Supporting Information

Mild Synthesis of Monodisperse Tin Nanocrystals and Tin Chalcogenide Hollow Nanostructures

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Materials

Tin (II) chloride (SnCl₂, 99%) and hexacarbonyl tungsten (W(CO)₆, 97%) were purchased from Alfa Aesar. hexamethyldisilazane (HMDS, 99%), oleylamine (OAm, 70%), 1-octadecene (ODE, 90%), tri-n-octylphosphine (TOP, 97%), S powder (99.99%), Se pellets (99.99%), and Te powder (99.99%) were purchased from Aldrich. OAm and ODE were dried by heating at 120 °C under vacuum for 1 h and then stored under an argon atmosphere prior to use. All other reagents were used as received.

Synthesis of Sn NCs

40 mg of SnCl₂ was placed into a 20 mL vial followed by the addition of 1 mL of OAm and 9 mL of ODE in the glovebox, and this was sonicated until a white suspension was obtained. In a typical synthesis of Sn NCs, W(CO)₆ was added to a 100 mL three-necked round-bottomed flask fitted with a condenser, thermometer adapter, thermometer, and rubber septum and then was degassed under vacuum at ambient temperature for 5−10 min. Next, under a constant flow of argon gas, the prepared suspension and 0.75 mL of HMDS was injected sequentially into the reaction flask. The mixture was then slowly heated to 60 °C at ~10 °C/min and held for ~10 min to ensure the complete dissolution of W(CO)₆ before sublimation. The final reaction mixture was then heated to 210 °C at ~10 °C/min and held for different time (1-20min), forming a black solution. The reaction was quickly cooled by transferring the flask from the heating mantle to a cold water bath. The solution was firstly diluted by adding 10 mL of hexane, and then 20 mL of ethanol was added to precipitate the NCs, which were collected by centrifugation at 4000 rpm for 3 min. After dispersion in 10 mL of oleic acid/hexane mixture (1:100 vol/vol), the as-synthesized NCs were then purified again using the same precipitation method and finally suspended in hexane to form a colloidal suspension for further characterizations. Sn NCs with average diameters of 11±0.73 and 16±1.27 nm were
synthesized by reduction of 0.21 mmol Sn$^{2+}$ with 0.0534 mmol W(CO)$_6$ at 210 °C for 1 and 20 min, respectively. Sn NCs with the average diameter of 13.5±0.97 nm were prepared by reduction of 0.21 mmol Sn$^{2+}$ with 0.0267 mmol W(CO)$_6$ at 210 °C for 10 min.

**Synthesis of hollow SnO$_x$ NPs**
Hollow SnO$_x$ NPs were synthesized through a one-pot, two-step method. The first step is the same as that in the synthesis of 11 nm Sn NCs before the post-treatment. When the black solution was cooled to room temperature, air was poured into the reaction flask after evacuation. The reaction mixture was then heated to 180 °C at ~10 °C/min and held for 30 min to produce hollow SnO$_x$ NPs. The post-treatment process is similar to that of Sn NCs.

**Synthesis of hollow SnS, yolk-shell SnSe and hollow SnTe NCs**
TOP-S, TOP-Se and TOP-Te solutions (1 mol/mL) were prepared inside the glovebox by stirring the certain amounts of TOP with S, Se and Te at proper temperatures (room temperature for TOP-S, 150 °C for TOP-Se and 80 °C for TOP-Te), respectively. Hollow SnS NCs were synthesized through a two-step method. The first step is the same as that in the synthesis of 16 nm Sn NCs before the post-treatment. When the black solution was cooled to room temperature, 0.4 mmol TOP-S were injected into the reaction flask. The reaction mixture was then heated to 180 °C at ~10 °C/min and held for 60 min to produce hollow SnS NCs. The yolk-shell SnSe and hollow SnTe NCs were prepared by a similar synthetic route by using TOP-Se or TOP-Te solutions instead of TOP-S. The post-treatment process is similar to Sn NCs.

**Characterizations**
X-ray diffraction (XRD) patterns were recorded on an X-Ray diffractometer (Rigaku SmartLab) with Cu Kα radiation ($\lambda = 0.15418$ nm) at a voltage of 45 kV and a current of 20 mA. Transmission electron microscopy (TEM), HAADF-STEM and energy-dispersive spectroscopy (EDS) were characterized by transmission electron microscope (TEM, Tecnai F30).
Fig. S1 TEM images and size statistics for Sn NCs with different diameters.
Fig. S2 EDS spectrum (A), HAADF-STEM image (B) and EDS line scan profile (C) of Sn NCs.

Fig. S3 XRD patterns for Sn NCs prepared with different amounts of oleylamine (0–5 mL).
Fig. S4 TEM images for Sn NCs prepared with different amounts of oleylamine (0–5 ml). (A) 0 ml; (B) 1 ml; (C) 2 ml; (D) 5 ml.

Fig. S5 TEM image (A), XRD pattern (B), HAADF-STEM image (C) and EDS line scan profile of hollow SnO$_x$ NPs.
Fig. S6 EDS spectra, EDS line scan profiles and HAADF-STEM images of hollow SnS (A, B and C), yolk-shell SnSe (D, E and F), and hollow SnTe NCs (G, H and I).
**Fig. S7** (A) TEM and (B) HRTEM images for yolk-shell SnS NCs. (C) TEM and (D) HRTEM images for yolk-shell SnSe NCs. (E) TEM and (F) HRTEM images for yolk-shell SnTe NCs.
**Fig. S8** TEM image and size distribution based on statistics collected over 300 particles for hollow SnS NCs (A), yolk-shell SnSe NCs (B) and hollow SnTe NCs (C).