

## **Electronic Supporting Information (ESI†)**

### **Highly efficient and stable quantum dot-sensitized solar cells based on Mn-doped CuS counter electrode**

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### **Experimental section:**

#### **Materials**

Cadmium acetate dehydrate [Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O], manganese(II) acetate tetrahydrate [Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O], zinc acetate dehydrate [Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O], sodium sulfide (Na<sub>2</sub>S), sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>), sulfur (S), selenium (Se), potassium chloride (KCl), copper(II) sulfate pentahydrate [CuSO<sub>4</sub>·5H<sub>2</sub>O], sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>), urea (CH<sub>4</sub>N<sub>2</sub>O), and TiO<sub>2</sub> paste (Ti-

Nanoxide HT/SP) were supplied by Solaronix. All other chemicals were commercially available and of analytical grade.

### **Preparation of CuS, Mn-CuS and Pt counter electrodes:**

The copper sulfide (CuS) nanostructures were prepared by a facile chemical bath deposition (CBD) method. All chemicals used for the preparation of the CuS and Mn-CuS thin films were purchased from sigma-Aldrich and used without any further purification. In the experiment, prior to deposition, the FTO samples were cleaned ultrasonically with acetone, ethanol, and DI water for 10 min each. The cleaned substrates were dried with N<sub>2</sub> gas. The CuS growth solution was prepared using cationic and anionic precursors of 0.1 M CuSO<sub>4</sub>·5H<sub>2</sub>O and 0.4 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, which act as sources of Cu<sup>2+</sup> and S<sup>2-</sup> ions, respectively. 0.4 M CH<sub>4</sub>N<sub>2</sub>O was used as a reagent for depositing CuS thin films. To introduce Mn<sup>2+</sup> into the CuS electrode, appropriate molar percentages of 5%, 10%, and 20% (5 mM, 10 mM, and 20 mM) of Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0-20%) were blended with CuSO<sub>4</sub>·5H<sub>2</sub>O. The experimental molar ratios of CuSO<sub>4</sub>·5H<sub>2</sub>O to Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O are 20:1, 10:1, and 5:1, respectively. The substrate was then immersed horizontally into the growth solutions of CuS and Mn-CuS in a hot air oven at 65 °C for 2 hours. Finally, the CuS and Mn-CuS coated films (active area of ~0.7 cm<sup>2</sup>) were washed several times with DI water and ethanol. The films were denoted as CuS, 5%Mn-CuS, 10%Mn-CuS, and 20%Mn-CuS, respectively, and used for further characterization.

The cleaned FTO glass substrate was coated with Pt paste (Pt-catalyst T/SP, Solaronix) with an active area of ~ 0.7 cm<sup>2</sup> using the doctor blade method and sintered at 450 °C for 10 min.

### **Fabrication of TiO<sub>2</sub> Photoanodes:**

The preparation of the photoanode is discussed in the elsewhere.<sup>1</sup> Fluorine-doped tin oxide (FTO, 13 Ω sq<sup>-2</sup>, Hartford Glass Co. Inc.) glass was used as the substrates for the photoanode and counter electrode. The TiO<sub>2</sub> photoanodes were fabricated on ultrasonically well-cleaned FTO substrate via the doctor blade method. 20-nm-sized anatase TiO<sub>2</sub> particles (Ti-Nanoxide HT/SP, Solaronix) were first deposited on FTO substrates with an active area of 0.27 cm<sup>2</sup>, followed by sintering at 450 °C for 30 min. A thickness of 7.5 μm was obtained after solvent evaporation. The as-prepared TiO<sub>2</sub> electrodes were used for further sensitization with CdS and CdSe QDs.

### **Fabrication of CdS/CdSe QDs:**

The SILAR method was used to assemble QDs on the TiO<sub>2</sub> photoelectrode. In brief, for CdS QDs, the TiO<sub>2</sub> film was dipped into an aqueous solution containing 0.1 M Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O for 5 min to allow Cd<sup>2+</sup> to adsorb onto the TiO<sub>2</sub>. It was then rinsed with DI water and dipped for another 5 min into an aqueous solution of 0.1 M Na<sub>2</sub>S, where the pre-adsorbed Cd<sup>2+</sup> reacts with S<sup>2-</sup> to form the desired CdS. The film was rinsed again with DI water and dried with a drier. This two-step process is called one CBD cycle. Repeat this process for 5 cycles.

For CdSe QDs, sodium selenosulphate (Na<sub>2</sub>SeSO<sub>3</sub>) was used as an Se source for SILAR. An Na<sub>2</sub>SeSO<sub>3</sub> aqueous solution was prepared by refluxing Se (0.2 M) in an aqueous solution of Na<sub>2</sub>SO<sub>3</sub> (0.4 M) at 120 °C for 4 h. The as-prepared CdS electrodes were then dipped into an aqueous solution of 0.1 M Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O for 5 min at room temperature, and rinsed with

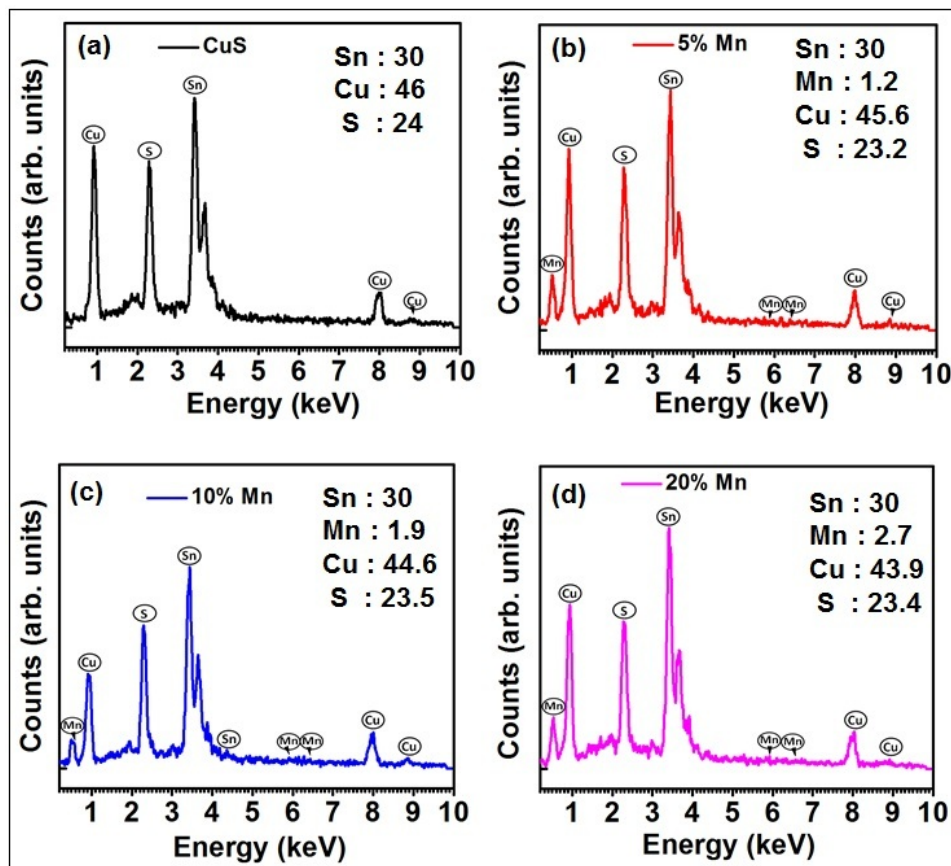
DI water. Then, samples were dipped into an aqueous solution of  $\text{Na}_2\text{SeSO}_3$  for 5 min at 50 °C and rinsed again with DI water. Repeat this process for 8 cycles.

Finally, all of the electrodes were coated with a ZnS passivation layer using 2 cycles, which decreases the rate of recombination and assists in electron transport. The electrodes were alternately dipped into an aqueous solution of 0.1 M  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  for 5 min and a solution of 0.1 M  $\text{Na}_2\text{S}$  for 5 min. They were then rinsed with DI water and dried with a drier.

### **Characterizations:**

The surface morphology, thickness, and elemental compositions of the electrodes were investigated using a field emission scanning electron microscope (FE-SEM, S-2400, Hitachi) equipped with energy-dispersive X-ray spectroscopy (EDX) operated at 15 kV. The crystalline nature of the Mn-doped and undoped counter electrodes was analyzed by X-ray diffraction (XRD, D/Max-2400, Rigaku) using a  $\text{Cu K}\alpha$  source operated at 40 kV and 30 mA in the  $2\theta$  range of 20-80°. The UV-visible absorption spectra of photoelectrodes were recorded using an OPTIZEN 3220UV spectrophotometer. The current-voltage characteristics of the QDSSCs were studied under one-sun illumination (AM 1.5G, 100  $\text{mW}/\text{cm}^2$ ) using an ABET Technologies (USA) solar simulator with an irradiance uniformity of  $\pm 3\%$ . Electrochemical impedance spectroscopy (EIS) was conducted on symmetrical cells using a BioLogic potentiostat/galvanostat/EIS analyzer (SP-150, France) under dark conditions (measured under 0.6 V bias potential in the frequency range of 100-500 kHz with the applied AC amplitude set to 10 mV). During irradiation and characterization, the cells were covered with a black mask fitted around the active area ( $0.7 \text{ cm}^2$ ) of the cell. Tafel polarization (scan rate of  $10 \text{ mVs}^{-1}$ ) was also performed for the symmetrical dummy cells of CuS, Mn-CuS and Pt CEs in dark conditions. Cyclic voltammetry were performed at a scan rate of  $100 \text{ mV s}^{-1}$  with a symmetrical dummy cell

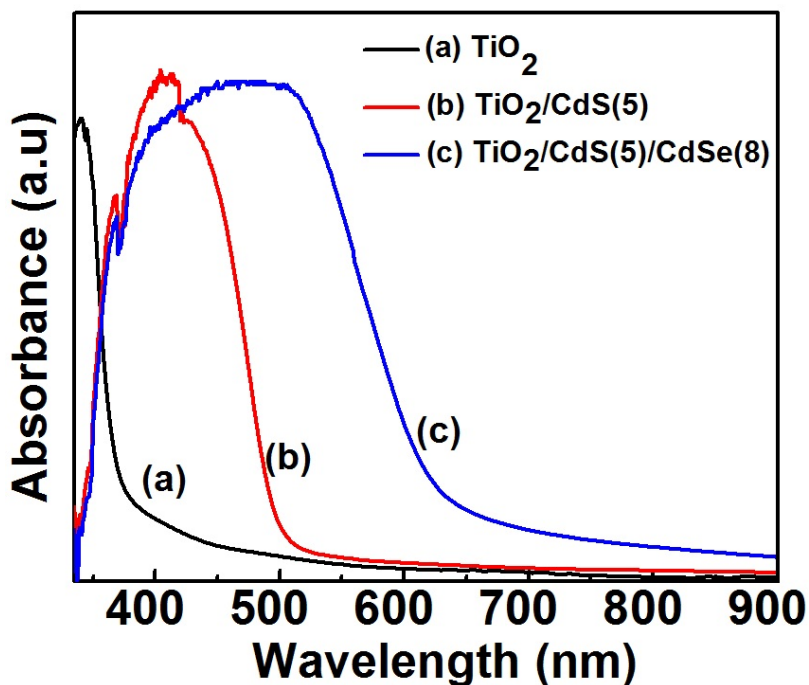
fabricated with two identical CEs in dark conditions using a BioLogic potentiostat/galvanostat/EIS analyzer (SP-150, France).



**Fig. S1. EDX result of Mn-doped and undoped CuS thin film on FTO substrate: (a) CuS, (b) 5% Mn-CuS, (c) 10% Mn-CuS, and (d) 20% Mn-CuS.**

EDX analysis was used to find the elemental composition of the as-prepared samples. Fig. S1 shows the EDX analysis of the CuS and Mn-doped CuS electrodes. Due to the low thickness of the films, Sn was also detected in the FTO glass. The atomic percentages of Mn:Cu:S in the samples of CuS, 5% Mn-CuS, 10% Mn-CuS, and 20% Mn-CuS were found to be (0:46:24),

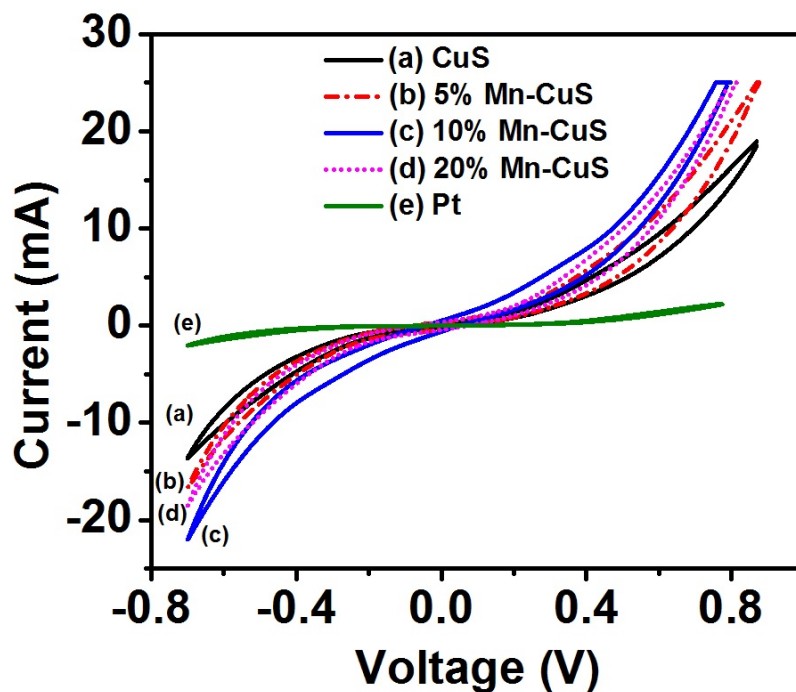
(1.2:45.6:23.2), (1.9:44.6:23.5), and (2.7:43.9:23.4), respectively. From the result, the atomic percentage of Cu depends on the appropriate amount of Mn content, and the sulfur content was almost similar in all cases. With increasing Mn content from 5% to 10%, the atomic percentage of Mn significantly increased (1.2% to 1.9%), and the atomic percentage of Cu was reduced (45.6% to 44.6%). The largest percentage of Mn (2.7%) was observed for the 20% Mn-CuS film. The atomic percentage of Mn in CuS is depending on the doping of the Mn content in the CuS. Most importantly, when the CE was replaced with a Mn-doped CE, the cell performance of the QDSSCs was further improved in regard to conversion efficiency. The presence of  $Mn^{2+}$  in the film was successfully confirmed by EDX analysis.



**Fig. S2:** UV-vis absorption spectra of a bare TiO<sub>2</sub> film and TiO<sub>2</sub> films sensitized by various QDs.

The variation of UV-vis spectra with SILAR cycles obtained in this work are similar to that shown in our previous paper.<sup>2</sup> From the Fig. S2, the absorption range for TiO<sub>2</sub>/CdS(5)/CdSe(8)

quantum dot sensitized extends up to 653 nm, much longer than those of bare  $\text{TiO}_2$  (386 nm) and  $\text{TiO}_2/\text{CdS}(5)$  (507 nm). Obviously, the broader light absorption ranges extending to 653 nm for  $\text{TiO}_2/\text{CdS}/\text{CdSe}$  QDs make them promising sensitizers in QDSSCs.



**Fig. S3** Cyclic voltammograms (CV) of the bare CuS, Mn-doped CuS and Pt symmetric dummy cells in dark condition

To investigate the electrocatalytic activities of the prepared counter electrodes, cyclic voltammetry (CV) was performed at a scan rate of  $100 \text{ mV s}^{-1}$  in a CuS, Mn-doped CuS and Pt symmetric dummy cells in dark condition, and the corresponding plots are shown in Fig. S3. The high current peak indicates active electrocatalytic reaction of the electrode for the  $\text{S}^{2-}/\text{S}_x^{2-}$  redox couples in the polysulfide electrolyte. The current peak of the 10% Mn-CuS CE is higher than those of the bare CuS, 5% Mn-CuS, 20% Mn-CuS and Pt CEs; therefore, 10% Mn-CuS CE exhibits the highest catalytic activity for the reduction of the polysulfide electrolyte. The Pt CE

shows the lowest catalytic activity, and CuS, 5% Mn-CuS and 20% Mn-CuS CEs show moderate catalytic activity.

**References:**

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2. H.J. Kim, S.W. Kim, C.V.V.M. Gopi, S.K. Kim, S.S. Rao, M.S. Jeong, *J. Power Sources*, 2014, **268**, 163.