution on an ultrathin-carbon-coated grid and allowed the sample to dry. X-Ray photoelectron spectroscopy (XPS) data were recorded on VG Multilab 2000 using an aluminium anode radiation source. The product was purified by Amicon Centrifugal Filter Unit (MWCO 100 kDa) to remove free agents for the above characteristic.

High-performance liquid chromatography coupled with Mass Spectrometry (HPLC-MS).

Measurements were performed on an HPLC system (Agilent1100 series) for chromatographic separations. The components of the reduction of Na_2SeO_3 were separated and confirmed by HPLC-MS as previously reported[1,2]. All separations were performed on a Tigerkin C18TDE column (5 μm，2.1×150 mm, DALIAN SIPORE CO., LTD) column, operating at a mobile phase flow rate of 0.2 mL/min and a column temperature of 30°C. The mobile phase consisted of 0.1% formic acid solution/acetonitrile (100:1, v/v). Electrospray ionization instrument was used in the current investigation. Ionization parameters were adjusted as follows: capillary voltage, 3.5 kV; temperature of drying gas, 325 °C; flow rate of the drying gas, 5.0 L/min. GSH (3.69 mg) was dissolved in 120 μL of ultrapure water. Then, the mixture of 20 μL of 0.1 M Na_2SeO_3, 120 μL of 0.1 M HCL and 80 μL of 0.1 M GSH was incubated for 1 min and injected into the stainless steel ESI target.

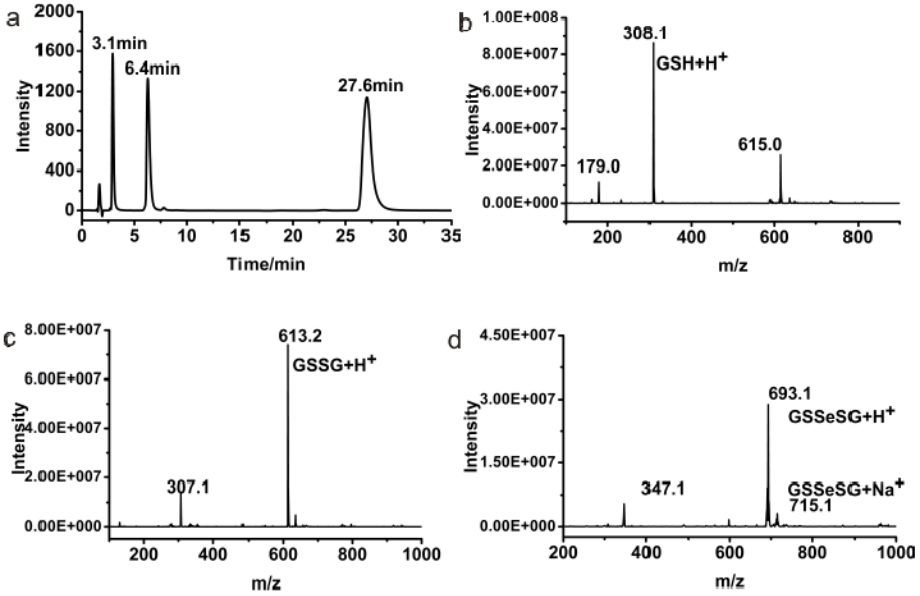

Fig. S1. HPLC-MS analysis of the components formed in the biomimetic reduction of Na_2SeO_3 *in vitro*. (a) HPLC chromatogram of the components involved in chemical reaction 1; (b) (c) and (d) are the mass spectra of compounds with peaks at 3.1 min, 6.4 min and 27.6 min in (a) respectively

The influence of pH conditions on the reducibility of NADPH.

0.2 mM GSSeSG and 0.1 mM NADPH were prepared and stored at 4°C before use. A series of Britton-Robinson (BR) buffer solutions with pH from 4 to 9 were also prepared. A typical procedure was as follows: 2.3 mL of BR buffer solution and 60 μL of GSSeSG solution were mixed in a 4 mL cuvette. Subsequently, once 30 μL of NADPH solution plus 1 unit of GR were added to the cuvette, the absorbance at 340 nm was quickly measured. The reaction, which occurred in the cuvette, was allowed to proceed at 37 °C for 2 minutes before the absorbance at 340 nm was recorded again. The absorbance at 340 nm was recorded on a Shimadzu UV-2550 UV-vis spectrophotometer.

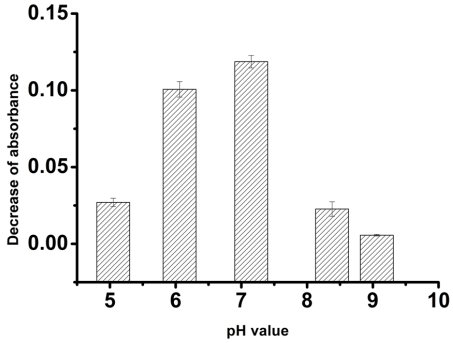

Fig. S2. The decreases of absorbance at 340 nm versus different pH values. The decrease was calculated by subtracting the absorbance of NADPH in the GSSeSG solution after two minutes from the absorbance at the initial time.

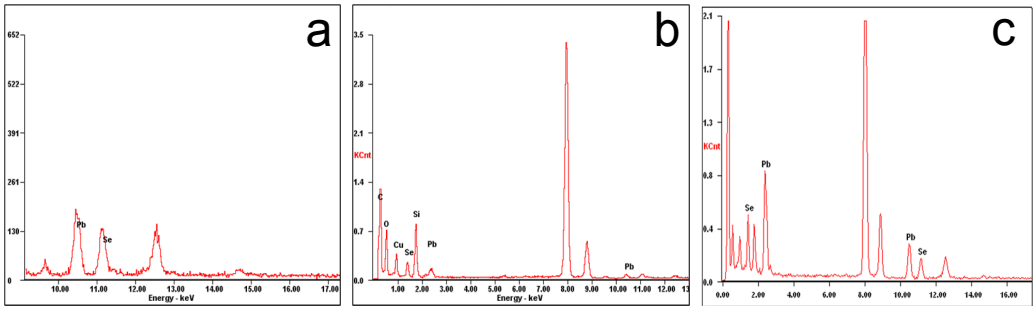

Fig. S3. EDX Spectra of the as-prepared amorphous precursors (a) and meso-crystals (b) and PbSe nanocubes (c).

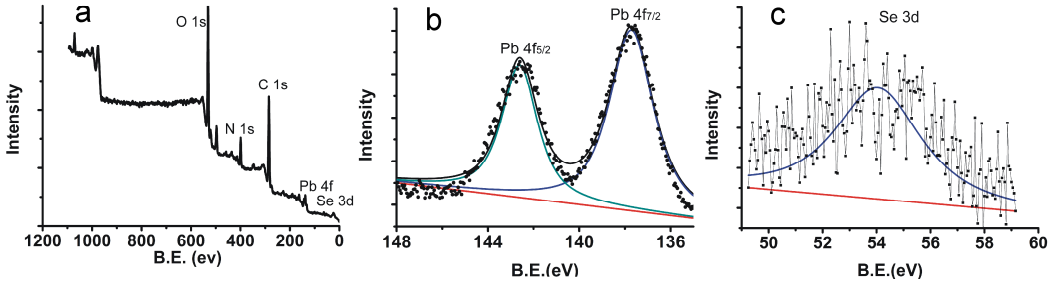

Fig. S4. XPS analysis of the as-prepared PbSe nanocubes. a) the survey-scan XPS picture and b) narrow-scan of the Pb 4f region and c) Se 3d region

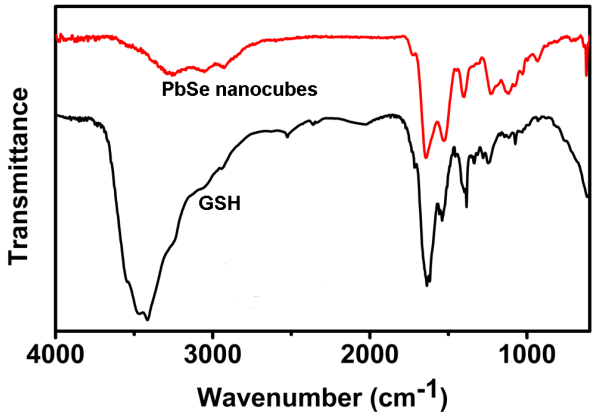

Fig. S5. Infrared spectra of GSH and a purified PbSe nanocubes sample.

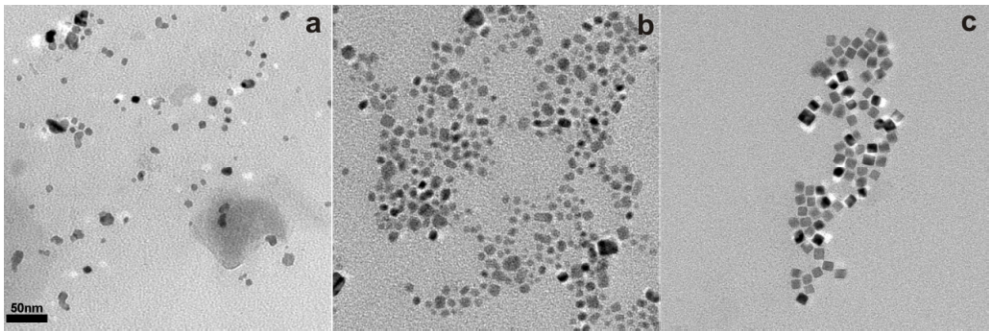

Fig. S6. TEM images showing the different shape of PbSe nanocrystals synthesized at 90 °C using $[Pb\text{-}GSH]^{2+}$ and Se precursors with different components: a) GSSeSG reacted with NADPH and GR; b) the mixture of GSSeSG, GSH and GSSG reacted with NADPH and GR; c) the mixture of GSSeSG, GSH, GSSG and Na_2SeO_3 reacted with NADPH and GR.

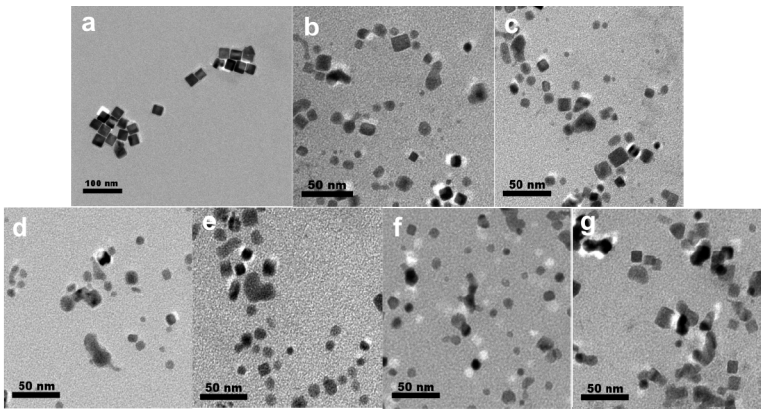

Fig. S7. TEM images of PbSe nanoparticles synthesized with different salt concentrations. a) PbSe nanocubes synthesized by using the quasi-biosystem without

the NaCl; b-g) PbSe nanoparticles synthesized by $[Pb\text{-}GSH]^{2+}$ and the Se precursors without excess SeO_3^{2-} ions at 0.05 mmol/L, 0.1 mmol/L, 0.5 mmol/L, 1 mmol/L, 10 mmol/L, 100 mmol/L NaCl concentrations.

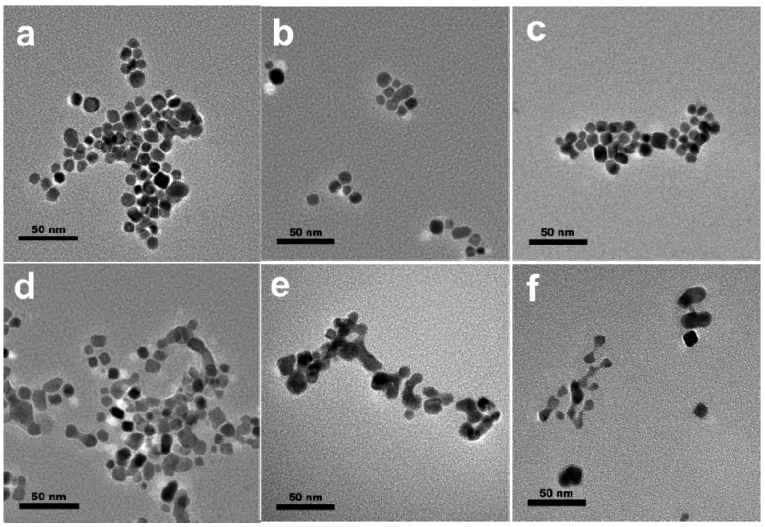

Fig. S8. PbSe nanoparticles synthesized in the quasi-biosystem with different salt concentrations: a) 0.001 mol/L; b) 0.005 mol/L; c) 0.01 mol/L; d) 0.05mol/L; e) 0.1mol/L; f) 0.25mol/L.

SI References

(1) M. Björnstedt, S. Kumar, A. Holmgren, *J. Biol.Chem.* **1992**, *267*, 8030-8034.
(2) M. Björnstedt, S. Kumar, A. Holmgren, *Method. Enzymol.* **1995**, *252*, 209-219.