Supporting information for

Low-temperature Colloidal Synthesis of $CuBiS_2$ Nanocrystals for Optoelectronic Device

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Experimental Details:

Chemicals:

Cu(I) acetate, hexamethyldisilathiane (HMS), 1-octadecene (ODE), oleic acid, toluene, 1,2-ethanedithiol (EDT), 1-ethyl-3-methylimidazolium iodide (EMII), InCl3, titanium tetrachloride (TiCl4) 99% were purchased from Aldrich. Bi(III) acetate was purchased from Alfa Aesar and poly(3-hexylthiophene) (P3HT) was purchased from Rieke Metals. 90T titania paste was purchased from Dyesol Ltd.

Materials Characterizations:

Transmission and scanning electron microscopy: The morphology of CBS nanocrystals was characterized by transmission electron microscopy (TEM) and angular dark-field scanning transmission electron microscopy using a JEOL 2100 microscope operating at an accelerating voltage of 200 kV.

X-Ray diffraction analysis: X-Ray diffractograms of drop-cast films of CBS nanocrystals on a glass substrate were carried out on a PANalytical X'Pert PRO MPD Alpha1 powder diffractometer in Bragg–Brentano θ/2θ geometry with a radius of 240 mm, Cu Kα radiation (λ = 1.5406 Å) and a power of 45 kV–40 mA.

Raman spectroscopy: Raman spectroscopy measurements were performed on a Renishaw InVia spectrometer and 532 nm laser at room temperature. An objective lens (×50) was used to focus the lasers on the samples.

UV-Vis-NIR absorption spectra: UV-Vis-NIR spectroscopy of CBS nanocrystal solution was carried out on a Cary 5000 UV-Vis-NIR spectrophotometer.

X-ray photoelectron spectra: XPS measurements were performed with a Phoibos 150 analyser (SPECS) in ultrahigh-

vacuum conditions (base pressure of 1×10^{-10} mbar) with a monochromatic Kα X-ray source (1,486.74 eV).

FTIR spectra: FTIR measurements were performed on a Cary 600 FTIR spectrophotometer in transmission mode.

Device fabrication and characterization

The TiO_2 films on FTO substrate were fabricated according to previous reports. Solutions of 20 mg/ml of CBS nanocrystals were prepared by adding toluene to the original concentrated solution. The desired film thickness was obtained via a layer-by-layer spin coating process. A few drops of NCs was dispensed on the top of a substrate, then spinning at 2000 rpm for 15s, followed by 1 drops of 1,2-ethanedithiol (EDT) 2% vol. in acetonitrile. The ligand was left to react for 20 seconds prior to the dispensing of a flush of acetonitrile and a flush of toluene. For the doped film, a few drops of InCl3 solution in acetonitrile (0.5 mg/ml) was dispensed on the top of CBS layer and then spinning at 2000 rpm for 40s. For EMII treated films, the EDT solution was replaced by 7 mg/ml of EMII solution in methanol with flushing by using methanol and toluene. A 5mg/ml P3HT solution in dichlorobenzene was prepared by stirring overnight. A P3HT layer was spin-coated onto the CBS layer at a 2000 rpm spin velocity for 40s. Then, gold deposition was carried out on a Kurt J. Lesker Nano 36 system. The device area was determined using a shadow circular mask of 2 mm in diameter. The final thickness was controlled together with the deposition rate and monitored via a quartz crystal. 150 nm of Au was deposited to achieve the top electrical contact. The devices were annealed at 100 °C for 10 min in air.

All device characterization was performed under ambient conditions. Current−voltage characteristics of FET devices were acquired using an Agilent B1500A semiconducting device analyzer. Current–voltage characteristics of solar cells were obtained using a Keithley 2400 source measuring unit under dark and simulated AM1.5G 100 mW cm-2 illumination conditions (Newport 96000). External quantum efficiency (EQE) measurements were performed using a Newport Cornerstone 260 monochromator and a Keithley 2400 source measuring unit providing short circuit conditions.

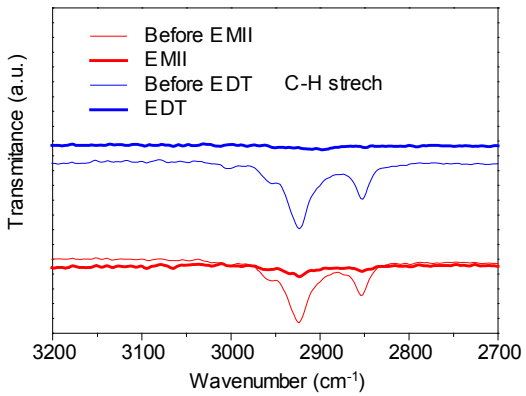

Figure S1. FTIR spectra of films before and after treated with EDT and EMII.

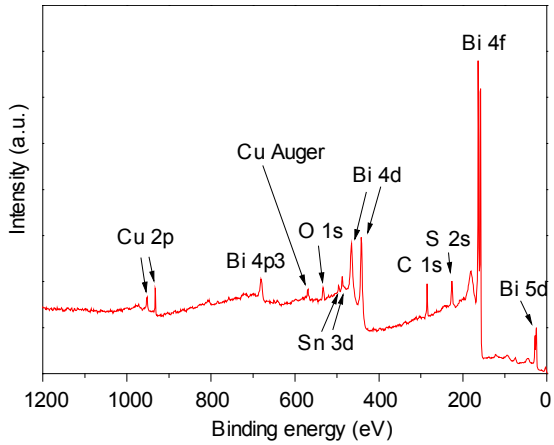

Figure S2. A survey spectrum of XPS. The signal of Sn 3d is from the substrate of ITO.

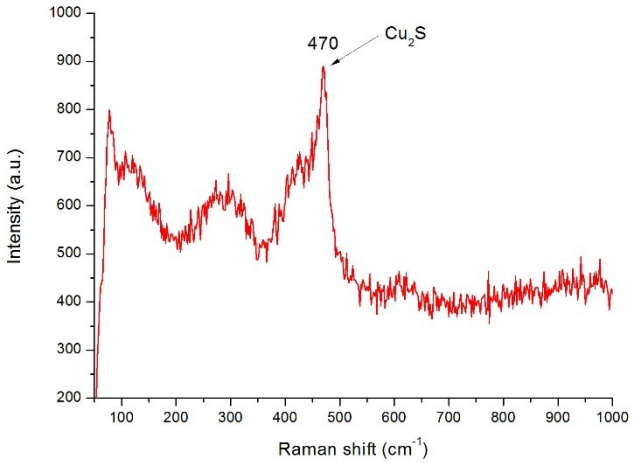

Figure S3. The Raman spectrum of the nanocrystals using more Cu precursor, and the formation of Cu2S was observed.

Table S1. The composition analysis of the as-synthesized CBS nanocrystals by XPS and EDX.

	Name	Bi 4f	S 2s	Cu 2p	C 1s	O 1s
XPS	%Conc	19.064	29.111	4.162	39.998	7.665
EDX	%Conc	35.6	56.7	7.64	------	-------

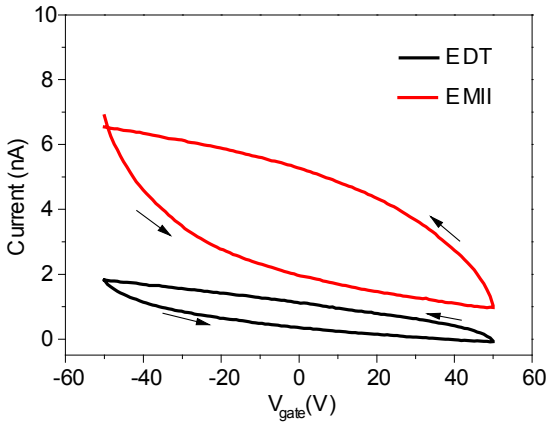

Figure S4. The transfer curves of field effect transistors.

Table S2. The summary of solar cell performance.

Device	Voc (V)	Jsc (mA/cm2)	FF	PCE (%)
EMII-treated without doping	0.28	0.31	0.34	0.0292
EMII-treated with In doping	0.04	1.46	0.18	0.0107
EDT-treated with In doping	0.22	7.32	0.42	0.682
EDT-treated without doping	0.18	0.81	0.32	0.0473