

Supporting Information

Enhanced Photocurrent by Co-sensitization of ZnO with Dye and CuInSe Nanocrystals

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Experimental Section

I. Chemicals

Zinc chloride (ZnCl₂), Oxalic acid dihydrate (C₂H₂O₄ • 2H₂O), Phosphoric acid (H₃PO₄, ≥85%), Copper chloride (CuCl₂), Indium(III) chloride tetrahydrate (InCl₃ • 4H₂O, 39%), ethyl alcohol absolute, Selenium (Se), Sodium sulfate anhydrous (Na₂SO₃), Ethyl cellulose (200 cPa • s, 48%~49.5%), Terpeneol were purchased from Sinopharm Chemical Reagent Co., Ltd; Dioctyl sulfosuccinate sodium salt (AOT, 94%) was purchased from J&K Chemical Technology. The sensitizer N719 (Cis-di(thiocyanato)-N,N-bis(2,2'-bipyridyl-4,4'-dicarboxylate)Ru(II)bis-tetrabutylammonium), electrolyte, surlyn film were purchased from Yingkou Opvtech New Energy Co., Ltd.

II. Synthesis of the ZnO@CuInSe film and fabrication of Dye Sensitized Solar Cells (DSSCs)

2.1 Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized by using the following template-free method. 13.86g ZnCl₂ and 8.88g AOT were dissolved in 320mL deionized water under 80°C with stirring for 90 minutes to form a pellucid solution. Then 4g Oxalic acid dehydrate and 0.25mL phosphoric acid were dissolved in 80mL deionized water under 30°C with stirring for 120 minutes to form a clear solution, afterwards, the solution was heated to boiling. The latter solution was added to the former solution within 20 minutes. Whereafter, the mixed solution was stirred under 80°C for 20 minutes and then stewing for a while to make the solution layered. The lower turbid liquid was rinsed with deionized water and ethyl alcohol absolute for five times respectively. Subsequently, the products were dried under 50°C. Finally, the powders were sintered at 350°C for 7 hours to obtain ZnO nanoparticles.

2.2 Preparation of ZnO@CuInSe nanoparticles

In step A, a certain amount of ZnO nanoparticles were put into a vessel and subjected to vacuum. After thirty minutes' vacuum, the 5mL solution of InCl₃ aqueous (0.2mol/L) was allowed to enter the system until normal atmospheric pressure was achieved, then, the system was held for ten minutes before the solution of InCl₃ was removed by evaporation. The precipitate was dried under flowing air at 80°C. After drying, the powder was rinsed with ethyl alcohol absolute. Then, the powder was dried under flowing air at 80°C again. Step B and step C were repeated as described step A other than the InCl₃ aqueous, which was replaced by 5mL CuCl₂ aqueous (0.2 mol/L) and 10mL Na₂SeSO₃ aqueous (0.2mol/L), respectively. After step A, B and C, the samples were calcined in N₂ gases at 400°C for 1h to obtain ZnO@CuInSe nanocomposite, which was named ZnO@CIS.

2.3 Preparation of ZnO film and ZnO@CIS films

The ZnO film was prepared by the doctor-blade method. First of all, the ZnO paste was made with the ZnO nanoparticles synthesized in section 2.1. Briefly, 0.4g ethyl cellulose was dissolved in 10mL ethyl alcohol absolute with stirring. Subsequently, 1g ZnO nanoparticles powder and 3.5mL terpineol were added to the above solution. The obtained mixed solution was stirred at 40°C for 8h, afterwards, the temperature was increased to 80°C to volatilize alcohol absolutely. Then they were grinded into ropiness in agate mortar. A mask, with a window encompassed by 3M scotch tape, was used to define the 5mm×5mm area, which was used to spread the paste dropped one edge of the window with a scraper on the conductive glass (SnO₂:F coated glass, FTO). Finally, the as-prepared ZnO film was sintered in air with the heating rate of 4°C/min to 120°C for 60 min, 2°C/min to 450°C for 120 min.

The procedure of synthesis of mesoporous ZnO@CIS film was the same as described above^[1].

2.4 Fabrication of Dye Sensitized Solar Cells (DSSCs)

The ZnO film and ZnO@CIS film were sensitized with N719 dye by direct adsorption. Firstly, the as-prepared ZnO film and ZnO@CIS film were heated to 80°C and immersed in the in the N719 ethanol solution (0.5mM) for 1h. After rinsing the film by ethanol and drying, the desired ZnO/N719 film and ZnO@CIS/N719 film electrodes were obtained.

The photovoltaic cells were assembled with the ZnO/N719 film and ZnO@CIS/N719 film electrodes, Pt coated counter electrode, and 60μm thick sealing material (OPV-SN-60). Commercially available electrolyte of I₃⁻/I⁻ was injected into the space between the photoelectrode and counter electrode.

III. Characterization

XRD patterns of powders were obtained using D8 Advance (Germany) diffractometer with Cu K α radiation (40 kV and 40 mA) with the scanning rate of 4°/min for wide angle tests. The N₂ sorption measurements were performed using Micromeritics Tristar 3000 for mesoporosity and Micromeritics ASAP 2020

porosimeters and microporosity at 77 K, respectively. The mesoporous specific surface area and the pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) methods. SEM (Scanning Electron Microscopy) analysis was performed on a Hitachi-S-4800 electron microscope. TEM (Transmission electron microscopy) images were obtained on a JEOL-2010F electron microscope operated at 200 kV.

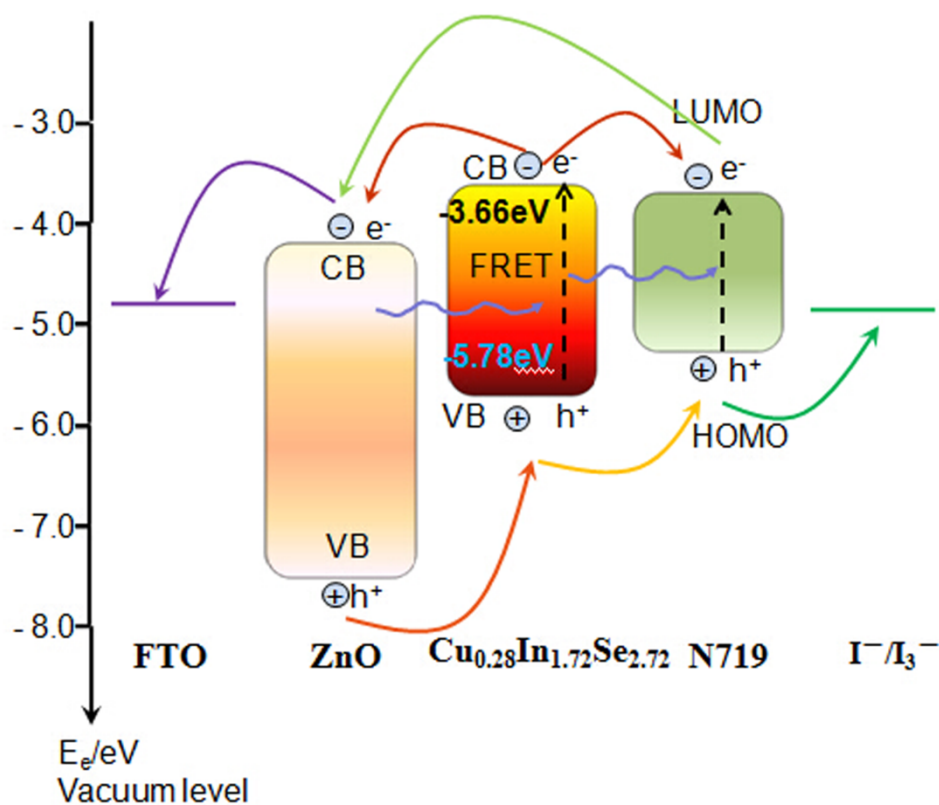
XPS (X-ray photoelectron spectroscopy) signals were collected on a VG Micro MKII instrument using monochromatic Mg Ka X-rays at 1486.6 eV operated at 200 W. All the elemental binding energies were referenced to the C (1s) line situated at 284.6 eV. The UV-Vis absorption and Fluorescence spectra were recorded with a Shimadzu UV-2550(300-600nm: xenon lamp, 300W; 600-900nm: tungsten-halogen lamp, 150W) and Fls-800 spectrometers, respectively. Photovoltaic measurement was recorded with a Newport Oriel class AAA solar simulator (model 92250A-1000) equipped with a class A 300 W xenon light source powered by a Newport power supply (model 69907). The power output of the lamp was calibrated to 1 Sun (AM1.5G, 100 mW/cm²) using a certified Si reference cell (VLSI standard, S/N 10510-0031). The current-voltage characteristics of each cell were recorded with a Keithley-2400 digital source meter. Photovoltaic performance was measured using a mask with an aperture area of 0.25cm². The incident photon-to-current efficiency (IPCE) was measured in DC mode with a 1/4 m double monochromator (Crowntech DK242), a multi-meter (Keithley 2000), and two light sources depending on the wavelength range required (300–600 nm: xenon lamp, 300 W; 600–900 nm: S4tungsten-halogen lamp, 150 W). The monochromatic light intensity for IPCE efficiency was calibrated with a reference silicon photodiode.

Symmetric dummy cells were used for the electrochemical impedance spectroscopy (EIS) measurements. The electrochemical impedance spectroscopy measurements were conducted using a computer-controlled electrochemical workstation (CHI660A, Chenhua, Shanghai) under 1 Sun (100 mW/cm²). The measured frequency ranged from 0.1Hz to 1 MHz with a bias potential of -0.75 V, and the 10 mV of AC amplitude. The resultant impedance spectra were analyzed with an appropriate

equivalent circuit by means of Z-view software. The electrochemical station was used for linear sweep Cs^{-2} -V measurements of Mott-schottky curve. The measured potentials vs. the Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale via the Nernst equation^[2]

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + E^{\circ}_{Ag/AgCl}$$

where E_{RHE} is the converted potential vs. RHE, $E_{Ag/AgCl}$ is the experimental potential measured against Ag/AgCl reference electrode, and $E^{\circ}_{Ag/AgCl}$ is the standard potential of Ag/AgCl at 25 °C (0.1976 V), PH=13.09. All the measurements were conducted under ambient conditions.



Scheme S1. A schematic showing the relative band energy levels for charge transfer in the FTO/ZnO/CIS/N719 electrolyte.

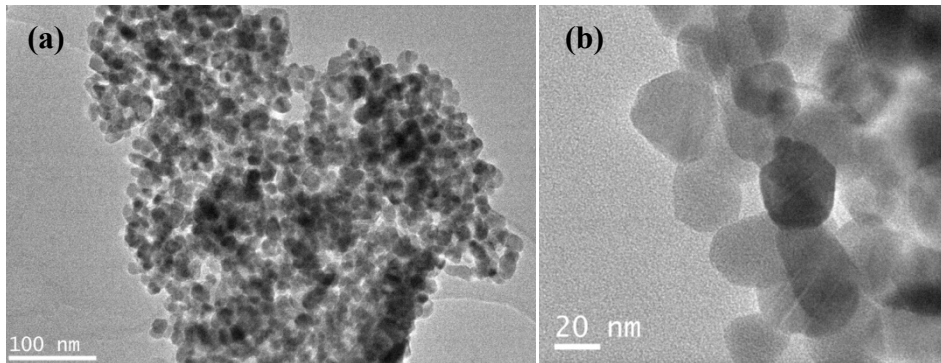


Fig. S1 TEM images (a, b) of the ZnO nanocomposite

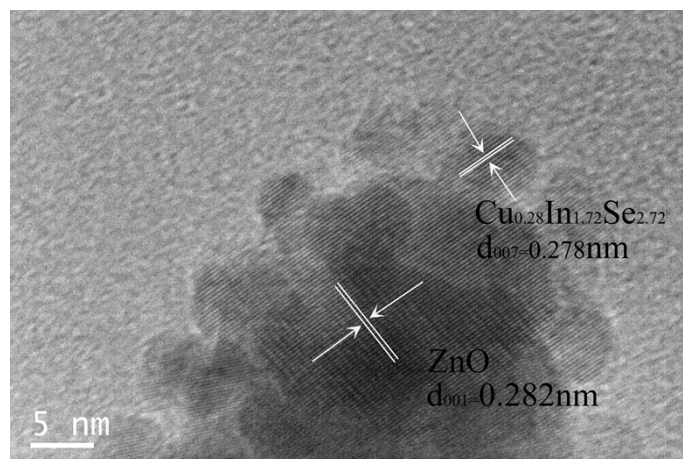


Fig. S2 HRTEM image of the ZnO@CuInSe nanocomposite

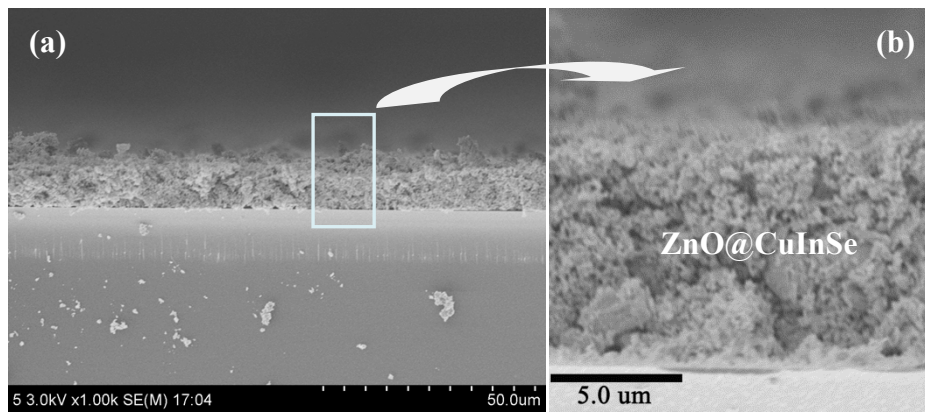


Fig. S3 SEM cross section images (a, b) of ZnO@CuInSe film with the thickness of $\sim 9\mu\text{m}$

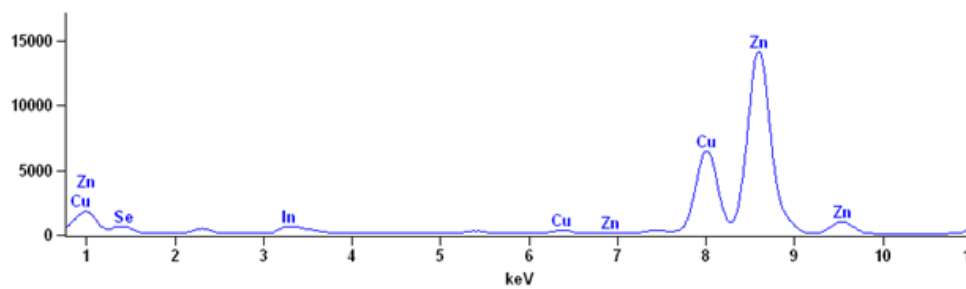


Fig. S4 TEM-EDS spectra of sample ZnO@CIS nanoparticles

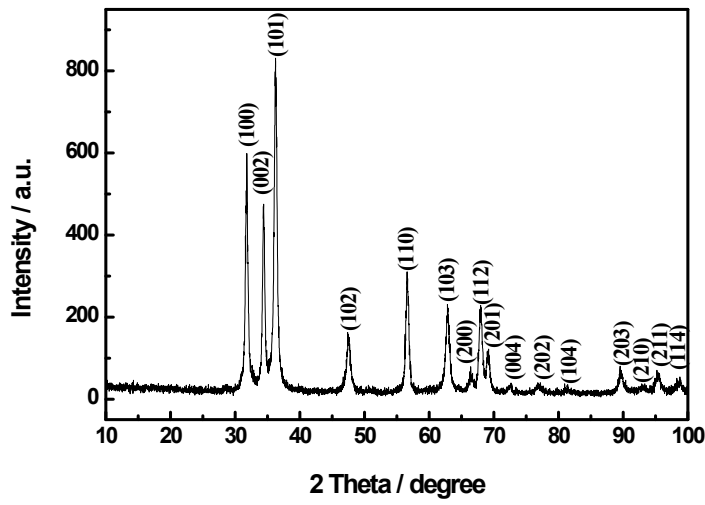


Fig. S5 XRD pattern of ZnO nanoparticles

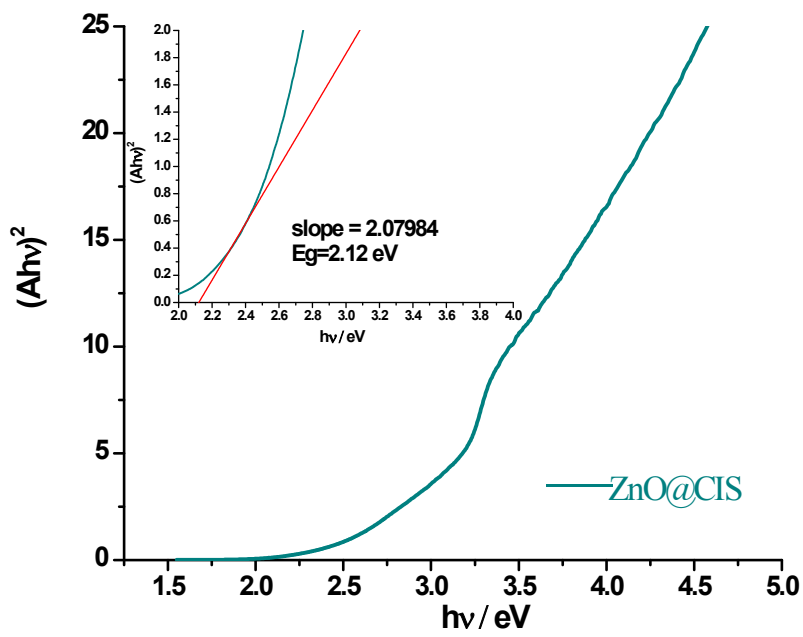


Fig. S6 Plots of $(Ah\nu)^2$ against the photon energy($h\nu$) for ZnO@CIS film

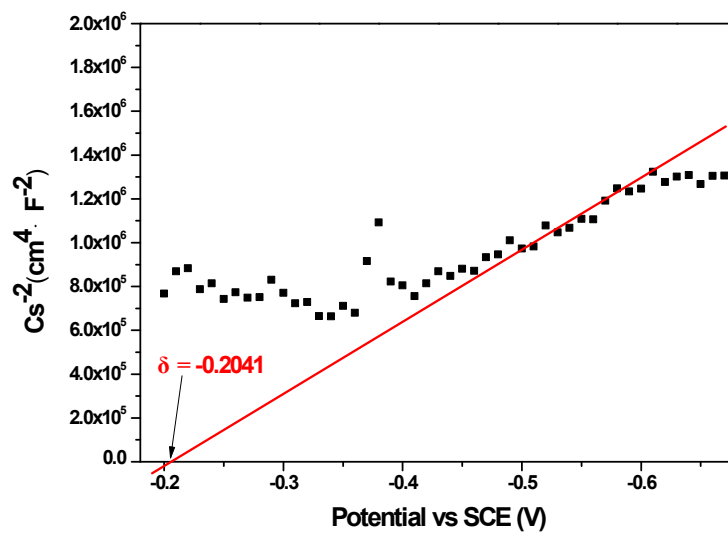


Fig. S7 Mott-schottky curve of $\text{Cu}_{0.28}\text{In}_{1.72}\text{Se}_{2.72}$ QDs

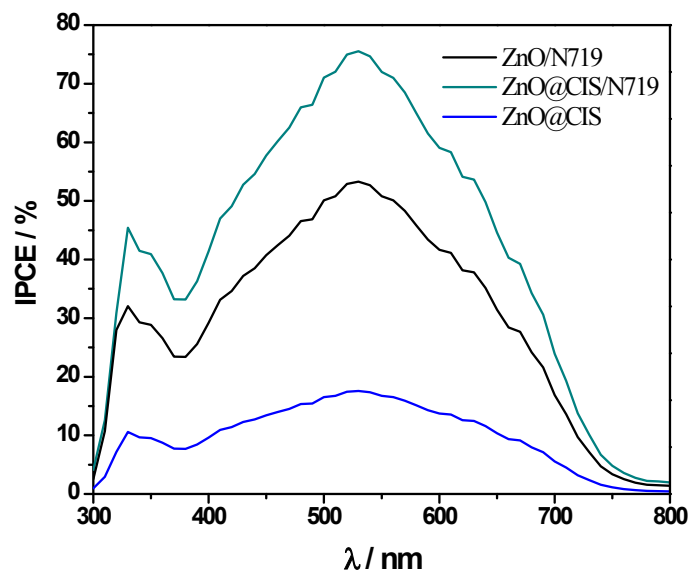


Fig. S8 IPCE spectra of solar cells fabricated with different photo-anodes

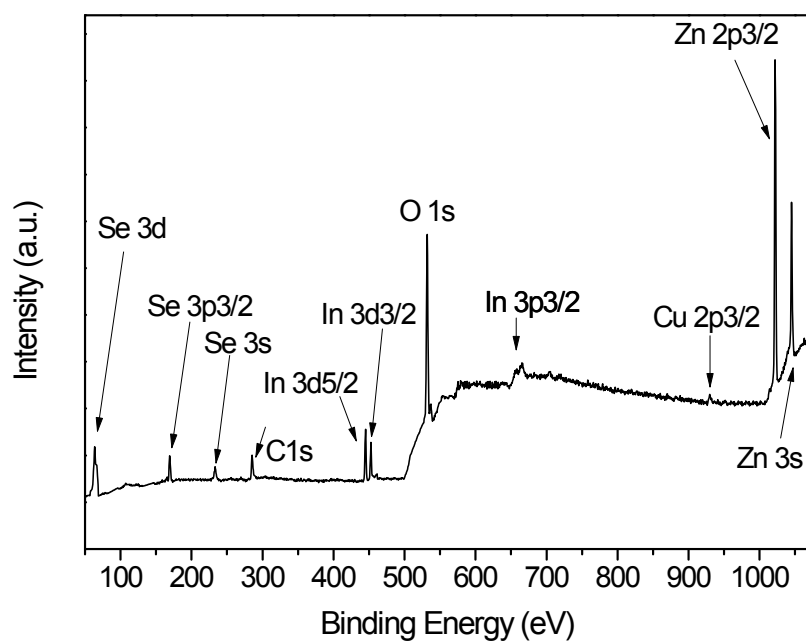


Fig. S9 XPS survey spectra of ZnO@CIS nanocrystals.

Table S1 Structural parameters of samples of ZnO NPs and ZnO@CIS

	BET / $\text{m}^2 \cdot \text{g}^{-1}$	Mesopore Volume / $\text{cm}^3 \cdot \text{g}^{-1}$	Mesopore Size / nm
ZnO NPs	44.33	0.193	46
ZnO@CIS	3.76	0.03	30

Table S2 Photovoltaic Parameters of Different Solar Cells

	V_{OC} / mV	J_{SC} / $\text{mA} \cdot \text{cm}^{-2}$	η / %	FF / %
ZnO/N719	718	11.20	4.23	53
ZnO@CIS	706	3.62	1.54	60
ZnO@CIS/N917	832	15.60	6.66	51

Reference:

1. J. J. Zhao, J. B. Zhang, W. N. Wang, P. Wang, F. Li, D. L. Ren, H. Y. Si, X. G. Sun, F. Q. Ji and Y. Z. Hao, Dalton Trans., 2014, 43, 16588.
2. S. Hoang, S. Guo, N. T. Hahn, A. J. Bard, and C. B. Mullins, Nano Lett. 2012, 12, 26.