Electronic Supplementary Information for

**Copper-Indium-Selenide Quantum Dot-Sensitized Solar Cells**

Jiwoong Yang,‡\(^{ab}\) Jae-Yup Kim,‡\(^{c}\) Jung Ho Yu,\(^{ab}\) Tae-Young Ahn,\(^{ab}\) Hyunjae Lee,\(^{ab}\) Tae-Seok Choi,\(^{ab}\) Young-Woon Kim,\(^{d}\) Jin Joo,\(^{e}\) Min Jae Ko\(^{ac}\) and Taeghwan Hyeon\(^{ab}\)

\(^{a}\) School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Republic of Korea. E-mail: thyeon@snu.ac.kr; Fax: +82 2 880 7150

\(^{b}\) Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul 151-742, Republic of Korea.

\(^{c}\) Photo-Electronic Hybrids Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea. E-mail: mjko@kist.re.kr; Fax: +82 2 958 5518

\(^{d}\) Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Republic of Korea.

\(^{e}\) Department of Applied Chemistry, Kyungpook National University, Daegu 702-701, Republic of Korea.

**Cyclic voltammetry measurement of QDs:**

To examine the conduction band minimum (CBM) of QDs, cyclic voltammetry (CV) analysis was performed using an electrochemical analyzer (CH Instruments Inc., Austin, TX). A glassy carbon electrode was used as a working electrode, on which QDs in dichloromethane (concentration ~5 mg mL\(^{-1}\)) were drop-casted. Platinum wire and Ag/Ag\(^+\) electrode were used as a counter and reference electrode, respectively. The electrolyte was 0.1 M tetra-\(n\)-butylammonium perchlorate (TBAP) in acetonitrile. Before every measurement, the electrolyte was deaerated by nitrogen bubbling for 30 min. The potential range was from 1.2 to \(–1.0\) V versus Ag/Ag\(^+\) with a scan rate of 50 mV s\(^{-1}\). The measured potential was calibrated and converted to the values versus a normal hydrogen electrode (NHE) by using the Fe/Fe\(^+\) couple. The CBM was determined from the first reduction peak potential in the CV.\(^1\) The valence band maximum was estimated from the CBM and optical band gap. Exciton binding energy was ignored because it is smaller than the precision of CV measurement.\(^2\)
Band energy calculation of QDs:

The wave functions for CISe region, which is composed of spherical Bessel and Neumann functions, and for organic ligand region, which is composed of Hankel functions, are obtained from the following boundary conditions, where \( R(r) \) is radial eigenfunction and \( R_0 \) is the QD radius.

\[
\frac{dR_{n=1,\text{CISe}}(R_0)}{dR_{n=1,\text{CISe}}} = \frac{dR_{n=1,\text{organic}}(r)}{dR_{n=1,\text{organic}}}
\]

The effective mass of electron and hole used in this work are 0.09 and 0.76 for CuInSe\(_2\),\(^3\) and 0.16 and 1.1 for CuIn\(_3\)Se\(_5\), respectively.\(^4\) Effective masses of electron and hole for organic ligand are assumed as 3.03 and 0.3, respectively.\(^5\) Electron affinity and ionization potential are \(-4.48\) eV and \(-5.52\) eV for CuInSe\(_2\),\(^6\) and \(-1.5\) and \(-11.8\) eV for organic ligand, respectively.\(^7,8\) The conduction- and valence band offsets between CuInSe\(_2\) and CuIn\(_3\)Se\(_5\) are 20 and 260 meV, respectively.\(^9\) Exciton Bohr radius was calculated using the same parameters.

References

**Fig. S1** The size distribution histograms of a) 2.4 nm; b) 2.9 nm; c) 3.9 nm; d) 5.0 nm; e) 7.0 nm; and (f) 10.0 nm-sized CISe QDs.

**Fig. S2** CISe QD powder synthesized in a large-scale and their TEM image.
Fig. S3 XRD patterns of a) 10 nm- and b) 7.0 nm-sized CISe QDs. The insets show the existence of (211) reflection, which is a characteristic of chalcopyrite copper indium selenide crystal structure.

Fig. S4 Extrapolated plot of $(\alpha h\nu)^2$ vs. energy from absorption spectrum used to determine the band gap of CISe QDs of various size.
**Fig. S5** Photoluminescence spectra of CISc QDs.
Fig. S6 Cyclic voltammograms (CVs) of CISe QDs depending on the QD size.
**Fig. S7** Optical images showing the illumination side of the TiO$_2$/QD films on FTO glasses depending on the QD size.

**Fig. S8** TEM images of 4 nm QD-adsorbed TiO$_2$ nanoparticles.
Fig. S9 (a) Recombination resistance, (b) chemical capacitance, and (c) electron lifetime of the CISe QDSCs with various-sized QDs, evaluated from the impedance spectra in the dark state.