Electronic Supplementary Information

Noble metal free counter electrode utilizing Cu₂ZnSnS₄ loaded with

MoS₂ for efficient solar cells based on ZnO nanowires co-sensitized

with CuInS₂–CdSe quantum dots

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S.1. EXPERIMENTAL DETAILS

1. Synthesis of Cu₂ZnSnS₄ (CZTS) microspheres

A simple hydrothermal route was applied to synthesize the CZTS microspheres.¹ Typically, copper acetate monohydrate (0.472 g, 0.04 M), zinc nitrate hexahydrate (0.356 g, 0.02 M), and stannous chloride dihydrate (0.268 g, 0.02 M) were dissolved in a 15 mL ethylenediamine/water (1:9, v/v) mixture, where ethylenediamine performs the role of a chelating agent and a stabilizer. A 0.16 M thiourea aqueous solution (30 mL) was then added drop wise to the above solution. The system was degased under high-vacuum for 30 min to remove oxygen and purged with Ar. The reaction mixture was purged (aerated) further with Ar for 1 h to remove the dissolved oxygen. The reaction mixture was then transferred into a Teflon vessel (100 mL capacity) and sealed inside a stainless steel autoclave, heated to 180 °C in an electronic oven, and maintained for 24 h. In the hydrothermal process, CZTS is formed by the reduction of Cu²⁺ ions to Cu⁺ and oxidation of Sn²⁺ ions to Sn⁴⁺ via oxidation-reduction reactions due to the strong reducing nature of SnCl₂. The autoclave was cooled down to room temperature and the solid was separated by centrifugation at 5000 rpm, washed three times with each of distilled water and ethanol. The powder form of CZTS was finally obtained by drying the sample overnight at 50 °C in an electronic oven. Yield: 51 %.

2. Synthesis of MoS₂ Co-catalyst

Synthesis of MoS_2 co-catalyst was carried out using a reported hydrothermal route with slight modifications.² First, ammonium heptamolybdate (0.736 g, 0.63 mmol) and an excess of thiourea (1.2 g, 15.7 mmol) were dissolved in water (80 mL) in a Teflon vessel. Cetyl trimethylammonium bromide (CTAB; 0.096 g, 0.26 mmol) was then added to the solution as a surfactant and stirred further for 30 min. The Teflon vessel was sealed inside a stainless steel autoclave, heated to 200 °C in an electronic oven, and maintained for 24 h. The autoclave was cooled to room temperature. Black solid product obtained was then separated by centrifugation (5000 rpm), followed by repeated washing with each of distilled water and ethanol for three times to remove the inorganic impurities. Finally, the sample was dried at 50 °C for 8 h in an electronic oven to obtain MoS₂ co-catalyst in powder form. Yield: 62 %.

3. Loading of 1.0 wt % of MoS₂ to CZTS

Loading of 1.0 wt % of MoS₂ to CZTS was carried out hydrothermally by slightly modifying the procedure followed for the synthesis of CZTS. Typically, a precursor solution (80 mL) of CZTS was prepared in a Teflon vessel, which was degased and purged with Ar to remove the dissolved oxygen. A calculated amount (with respect to the yield of CZTS) of presynthesized MoS₂ co-catalyst was then added to this precursor solution. The reaction mixture was sonicated for ~3 h under Ar atmosphere to get a homogeneous distribution of CZTS precursor solution and MoS₂ nanosheets. The Teflon vessel was then sealed in a stainless steel autoclave, heated to 180 °C in an electronic oven, and maintained for 24 h. The black solid product was collected by centrifugation and repeatedly washed for three times with each of distilled water and ethanol. Finally, CZTS–MoS₂ was obtained in powder form by drying overnight at 50 °C in an electronic oven. Yield: 58%.

4. Epitaxial Growth of One-dimensional ZnO Nanowires

Epitaxial growth of one-dimensional ZnO nanowires onto ZnO seeded Fluorine doped tin oxide (FTO) coated glass substrates were carried out following a simple hydrothermal route.^{3,4} Typically, a seed solution of ZnO was prepared by dissolving $Zn(CH_3COO)_2.2H_2O$ (0.2 g) and ethanolamine (55 µL) in 2-methoxyethanol (3.0 mL) and filtering through a 0.2 µm PTFE membrane filter. FTO coated glass substrates were cleaned with soap solution, washed with distilled water, and then treated under an ultrasonic bath (15 min) in acetone and 2-propanol, dried by blowing Ar and finally subjected to ozone treatment for 30 min. ZnO seed solution was spin coated on FTO substrates and heated at ~175 °C (10 min). Spin coating and heating were repeated for one more time to obtain a uniform ZnO seed layer on FTO substrates. ZnO seed layered FTO substrates were then dipped in Zn(NO₃).6H₂O (50 mM) and hexamethylenetetramine (50 mM) aqueous solution (30.0 mL) in Teflon vessels, sealed inside a stainless steel autoclave and then maintained at 90 °C (2 h) in an electronic oven to carry out a uniform growth of ZnO NWs. ZnO NW grown FTO substrates were then rinsed with ethanol and heated at 175 °C (10 min) to remove any traces of water and ethanol.

5. Synthesis of CuInS₂ quantum dots

Readily dispersible CuInS₂ quantum dots (QDs) were synthesized by following a reported protocol with slight modifications.^{5,6} Typically, indium(III) chloride (0.226 g, 1 mmol) and copper(I) iodide (0.190 g, 1 mmol) were added to 1-dodecanethiol (5 mL) in a three-necked round bottom flask. An inert atmosphere was created inside the flask by degassing under high-vacuum for 10 min, followed by purging with Ar. Degasing and purging processes were repeated for two more times. The reaction mixture was heated to 100 °C till a clear yellow coloration appeared and the temperature was slowly raised to 180 °C. The reaction was constantly monitored until the color of the reaction mixture was changed from yellow to orange and finally to dark red, which is indicative of nucleation and growth of CuInS₂. Any further crystal growth of CuInS₂ was instantly resisted at this point by dropping the temperature of reaction to ~40-45 °C using a water bath. The reaction mixture was poured into chloroform and then excess of methanol was added to precipitate the QDs, which were collected by centrifugation at 10000 rpm. The procedure to wash the QDs with chloroform and methanol was repeated further for three times to eliminate the excess organic ligand (1-dodecanthiol). CuInS₂ QDs were finally dispersed in chloroform and stored inside the glove box for further use.

6. Fabrication of ZnO–CuInS₂ photoanode

The loading of CuInS₂ QDs onto ZnO nanowires was performed by electrophoretic deposition (EPD) technique.⁷ To deposit CuInS₂ QDs, a ZnO nanowire grown FTO substrate (ZnO/FTO) and a platinized FTO substrate (Pt/FTO) were vertically fixed at a parallel distance of ~0.5 cm inside a glass cell. Pt/FTO electrodes were prepared by spin coating a 5 mM hexachloroplatinic acid solution in 2-propanol onto cleaned and ozonized FTO substrates, followed by calcination at 450 °C for 15 min. ZnO/FTO and Pt/FTO electrodes were connected (using the alligator clips) to the positive and negative terminals of a Keithley SourceMeter 2420, respectively. The glass cell was filled with a CuInS₂ QD dispersed solution in chloroform and then a bias voltage of ~150 V cm⁻¹ was applied for a couple of min to deposit the QDs. CuInS₂ deposited ZnO photoanodes (hereafter, ZnO–CIS) were taken out, rinsed with ethanol, dried by blowing Ar, and used for the device fabrication.

7. Fabrication of ZnO–CdSe photoanode

To fabricate CdSe QD deposited ZnO nanowire photoanode (hereafter, ZnO–CdSe), CdSe QDs were deposited onto ZnO/FTO using a similar EPD setup as used for the fabrication of ZnO–CIS. In brief, an aqueous solution of 0.02 M cadmium acetate, 0.04 M ethylenediaminetetraacetic acid disodium salt (EDTA) and 0.02 M sodium selenosulfate (Na₂SeSO₃) was used as the electrolyte and a constant bias current of 0.60 mA.cm⁻² was applied between the ZnO/FTO and Pt/FTO electrodes for a period of ~30 min.⁸ The solution of Na₂SeSO₃ was prepared by refluxing a mixture of selenium powder (0.48 g, 6.0 mmol) and sodium sulfite (2.0 g, 15.8 mmol) in distilled water for 3 h.

8. Fabrication of ZnO–CuInS₂–CdSe photoanode

The fabrication of CuInS₂–CdSe co-sensitized ZnO nanowire based photoanode (hereafter, ZnO–CIS–CdSe) was also performed using EPD method in two steps. First, CuInS₂ QDs were deposited under an applied bias of ~150 V.cm⁻¹ to fabricate the ZnO–CIS photoanode. In the second step, ZnO–CIS electrode was connected to the positive terminal of the power supply and CdSe QDs were deposited under an applied bias current of ~0.60 mA.cm⁻² against a Pt/FTO electrode (connected to the negative terminal).

9. Fabrication of counter electrodes

To fabricate the Pt-free counter electrodes, bare Cu_2ZnSnS_4 and Cu_2ZnSnS_4 –MoS₂ composite powders were separately dispersed in ethanol under an ultrasonic bath for a period of ~30 min. In the meantime, FTO coated glass substrates were cleaned with soap solution, washed with distilled water, and treated under ultrasonic bath for 15 min in acetone followed by 2-propanol. FTO substrates were then subjected to ozone treatment for a period of 15 min. The dispersed solutions of Cu_2ZnSnS_4 and Cu_2ZnSnS_4 –MoS₂ were spin coated onto these FTO substrates at 500–1000 rpm. FTO substrates were then calcined at 300 °C for 10 min under a sulfur atmosphere and used as such for the device fabrication.

10. Device Fabrication

To construct the QDSCs, photoanodes and respective CEs were sandwiched using an easy-melt thermoplastic sealant (thickness ~50 μ m). A drop of S^{2–}/S_n^{2–} electrolyte solution was then injected to each of the cells through the pre-drilled holes on CEs by a vacuum capillary filling method. The cells were sealed to avoid any leakage of the electrolyte. The aqueous electrolyte solution (S^{2–}/S_n^{2–}) was prepared by dissolving 2.0 M sulfur powder and 2.0 M sodium sulfite in distilled water. *Please note*: No methanol was added to the electrolyte solution.

S.2. MATERIALS AND DEVICE CHARACTERIZATION

Powder X-ray diffraction (XRD) patterns were recorded using Bruker D8 Advance X-ray diffractometer with Cu–K_{α} (λ = 1.54 Å) operating at a voltage of 40 kV and a current of 40 kA. A scan rate of 0.1–0.2 °/s was fixed to record the XRD patterns of the samples within a 20 scan range of 10-80°. Ultraviolet-visible (UV-Vis) absorption spectra of the solid powder and thin film samples were recorded by diffused reflectance mode using a JASCO Model V-650 spectrophotometer having an additional 150 mm integrating sphere Model JASCO ILV-724 against BaSO₄ as an internal reference. Steady-state photoluminescence (PL) spectra were recorded using a Horiba-Jobin Yvon Fluoromax 4P spectrophotometer. Laser micro Raman spectroscopic analysis was carried out in a Horiba LabRAM HR spectrometer equipped with a He-Ne laser having an excitation wavelength of 514.5 nm. Brunauer-Emmett-Teller (BET) surface area analysis of the CEs were performed using a Quantachrome surface area and pore size distribution analyzer instrument model Autosorb-IQ MP. Surface morphology of powdered samples and fabricated photoanodes were probed by field-emission scanning electron microscopy (FESEM) using a Zeiss (Gemini) instrument operating at a variable voltage of 3-15 kV. Energydispersive X-ray spectroscopy (EDS) mapping elemental analysis of the CE materials were performed by FESEM instrument. Transmission electron microscopy (TEM) analysis of the powder samples were carried out using JEOL JEM 2100 microscope with an operating voltage of 200 kV. Photovoltaic performance of the fabricated QDSCs were investigated from the measured current density-voltage $(J_{sc}-V)$ plots using a Keithley Sourcemeter series 2420 at 100 mW.cm⁻² under AM 1.5 G simulated solar illumination. A 450 W xenon lamp was equipped to a Newport

Oriel Sol3A solar simulator to illuminate the cells with an artificial solar spectrum. The incident light intensity of the lamp was calibrated using a standard Si photovoltaic cell provided by Newport Corp. Incident photon-to-current conversion efficiency (IPCE) of the cells were recorded using a Newport Oriel IQE-200 instrument fitted with a 250 W quartz tungsten halogen (QTH) lamp as the light source. The light illuminated from the QTH lamp was allowed to pass through a chopper and Cornerstone monochromator prior to fall onto the cells. The obtained signal was amplified by a Merlin lock-in amplifier radiometry unit and then detected by the internal detector. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a CH instrument model CHI600E.



Figure S1. Steady state photoluminescence spectra of hydrothermally grown 1D ZnO nanowires on FTO coated glass substrate showing the less prominent defect emission peak ~475–575 nm at an excitation wavelength of 410 nm.



Figure S2. Powder X-ray diffraction (XRD) patterns of (a) ZnO–CIS, (b) ZnO–CdSe, and (c) ZnO–CIS–CdSe photoanodes showing the retention of diffraction peaks for ZnO nanowires (orange circles), CuInS₂ quantum dots (black triangles), and CdSe quantum dots (red squares).



Figure S3. Comparison of the UV–vis absorption spectra for the MoS₂ nanosheets in solid state (black line) and in 1-methyl-2-pyrrolidone (NMP, red line). The four distinct peaks are defined as the following. *Peak A*: direct transition at the *K* point of the Brillouin zone, *Peak B*: $K_4 \rightarrow K_5$ transition at the *K* point (spin–orbit spilling), *Peak C*: $K_1 \rightarrow K_5$ transition at the *K* point (spin–orbit spilling), *Peak C*: $K_1 \rightarrow K_5$ transition at the *K* point (spin–orbit spilling), *Peak D*: direct transition from the deep valence band to the conduction band.



Figure S4. Energy-dispersive X-ray spectroscopy (EDS) maps of (a) Cu_2ZnSnS_4 microspheres (CZTS) and (b) 1.0 wt % of MoS₂ co-catalyst loaded Cu_2ZnSnS_4 microspheres (CZTS–MoS₂). Please note: EDS mapping was performed to overcome the experimentally observed elemental overlap issue between Mo and S atoms.



Figure S5. Field-emission scanning electron microscopy (FESEM) images of (a) ZnO–CIS, (b) ZnO–CdSe, and (c) ZnO–CIS–CdSe photoanodes fabricated at prolonged times periods for the CuInS₂ and CdSe quantum dot deposition.



Figure S6. (a) Transmission electron microscopy (TEM) and (b) high-resolution TEM (HRTEM) images of MoS_2 nanosheets showing an interplanar *d*-spacing of ~0.66 nm. (c) TEM image of hydrothermally grown one-dimensional ZnO nanowires. (d) HRTEM image and (d) inverse fast Fourier transform (IFFT) of the HRTEM image of CuInS₂ quantum dots showing an interplanar *d*-spacing of ~0.34 nm. Inset to trace (e) shows the SAED pattern of CuInS₂ quantum dots. (f) HRTEM image of CdSe quantum dots showing an interplanar *d*-spacing of ~0.35 nm.

S.3. CALCULATIONS FOR THE ESTIMATION OF BAND POSITIONS

Xu and Schoonen have reported a simple method to estimate the absolute band positions of the conduction and valence bands for semiconductors from the absolute electronegativity (χ) values.⁹ The top of the valence band (E_{VB}) at the semiconductor/electrolyte interface may be predicted from the χ value of the semiconductor, using eq (1). In general, the value of χ of a multi-atomic compound (e.g., M_aX_b) may be defined as the geometric mean of the χ values of the constituent atoms.¹⁰ The corresponding χ values for each atom can be derived from their ionization potential (IP) and electron affinity (EA) values, using eq (2) and Mulliken electronegativity scale.¹¹

$$E_{VB} = -(\chi_M^a \chi_X^b)^{\frac{1}{a+b}} - \frac{1}{2} \times E_g + 0.059(pH_{zpc} - pH) + E^e$$
(1)

$$\chi_M = \frac{1}{2} \times (IP_M + EA_M) \tag{2}$$

where χ_M and χ_X are the absolute electronegativities of M and X atoms, respectively, E^e is the energy of free electrons on the hydrogen scale (-4.5 eV), and E_g is the band gap of the material. Considering the point of zero charge, the eq (1) can be simplified to eq (3). The values of E_{VB} and E_{CB} can be then calculated, using eqs (3) and (4).

$$E_{VB} = \chi + \frac{1}{2} \times E_g - E^e \tag{3}$$

$$E_{CB} = E_{VB} - E_g \tag{4}$$

In the case of MoS₂, the IP and EA values for Mo atom are 7.10 eV and 0.746 eV, respectively, while the same for S atom are 10.36 eV and 2.08 eV, respectively.^{12,13} From the IP and EA values, the absolute electronegativities of Mo and S are found to be 3.9 eV and 6.22 eV, respectively, using eq (3). This further gives a χ value of 5.32 eV for MoS₂. The tauc plot from the UV–vis spectrum estimated a band gap for MoS₂ to be \approx 1.59 eV. The corresponding values of E_{VB} and E_{CB} of MoS₂ are calculated to be –5.9 eV and –4.3 eV, respectively, with respect to the vacuum level. Similarly, E_{VB} and E_{CB} for Cu₂ZnSnS₄ are found to be –5.1 eV and –3.4 eV, respectively.

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