Nanoscale

Electronic Supplementary Information

Highly Concentrated Synthesis of Copper-Zinc-Tin-Sulfide Nanocrystals with Easily Decomposable Capping Molecules for Printed Photovoltaic Applications

Youngwoo Kim,[a] Kyoohee Woo,[a] Inhyuk Kim,[a] Yong Soo Cho,[a] Sunho Jeong,[b] and Jooho Moon[a,*]

Experimental

1. CZTS nanocrystal synthesis

Copper (II) acetylacetonate (97%, Aldrich), zinc acetate (99.99%, Aldrich), tin (IV) acetate (anhydrous, 99.8%, Aldrich), sulfur powder (Aldrich), triphenylphosphate (99%, TPP, Aldrich), and oleylamine (70%, OLA, Aldrich) were purchased and used as received. All reaction conditions were performed under an inert atmosphere to prevent the formation of oxides. In a typical synthesis reaction, a mixture of initial precursors at a molar ratio of Cu:Zn:Sn:S = 1.70:1.22:1.00:3.99 with 16 mL of OLA was heated to 150°C for 30 min. During the heating, the solution turned dark blue, indicating the formation of chelated Cu, Zn, and Sn complexes with OLA. The temperature of the mixture was decreased to 125°C and the mixture remained at this temperature until hot injection was performed. In a separate vial, a 2.0 M solution of sulfur powder in OLA was sonicated until the dissolution of S took place. These two separate precursor solutions were injected into a three-neck round-bottom reaction flask in which either 0.17 mol of TPP for TPP-CZTS or 0.15 mol of OLA for OLA-CZTS was heated to 300°C under an inert atmosphere.

When the temperature reached 300°C, the metal and sulfur precursors were rapidly injected into the heated reaction flask. The reaction solution immediately changed to a dark black solution. After reaction for 0.5 h, the reactor was cooled to 80°C and 5 mL of hexane was added into the reaction flask to prevent nanocrystal aggregation. The CZTS nanocrystals were collected by centrifugation using equal amounts of hexane and isopropyl alcohol. Residual organic impurities were removed by repeated washing using a mixture of hexane/isopropanol (1:2 ratio) with centrifugation (10,000 rpm for 5 min). The final precipitate was dried under nitrogen and redispersed in 1, 2-dichlorobenzene (Aldrich) to form a stable ink with a concentration of ~20 wt%.

2. Device fabrication

The CZTS nanocrystal ink was applied directly onto Mo-deposited (400 nm) SLG substrates by spin-coating to form nanocrystal granular films. The nanocrystal films were dried on a hot plate at 300°C for 10 min. After drying, the CZTS nanocrystal films were soaked in a sodium salt solution for 10 min and dried on a hot plate at 80°C for 10 min. The sodium salt solution (0.2M) was prepared by dissolving the sodium acetate (Aldrich) in ethanol at room temperature. The CZTS nanocrystal films were annealed under a N_2 + H_2S (4%) atmosphere at 500°C for 30 min. The annealed absorber films were processed into photovoltaic devices following standard procedures including chemical bath deposition of CdS (~60 nm), DC sputtering of *i*-ZnO (~70 nm), RF sputtering of ITO (~250 nm), and thermal evaporation of a patterned Ni/Al grid as the top electrode. The final devices (2 cm x 2 cm) were mechanically scribed into cells with an area of 0.25 cm^2. We measured the current–voltage (I–V) characteristics of our CZTS nanocrystal-based solar cells measured in the dark and under AM 1.5 illumination. The integrated intensity was reduced to 1,000 W m^{-2} using neutral density filters.

3. Characterization and analysis

Scanning transmission electron microscopy (STEM) images were taken by a 1024 x 1024 digital CCD camera using a high-resolution transmission electron microscope (HR-TEM, Titan G2 60-300, FEI) operated at an accelerating voltage of 300 kV. The composition of the nanocrystals was analyzed by energy dispersive X-ray spectrometry (EDX) using an Oxford Inca250 system. The crystallographic structures of the nanocrystals and films were characterized using an X-ray diffractometer by scanning from 10^o to 80^o (Ultima IV, Rigaku). The microstructures of the annealed CZTS nanocrystal films were analyzed by field emission scanning electron microscopy (JEOL-JSM-6700F). TG analysis of each type of CZTS nanocrystal powder was performed under nitrogen flow (150 cc min^{-1}) using a SDT Q600 (TA Instruments). Absorption spectra were collected using a UV-vis spectrometer (V530, JASCO). The cell performance and EQE were analyzed by a solar simulator (Oriel Sol3A Class AAA, Newport Corporation, Irvine, CA, USA) and an incident photon conversion efficiency (IPCE) measurement unit (QEX 10, PV Measurements, Inc., Boulder, CO, USA), respectively.

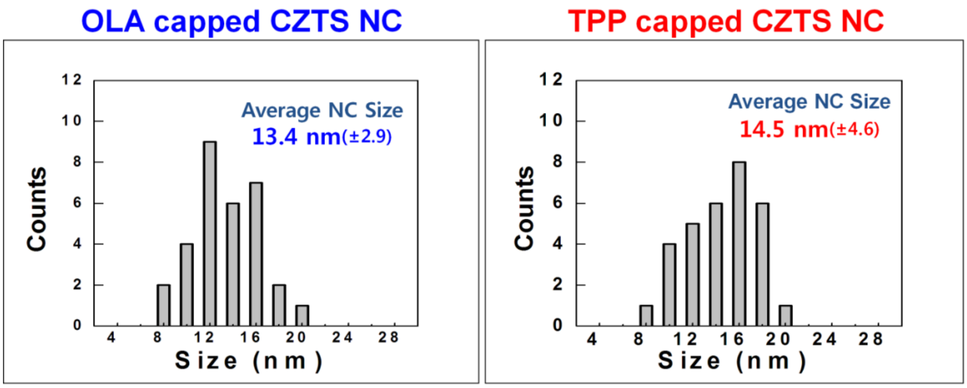
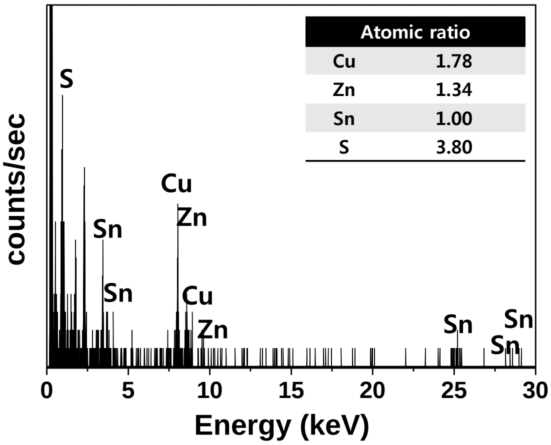


Figure S1. The nanocrystal (NC) size distribution plots for each capping ligand.



Atomic ratio	
Cu	1.78
Zn	1.34
Sn	1.00
S	3.80

Figure S2. Scanning transmission electron microscopy (STEM)-EDX drift-corrected spectrum image of the triphenylphosphate-capped CZTS nanocrystals.

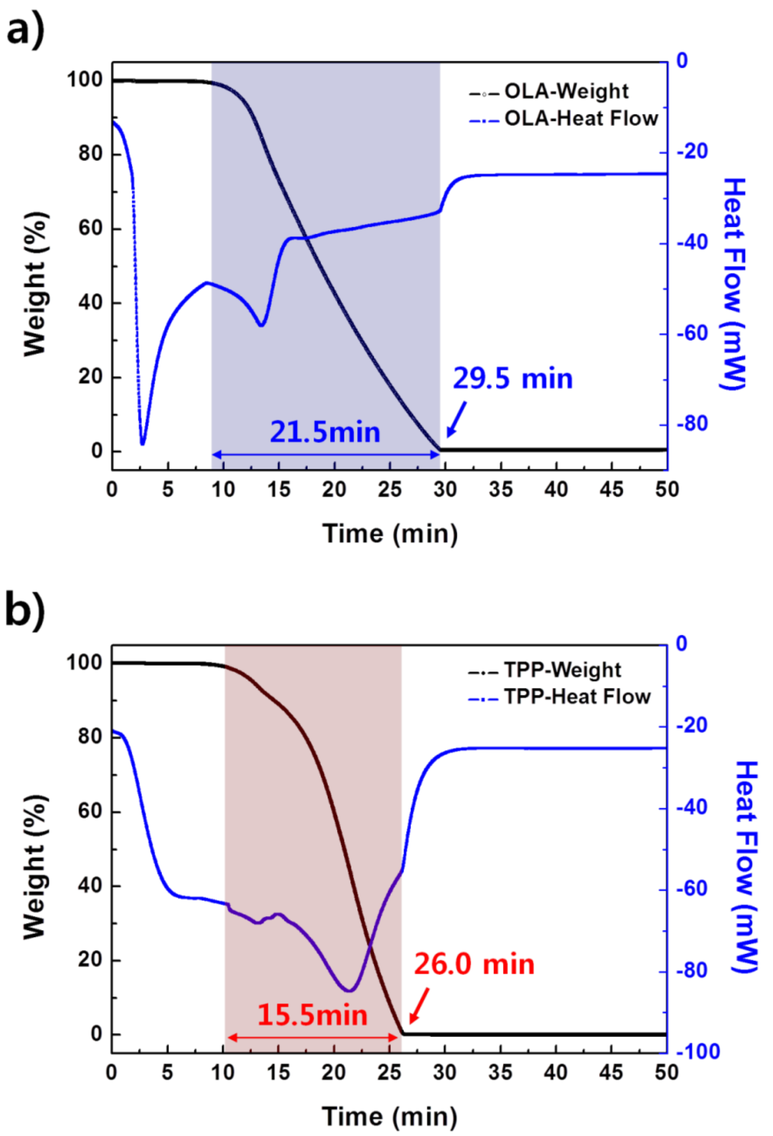


Figure S3. Isothermal analysis of (a) oleylamine (OLA) and (b) triphenylphosphate (TPP) performed at 300°C under a nitrogen atmosphere to determine their decomposition rates using TG-DSC.

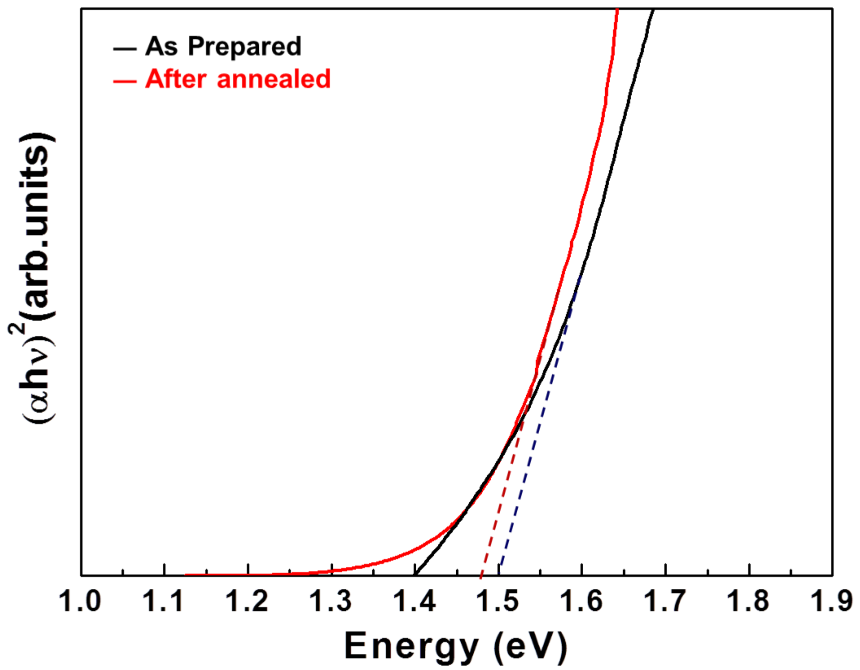


Figure S4. UV-vis absorption spectra of TPP-CZTS nanocrystals based films: as-prepared (blue) and annealed at 500°C (red). The band gap energy of the as-prepared nanocrystals (blue) was about 1.50 eV which decreased after annealing under a N_2+H_2S (4%) atmosphere (red) to about 1.47 eV.

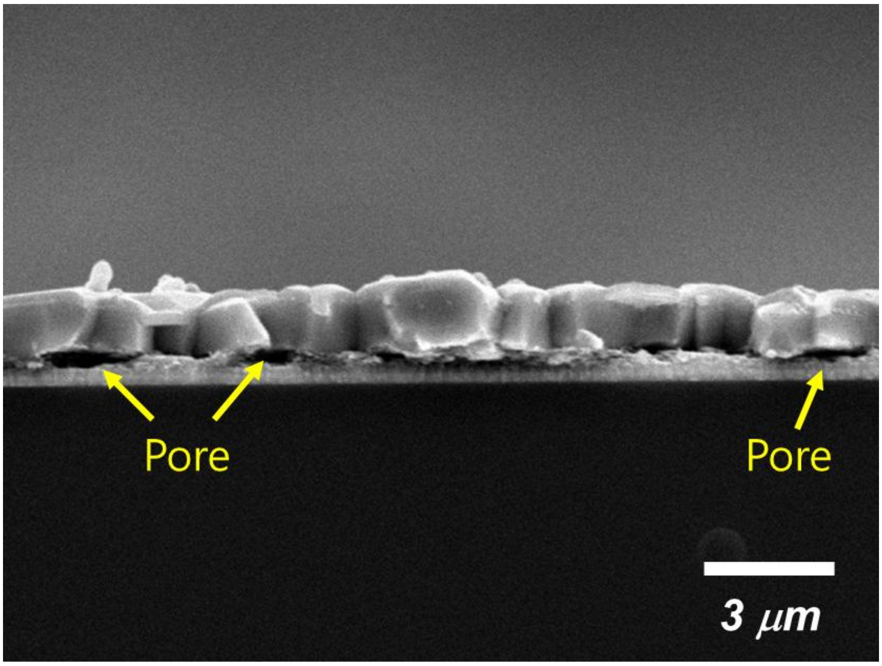


Figure S5. A cross-sectional microstructural SEM image of the partially porous CZTS absorber layer.