

Electronic Supplementary Information

Highly efficient core shell CuInS₂/Mn doped CdS quantum dots sensitized solar cells

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Synthesis and characterization of CuInS₂ quantum dots

The CuInS₂ quantum dots (CIS QDs) were synthesized by a mercaptoacetic acid (MAA) assisted aqueous method developed by our group with slight modification.¹ Briefly, Cu(CH₃COO)₂·2H₂O (0.2 mmol) and InCl₃·4H₂O (0.3 mmol) were dissolved in 150 mL N₂-saturated deionized water with constant magnetic stirring at room temperature. Afterwards, MAA (0.170 mL) was incorporated into this solution and the pH value of the mixture solution was adjusted to 4.0 by 1 mol/L NaOH solution. After stirring for 10 min, Na₂S (0.5 mmol) was injected swiftly into the above solution while rapidly stirring and kept at room temperature for 2 hours to complete CIS core growth. During this process, the color of the solution rapidly changed from colourless to dark brown. Subsequently, CdCl₂·2.5H₂O (0.1 mmol) was added into the obtained colloidal CIS QDs solution while rapidly stirring and kept at room temperature for 1 hour. Finally the resultant solution was concentrated to 20 mL via rotary evaporation for further use.

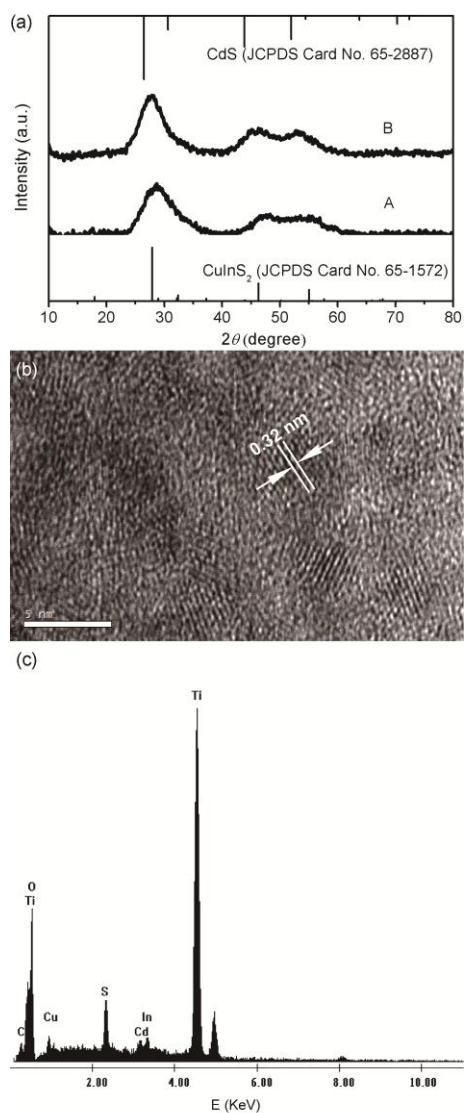


Fig. S1(a) XRD patterns of CIS QDs (A) without CdCl_2 treatment and (B) with CdCl_2 treatment, (b) typical HRTEM image of CIS QDs with CdCl_2 treatment, (c) EDS spectrum of CuInS_2 quantum dots treated with CdCl_2 . The corresponding atomic ratio for Cu, In, Cd, and S is 1:0.92:0.51:3.37.

The crystal structure of as-synthesized CIS QDs was characterized by powder X-ray diffraction (XRD). The XRD pattern of the obtained CIS QDs is illustrated in Fig.S1 (a). The three broadened diffraction peaks located at 28° , 47° and 55° can be properly assigned to (112), (220) and (116) planes of chalcopyrite tetragonal structure of CIS (JCPDS Card No. 65-1572). From Fig. S1(a), it can be clearly seen that the diffraction patterns of CIS QDs with CdCl_2 treatment slightly shift to lower angles, which indicate the incorporation of Cd. However, no typical diffraction peaks of CdS

are observed, suggesting the crystal structure is predominantly due to the CIS QDs. Energy dispersive X-ray (EDX) analysis confirms the existence of Cu, In, S, and Cd. The atomic ratio of Cu:In:Cd:S is found to be 1:0.92:0.51:3.37 (Fig. S1(c)). The morphology of CdCl₂ treated CIS QDs was also investigated by high resolution transmission electron microscope (HRTEM). Fig. S1(b) confirms that the average particle diameter of CIS QDs is about 4 nm, which is consistent with the value calculated by the Debye-Scherrer equation using XRD data. The well resolved lattice fringe of 0.32 nm corresponds to the (112) plane of CIS QDs.

Fabrication of TiO₂ photoanodes

The double layered TiO₂ photoanodes were fabricated on well-cleaned FTO glass via doctor blade technique. A 15 μm-thickness transparent layer of 20 nm sized anatase TiO₂ particles was first deposited on FTO substrates, followed by sintering at 450 °C for 30 min. and 5 μm-thickness light scattering layer of 300 nm sized rutile TiO₂ particles was further coated, subsequently annealed at 450 °C for 30 min. Finally, the obtained TiO₂ electrodes were treated with an aqueous solution of 40 mM TiCl₄ at 70 °C for 40 min, followed by a sintering process at 500 °C for 30 min. The as-prepared TiO₂ electrodes were used for further sensitization with CIS, CdS, Mn-CdS, CIS/CdS, and CIS/Mn-CdS QDs.

Synthesis and characterization of CuS counter electrodes

In a typical procedure, 3 mmol copper chloride dehydrate (CuCl₂·2H₂O) and 3 mmol thioacetamide as precursor were dissolved in 30 ml deionized water respectively. Then, the two solutions were mixed and stirred vigorously for 5 minutes, and the mixture was transferred into a 80ml Teflon-lined stainless steel autoclave and heated in an electric oven at 160 °C for 6 hours. After cooling, the precipitates were separated by centrifugation and washed with ethanol several times to remove any possible residual impurities. Finally, the obtained product was dried in a vacuum oven at 70 °C for 6 hours.

Fig. S2(a) shows the XRD pattern of the as-prepared CuS powers. All the

diffraction peaks are in good agreement with the standard data for hexagonal phase CuS structure (JCPDS Card No. 06-0464). The composition and the ratio 1:1 of Cu:S were determined by EDX (Fig. S2(b)). The low and high magnification SEM images of 5 μm -thickness CuS film on FTO, which consists of particles of 50-1000 nm in size, are illustrated in Fig. S2(c) and (d).

The counter electrode were prepared by mixing the resulting CuS powder (90 wt%) and polyvinylidene (PVDF 10 wt%) dissolved in 1-methyl-2-pyrrolidinone with constant stirring for 12 hours to form a homogeneous slurry. The well-mixed slurry was then coated on FTO by doctor blade method and dried in an electric oven at 80 $^{\circ}\text{C}$ for 12 hours for later use.

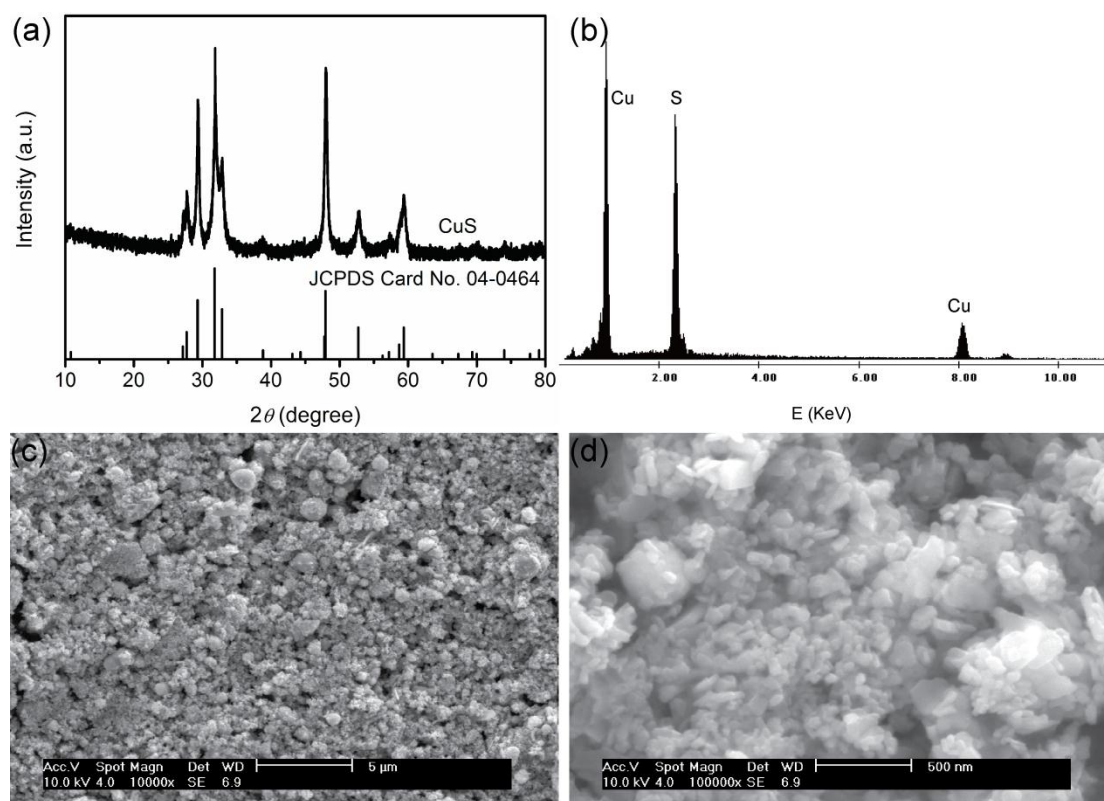


Fig. S2(a) X-ray diffraction pattern of as prepared CuS, (b) EDS spectrum of CuS, the corresponding atomic ratio of Cu and S is 1:1, (c) low resolution scanning electron microscopy images of CuS films on FTO, (d) high resolution scanning electron microscopy images of CuS films on FTO.

Fig. S3 shows the photographs of different QDs sensitized TiO_2 electrodes with different colors. Compared with the TiO_2/CdS electrode, the color changes from light yellow to orange with the doping of Mn in TiO_2/CdS electrode, which indicates the existence of Mn. This can be further verified by the Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis. The actual Mn concentration in CdS is found to be 1.24%. A red-shift is observed for Mn-CdS compared to CdS, which also suggests that the Mn^{2+} have been doped into the center of CdS rather than MnS bounded to the surface of CdS. The formation of MnS would lead to a blue shift in UV-vis absorption because of the larger bandgap energy of 3.0 eV. It is noticeable that the color of TiO_2/CIS QDs electrode turns black with the combination of CdS or Mn-CdS coating, which is consistent with the optical absorption properties of TiO_2/CIS QDs/CdS and TiO_2/CIS QDs/Mn-CdS in our work.

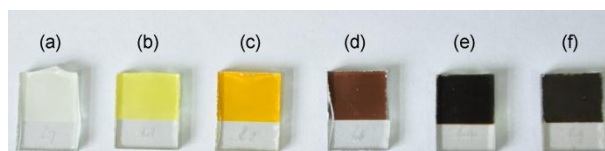


Fig. S3 Photographs of different QDs sensitized TiO_2 electrodes: (a) the bare TiO_2 film, (b) the TiO_2/CdS QDs film, (c) the $\text{TiO}_2/\text{Mn-CdS}$ QDs film, (d) the $\text{TiO}_2/\text{CuInS}_2$ QDs film, (e) the $\text{TiO}_2/\text{CuInS}_2$ QDs/CdS film, (f) the $\text{TiO}_2/\text{CuInS}_2$ QDs/Mn-CdS film.

Stability of CIS, CIS/CdS and CIS/Mn-CdS QSCs

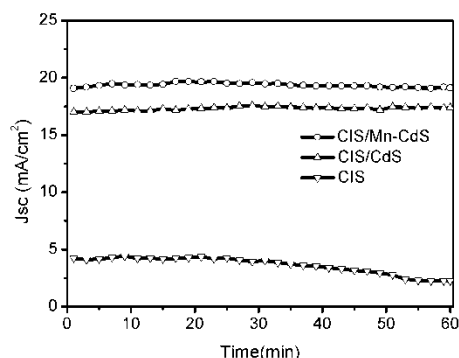


Fig. S4 Photocurrent stability of CIS, CIS/CdS and CIS/Mn-CdS QSCs under continuous illumination of $100 \text{ mW}/\text{cm}^2$.

Stability of the devices is evaluated by measuring J_{sc} with respect to time under continuous illumination of 100 mW/cm^2 . As shown in Fig. S4, for CIS/CdS and CIS/Mn-CdS based QSCs, a steady photocurrent is observed. While for the CIS based QSCs, the photocurrent decreases quickly after 30 min irradiation. Strong corrosion of the polysulfide electrolyte on the CIS QDs likely leads to the reduction in photocurrent during long period operation. Therefore, it can be concluded that the in situ growth of Mn-CdS shell on the core of CIS QDs is a promising strategy to enhance the photostability of CIS QDs.

Reference

1. X. Hu, Q. X. Zhang, X. M. Huang, D. M. Li, Y. H. Luo, Q. B. Meng, *J. Mater. Chem.*, 2011, **21**, 15903.