Scalable Noninjection Phosphine-Free Synthesis and Optical Properties of Tetragonal-Phase $CuInSe_2$ Quantum Dots

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Materials Characterization

The phase identification was carried out using a powder X-ray diffraction (XRD, TTR-III, Rigaku Corp., Japan). The morphology and crystal structure of the prepared samples were characterized using a field emission scanning electron microscopy (FESEM, FEI, Quanta 200FEG) and a high-resolution transmission electron microscopy (HRTEM, JEM-2100F, Japan). Energy dispersive X-ray spectroscopy (EDS) were performed with an energy dispersive spectrometer equipped on the SEM/TEM equipment. X-ray photoelectron spectroscopy (XPS) data were accumulated on an ESCA-LAB250 XPS system (Thermo, U.S.). Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on a Perkin-Elmer Optima 3000DV after dissolving the nanocrystals in aqua regia. UV-vis-NIR absorption spectra were obtained with a spectrophotometer (HITACHI, U-3900H, Japan). Current-voltage (*J-V*) characteristics of the solar cells were derived with a Keithley 2420 digital source meter (Keithley, USA) under a 450W xenon lamp (Oriel Sol3A Solar Simulator 94043, Newport Stratford Inc., USA).

Photovoltaic Device Fabrication

CISe QD-sensitized TiO_2 photoanodes were prepared as described in the main text. Solar cell devices were fabricated by sandwiching the photoanode and the CuSe counter electrode (prepared according to our previous report[1]) using a thermal adhesive film (Surlyn, 60 μm, Dupont). The polysulfide electrolyte (2 M S, 2 M Na_2S, and 0.2 M KCl in ultrapure aqueous solution) was then injected by vacuum backfilling followed by sealing with a Surlyn film and a cover glass. The active surface area of the mask-covered solar cells was measured to be 0.25 cm^2.

MPA Ligand Exchange

In our typical ligand exchange route, equal volume of MPA (Alfa Aesar, 99%) was added to the as-synthesized CISe QD chloroform solution, followed by sonication for 3 h. Products were then isolated with chloroform, collected by centrifugation and removal of the supernatant. MPA-capped CISe QDs thus achieved and can be freely dissolved in methanol. $CuInSe_2$ QDs can also be dissolvable in water, but we note that the solubility is not so good as in methanol. This is probably because the initial long-chain ligands (e.g.,

DDT) on QD surface still can not be thoroughly replaced by our MPA treatment.

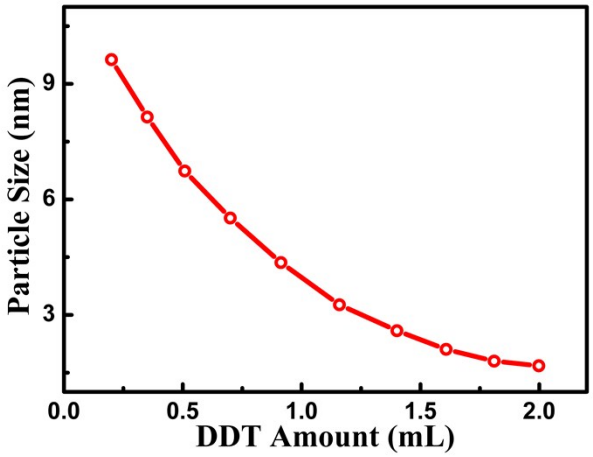

Figure S1. Particle size of the resulting CISe QDs as a function of DDT amount.

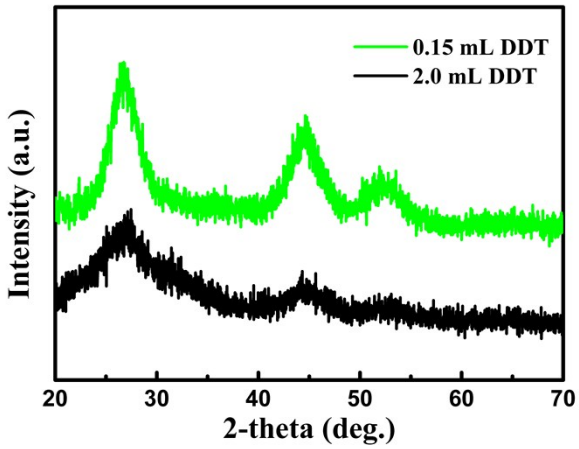

Figure S2. XRD spectra of the tetragonal CISe QDs synthesized with addition of 0.15 mL DDT and 2.0 mL DDT.

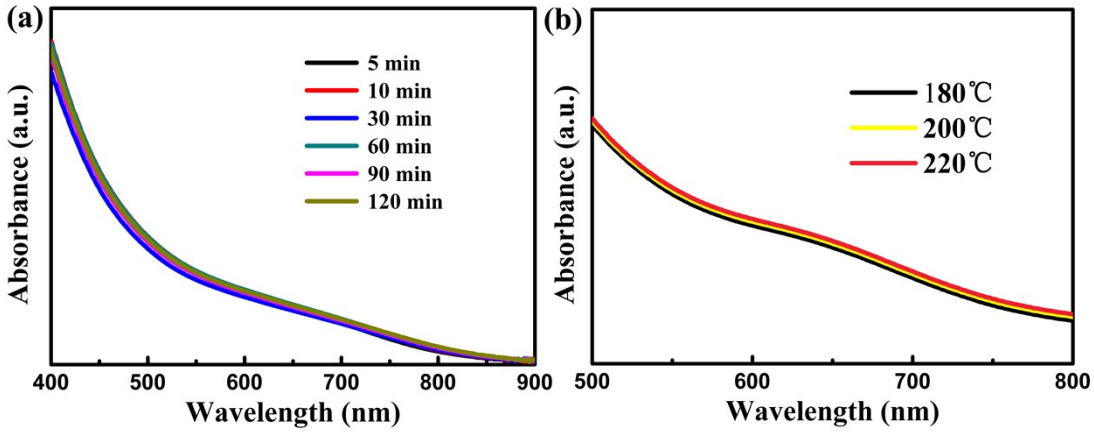

Figure S3. UV-vis absorbance of CISe QDs prepared with varying synthetic parameters. 0.75 mmol of CuI, 0.75 mmol of $In(OAc)_3$, 1.5 mmol of Se, and 1.5 mL of DDT. (a) The

reaction time was adjusted from 5 min to 120 min. (b) The final reaction temperature was set at 180°C to 220°C.

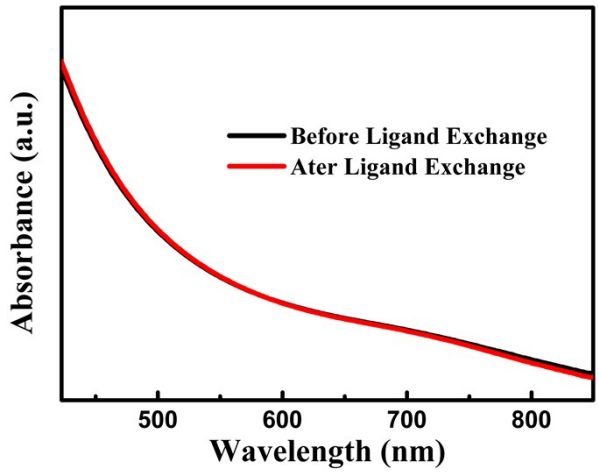

Figure S4. UV-vis absorbance of CISe QDs before and after MPA ligand exchange.

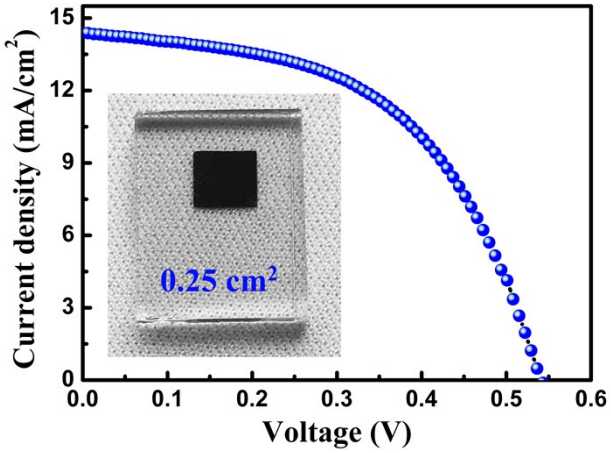

Figure S5. *J-V* curve of ~5 nm CISe QD-sensitized solar cells under simulated solar illumination at 100 mW cm^{-2}.

(1) Liu, F.; Zhu, J.; Hu, L. H.; Zhang, B.; Yao, J. X.; Nazeeruddin, M. K.; Gratzel, M.; Dai, S. Y. *J. Mater. Chem. A* **2015**, *3*, 6315.