

## Supporting information

# Interfacial Synthesis of SnSe Quantum Dots for Sensitized Solar Cells

Luting Ling, Qiang Zhang, Lin Zhu, Cai-Feng Wang, Su Chen\*

State Key Laboratory of Materials-Oriented Chemical Engineering, and College of Chemistry and Chemical Engineering, Nanjing Tech University, Nanjing 210009, P. R. China

### Experimental section

**Chemicals:** Selenium powder (99.99%), sodium borohydride (98%) and tin(II) octoate (95%) were purchased from Aldrich and used as received. Oleylamine (OLA, 95%), ethanol (99.8%, HPLC), thioglycolic acid (TGA, AR) and ammonium sulfide (20-24 wt% solution in water, ACS grade) were purchased from Aladdin-reagent Ltd. (ShangHai, China) and used without further purification. Toluene (99.5%), formamide (FA, 99.5%) and glycerol (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as received. Fluorine doped tin oxide (FTO) electrodes with a 6 mm\*6 mm square TiO<sub>2</sub> film and acetonitrile electrolyte were purchased from the Dalian Rainbow Solar Technology Development Co., Ltd. (DaLian, China).

**Synthesis of SnSe QDs:** In a typical procedure, 1.5 mmol tin(II) octoate and 6 mL OLA were dissolved in a mixed solution of 30 mL toluene and 30mL glycerol. The solution was purged with N<sub>2</sub> for 30 min and then heated to 95 °C. The NaHSe solution, prepared by the reaction of 1.5 mmol selenium powder and 3.5 mmol NaHB<sub>4</sub> with 3 mL H<sub>2</sub>O, was injected into the above solution. After reacting for another 8 h under stirring, the reactants were immediately cooled by air, with a dark brown upper phase and a nearly transparent lower phase. The upper phase was centrifuged at 4000 r/min to remove impurities and precipitated by plenty of ethanol. The precipitate was washed by ethanol several times, centrifuged and then dried under vacuum and stored in a glove box for further use.

**Ligand exchange of OLA-SnSe QDs:** 5 mL purified OLA-SnSe colloidal dispersion (~2 mg/mL) was diluted with 15 mL toluene. And then the toluene solution was mixed with an isometric formamide solution containing 3 mL (NH<sub>4</sub>)<sub>2</sub>S and stirred for 30 min. The colour of the toluene phase gradually changed from brown to transparent and the formamide solution from chartreuse to brownish red, which indicated the successful transfer of QDs from toluene to FA.

**Fabrication of solar cells:** The TiO<sub>2</sub> electrodes were prepared by screen printing TiO<sub>2</sub> paste (DHS-TPP2, HeptaChroma SolarTech Co., Ltd. China) on the FTO substrate, followed by sintering at 450 °C for 30 min. The thickness of the TiO<sub>2</sub> film was about 8 μm. After cooling to the room temperature, the electrodes were immersed in the colloidal solution of SnSe QDs for 48 h in the dark and then dried under vacuum. A platinum-coated FTO substrate (HeptaChroma SolarTech Co., Ltd. China) was used as the counter electrode. The electrodes were sealed with a polymer gasket (Surlyn) with the electrolyte (acetonitrile solution containing the I<sup>-</sup>/I<sup>3-</sup> redox couple, DHS-Et36, HeptaChroma SolarTech Co., Ltd. China).

**Characterization:** Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images were obtained from a JEOL JEM-2010 transmission electron microscope at an operating voltage of 200 kV equipped with a Gatan Orius CCD camera. Powder X-ray diffraction was performed on a ARL X'TRA powder X-ray diffractometer with Cu K $\alpha$  radiation source ( $\lambda = 0.15406$  nm) at a scanning speed of 6 °/min with  $2\theta$  range from 20 ° to 60 °. Ultraviolet-visible (UV-vis) spectra were recorded on a USB4000-UV-vis spectrometer (Ocean Optics, Inc.). X-ray photoelectron spectroscopy (XPS) was performed on a K-Alpha XPS System (THERMO FISHER SCIENTIFIC (USA)) using a monochromatic Al anode. I-V measurement was performed on an electrochemical workstation (CHI 660C Instruments), equipped with an Oriel Sol3A Class Solar Simulators.

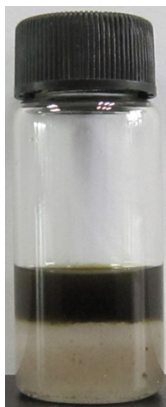


Figure S1. The photograph of the interface system after the reaction.

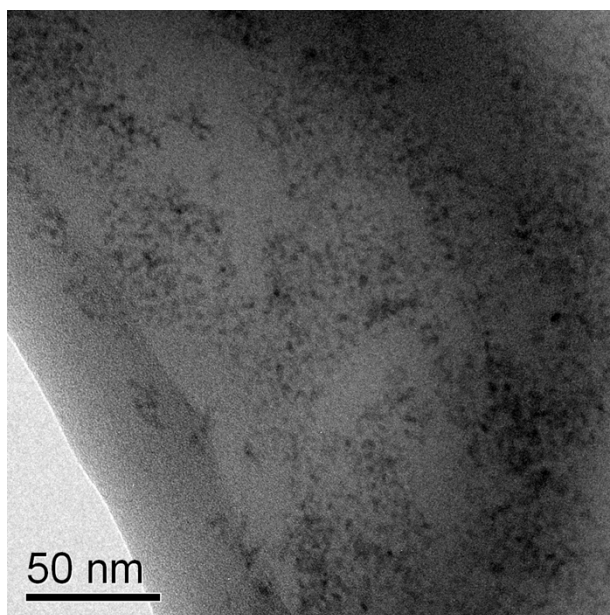


Figure S2. The additional TEM image of the as-prepared SnSe QDs.

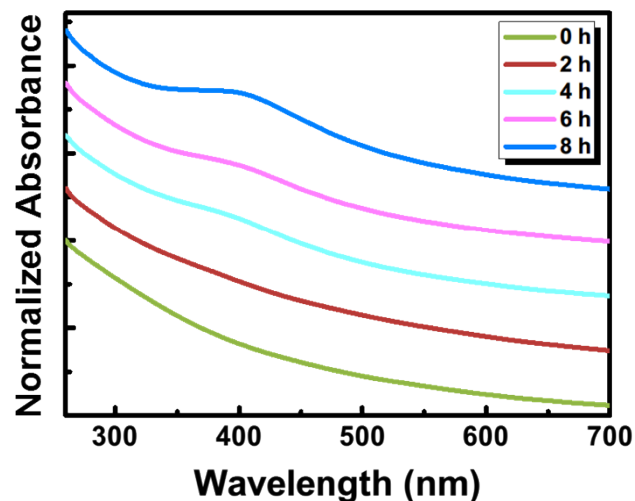


Figure S3. The temporal evolution on UV-vis spectra of the SnSe QDs.

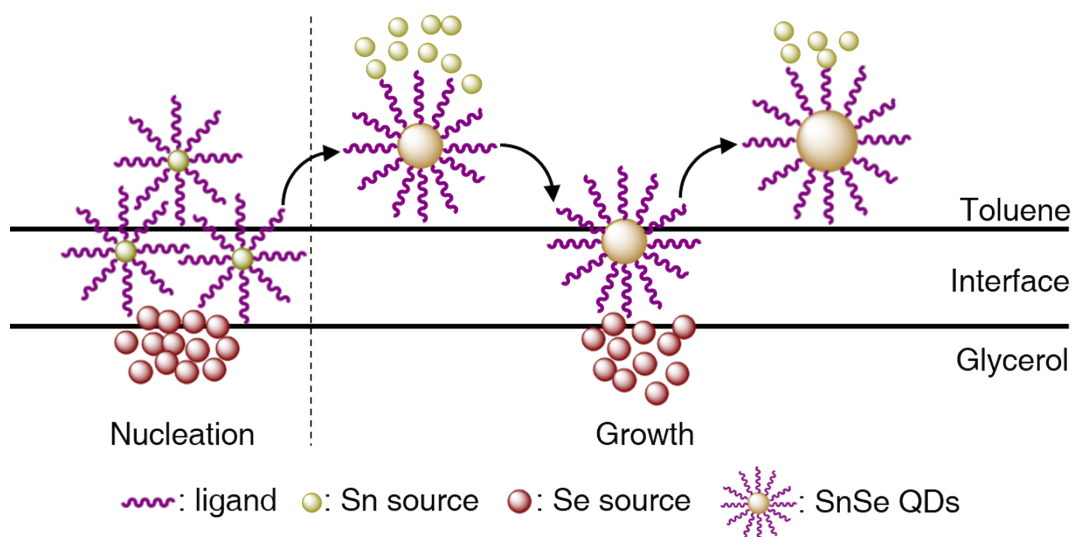


Figure S4. Schematic representation of the formation mechanism of SnSe QDs via the interfacial route.

A possible mechanism for the interfacial process may be explained as follows: in the two-phase liquid-liquid process, upon the addition of the NaHSe solution, large amounts of nuclei suddenly form at the liquid-liquid interface. And these nuclei move to the organic phase and stop growing. When they return to the interface, the nucleation and growth continue and result in the focusing of the size distribution. The repeated though slow growth and the separation of the nucleation and growth stages favor the monodispersity of the QDs. The limited reaction area of the interfacial strategy results in a longer nucleation and growth period.

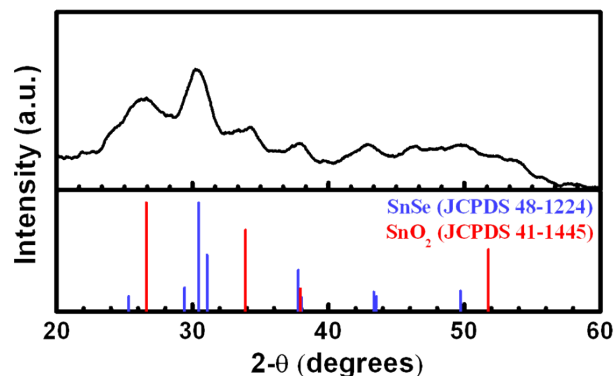


Figure S5. The XRD pattern of the OLA-SnSe prepared in the toluene/water system.

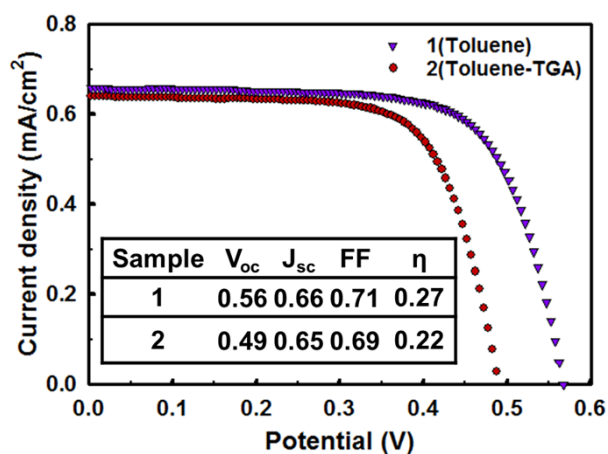


Figure S6. The J-V characteristics of solar cell devices with and without the bifunctional molecular linker (thioglycolic acid).

Bifunctional molecular linkers are widely used to improve the electron transfer ability. In most cases, a linker possesses a structure of HOOC-R-SH, where R is the hydrocarbon chain of the linker. The carboxyl group can attach to a TiO<sub>2</sub> film, while the mercapto group has a strong affinity to the metal sites on QDs surface. The experiment was conducted by immersing a TiO<sub>2</sub> film in a TGA solution for 2 h before fabrication, which enabled the full attachment of TGA molecules onto the film. However, the results showed in Fig. S6-2 gave a decreased  $J_{sc}$ ,  $V_{oc}$ , FF and efficiency compared with the above ones. This decrease can be attributed to the combination between the primary amine groups of the ligands OLA and the carboxyl groups of the molecular linkers, which induces the dissociation between the carboxyl groups and the TiO<sub>2</sub> film.