

Supporting information

A Simple Strategy to Achieve Shape-Control of Au-Cu_{2-x}S Colloidal Heterostructured Nanocrystals and Their Preliminary Use in Organic Photovoltaics

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Experiments

Materials: Chloroauric acid (HAuCl₄·3H₂O, 99.95%), sodium borohydride (NaBH₄) were purchased from Beijing Ouhe Technique Company. CuCl₂·2H₂O (99.99%), 1-dodecanethiol (DDT, 98%), di-*tert*-butyl disulfide (TBDS, 97%), didodecyldimethylammonium bromide (DDAB, 98%) were all purchased from Aldrich. Ethanol, isopropanol, chloroform, toluene and oleylamine (OLA) were of analytical grade and obtained from various sources.

Synthesis of Au NCs: The Au nanocrystals were synthesized following a reported protocol with slight modifications. In a typical synthesis, a solution comprising ~4 mg/mL HAuCl₄·3H₂O and ~10 mg/mL DDAB in toluene was sonicated for at least 30 min to form a clear dark red solution. Then 100 μL of 9.4 M NaBH₄ aqueous solution was introduced into the solution (10 mL) under vigorous stirring. After 15 minutes, 0.8 mL of DDT was injected and the solution was stirred for another 5 minutes (Figure S1).

Device fabrication: Photovoltaic devices based on P1:PC₇₁BM with different Au-Cu_{2-x}S NCs concentrations are fabricated. The device configuration is ITO/PEDOT:PSS/P1:PC₇₁BM: Au-Cu_{2-x}S NCs/LiF/Al (Figure S8(b)). ITO (20 Ω) glass was cleaned with detergent, acetone and isopropyl alcohol under ultrasonication. PEDOT:PSS (Baytron AI

4083 from H.C. Starck) was filtered with a 0.45 μm polyvinylidene difluoride (PVDF) film before use. A PEDOT:PSS thin layer was spin-coated on top of the ITO substrates at 3500 rpm/s for 30 s and dried subsequently at 150 $^{\circ}\text{C}$ for 15 min on a hotplate. Au-Cu_{2-x}S solution of 1.000 mg/mL was prepared in 1,2-dichlorobenzene (ODCB) and then diluted to 0.50 mg/mL, 0.10 mg/mL, 0.05 mg/mL and 0.01 mg/mL, respectively. Then five sets of ODCB solutions of P1 and PC₇₁BM (P1: PC₇₁BM = 1:2, 20 mg/mL) with 0 mg/mL, 0.50 mg/mL, 0.10 mg/mL, 0.05 mg/mL and 0.01 mg/mL Au-Cu_{2-x}S NCs were spin-coated onto the PEDOT:PSS layer at 1000 rpm to form the active layer. Finally, LiF (0.6 nm) and Al (100 nm) were sequentially evaporated under high vacuum onto the active layer as a cathode.

Measurements and instruments: The scanning electron microscope (SEM) were recorded with a field-emission scanning electron microscope (S-4800) operated at an accelerating voltage of 10 kV to 20 kV. The nanocrystal morphology and energy-dispersive X-ray spectroscopy (EDX) elemental mapping were further characterized by high-resolution transmission electron microscopy (TEM, Tecnai F20, FEI) with an accelerating voltage of 200 kV. Ultraviolet-visible (UV-vis) absorption spectra were measured on a PerkinElmer UV-vis spectrometer. X-Ray powder diffraction (XRD) was carried out on an X-ray diffractometer (PANalytical X' Pert PRO MPD) with Cu KR radiation. The current density-voltage (*J-V*) performances of the devices were measured on a computer-controlled Keithley 236 Source Measure Unit. The white light source we used is an Air Mass AM 1.5G AAA class solar simulator (model XES-301S, SAN-EI) solar simulator with an irradiation intensity of 100 mW/cm² and our light

intensity

was calibrated with a standard single-crystal Si photovoltaic cell before employment. The surface morphology and roughness analysis of active layer were performed by atomic force microscopy (AFM) with a Digital Instrument Multimode Nanoscope IIIA under ambient conditions operating in the tapping mode. The external quantum efficiency (EQE) of the device was measured with a 150 W xenon lamp (CTTH-150W) and a monochromator (M24-S).

Characterizations

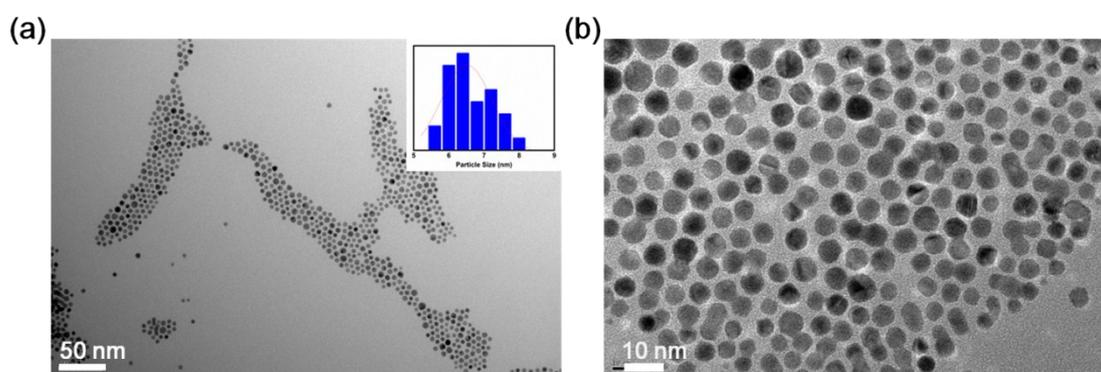


Figure S1. (a-b) TEM micrographs of Au nanoparticles. The inset image is particle size contribution of Au nanoparticles measured by randomly counting about 150 nanocrystals in the TEM image by Image Tool Software.

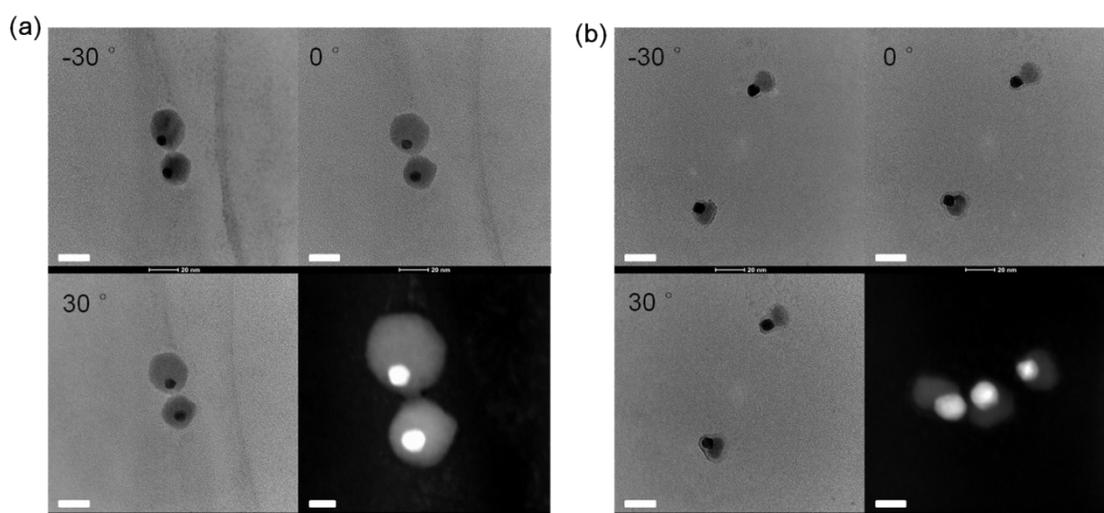


Figure S2. (a) TEM and STEM micrographs of Au-Cu_{2-x}S NCs (Shape I) at tilt angles of -30°, 0° and 30°; (b) TEM and STEM micrographs of Au-Cu_{2-x}S NCs (Shape II) at tilt angles of -30°, 0° and 30°. The scale bars correspond to 20 nm.

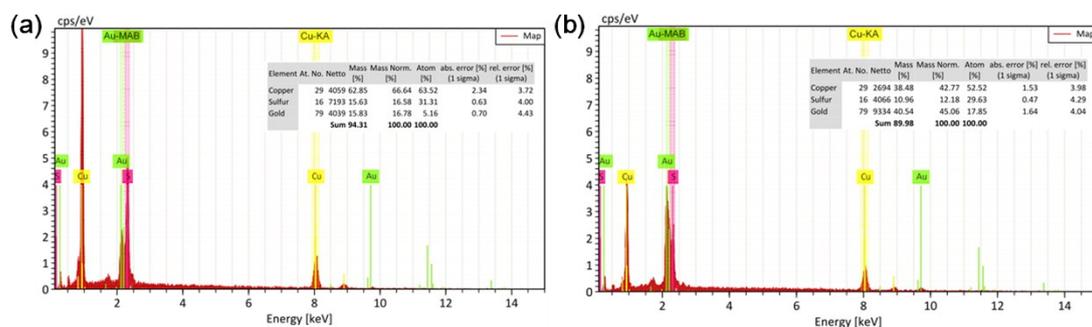


Figure S3. EDX spectroscopy of (a) Au-Cu_{2-x}S (Shape I) and (b) Au-Cu_{2-x}S NCs (Shape II).

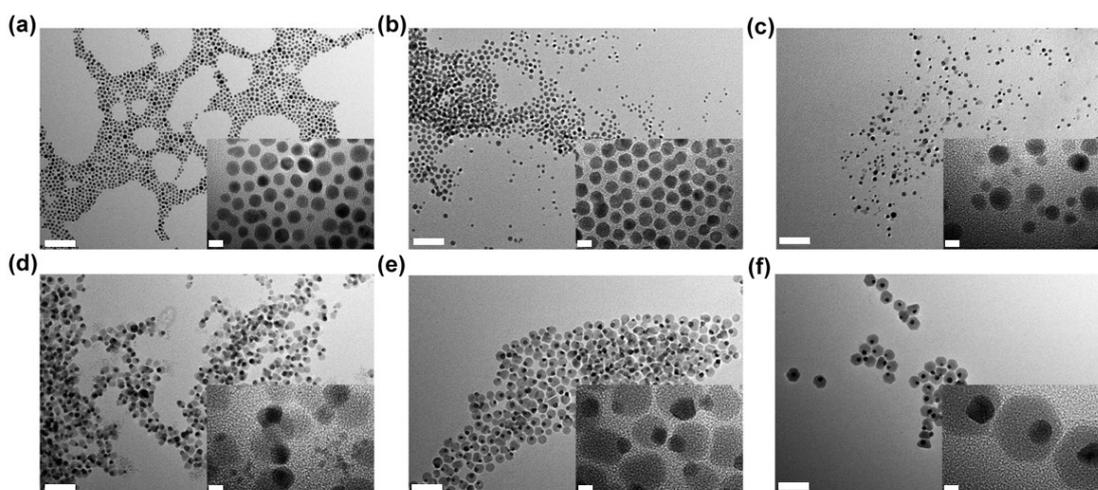


Figure S4. (a-f) TEM micrographs of Au-Cu_{2-x}S NCs (Shape I) fabricated in the different reaction time of 0, 6, 10, 30, 50 and 70 min, respectively. The scale bars correspond to 50 nm (insets correspond to 5 nm).

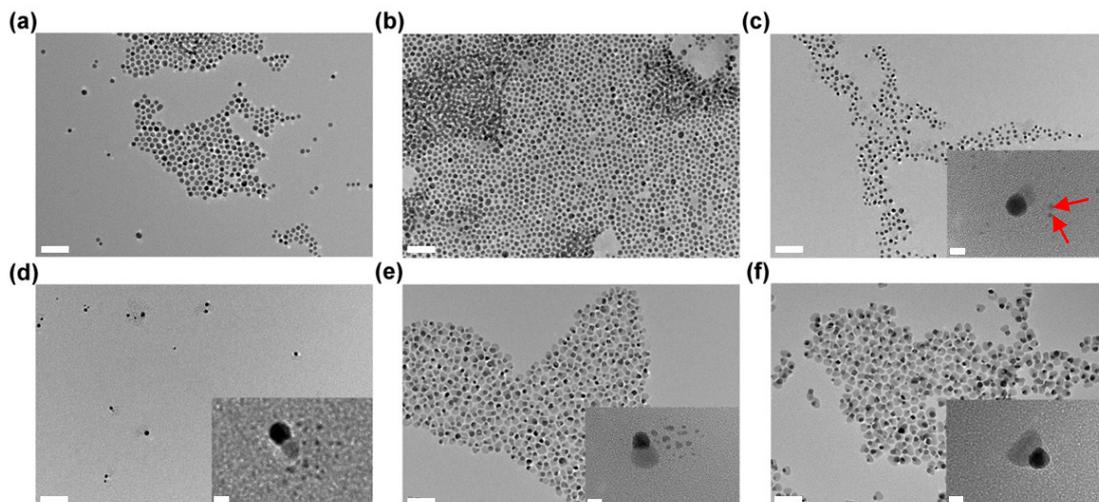


Figure S5. (a-f) TEM micrographs of badminton-like Au-Cu_{2-x}S NCs (Shape II) fabricated in the different reaction time of 0, 3, 10, 30, 50 and 70 min, respectively. The scale bars correspond to 50 nm (insets correspond to 5 nm).

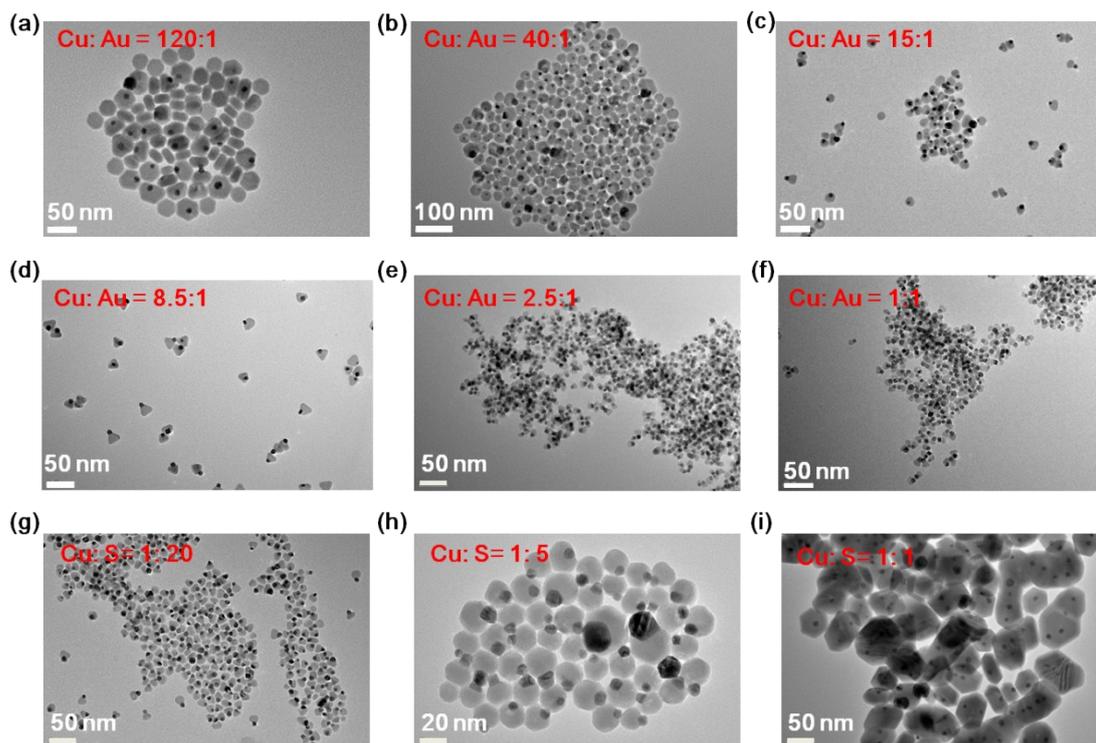


Figure S6. (a-i) TEM micrographs of Au-Cu_{2-x}S NCs obtained under different molar ratio of Au: Cu.

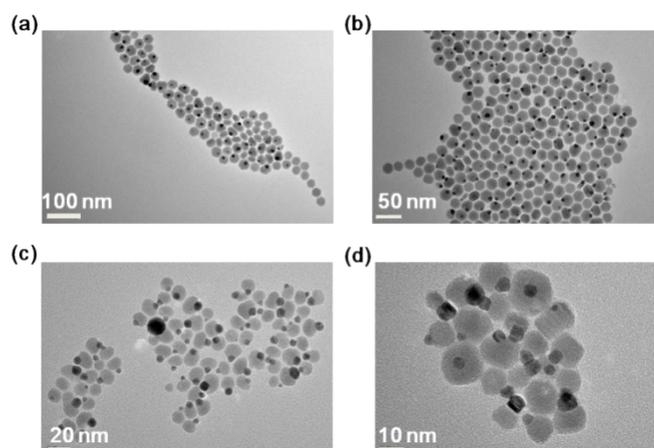


Figure S7. TEM micrographs of Au-Cu_{2-x}S NCs obtained under different conditions: (a) 10 mmol of TBDS was used; (b) 1 mmol of CuCl₂·2H₂O, 0.05 mmol of Au NPs and 10 mmol of TBDS was used; (c) DDT (20 mmol S precursor) was used instead of TBDS; (d) 5 mL of OLA and 5 mL of OA used instead of 10 mL of OLA .

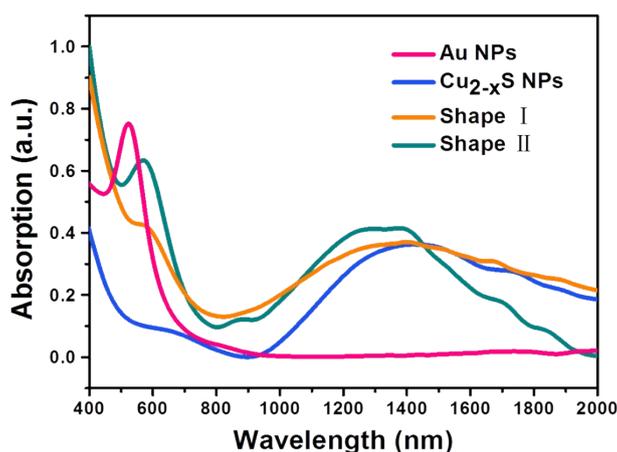


Figure S8. UV-vis spectra of Au, Cu_{2-x}S and Au-Cu_{2-x}S NCs dispersed in chloroform.

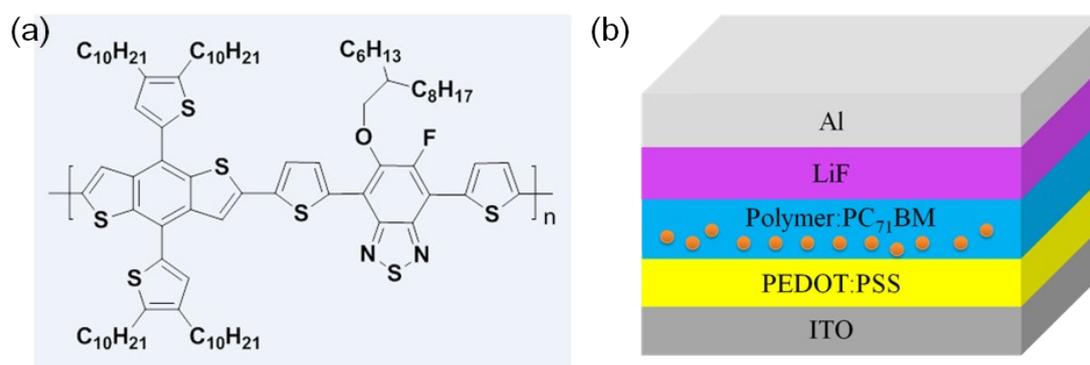


Figure S9. (a) Molecular structure of the polymer (P1) used in the active layer; (b)

Configuration of the photovoltaic device.

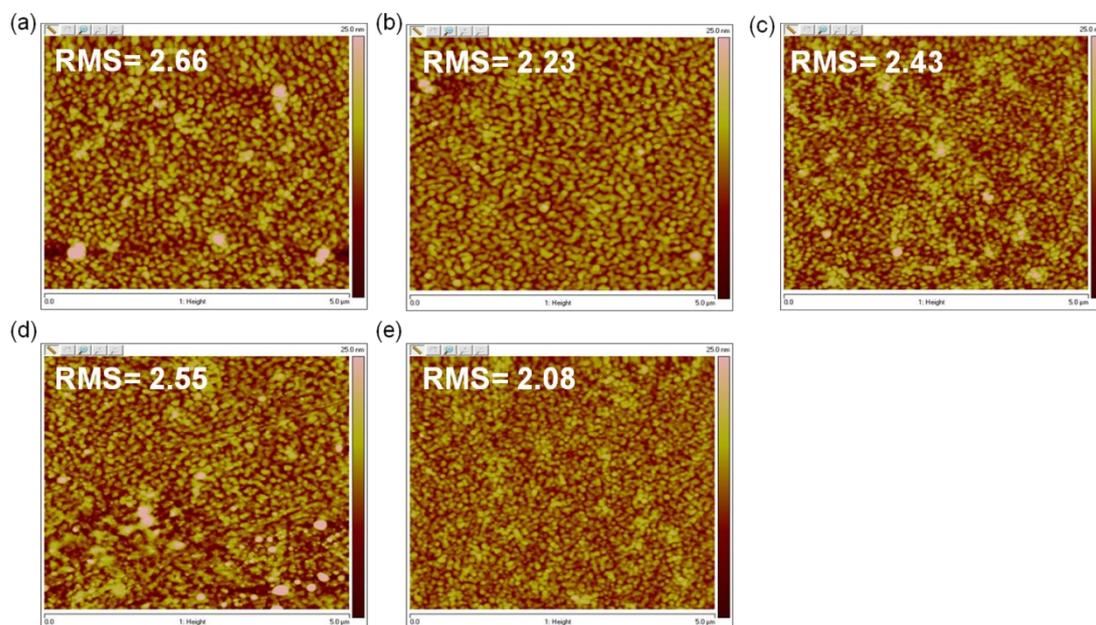


Figure S10. AFM height images for ITO/PEDOT: PSS/ P1: PC₇₁BM films (a) 0 mg/mL; (b) 0.50 mg/mL; (c) 0.10 mg/mL; (d) 0.05 mg/mL and (e) 0.01 mg/mL Au-Cu_{2-x}S NCs. The corresponding mean roughnesses (RMS) of the films are 2.66 nm, 2.23 nm, 2.43 nm, 2.55 nm and 2.08 nm, respectively.