A structure of CdS/Cu_xS quantum dots sensitized solar cells

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This work introduces a type of CdS/Cu_xS quantum dots (QDs) as sensitizers in quantum dot sensitized solar cells by *in-situ* cationic exchange reaction method where CdS photoanode is directly immersed in CuCl₂ methanol solution to replace Cd²⁺ by Cu²⁺. The p-type Cu_xS layer on the surface of the CdS QDs can be considered as hole transport material, which not only enhances the light harvesting of photoanode but also boosts the charge separation after photo-excitation. Therefore, both the electron collection efficiency and power conversion efficiency of the solar cell are improved from 80% to 92% and from 1.21% to 2.78%, respectively. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4952435>]

Various types of quantum dot solar cells (QDSC) have been intensively studied ever since Vogel and Weller¹ reported PbS and CdS QDSCs. The advantages of quantum dots (QDs) as light harvesters in solar cells include the size-tunable band-gaps,² high extinction coefficient,³ and possible hot carrier injection.⁴ In particular, the multiple exciton generation (MEG) of QDs⁵ can suppress Shockley-Queisser limit^{6,7} and rise the theoretical maximum power conversion efficiency (PCE) from 31% up to 44%. However, the state of art chalcogenide QDs based QDSCs (e.g., CdSe,⁸ CdS,⁹ PbS,¹⁰ CdSe/CdS,¹¹ CuInS₂,¹² CuInSe,¹³ and CdSe_{1-x}Te_x¹⁴ QDs) shows the highest PCE up to 9.48% (Ref. 15) still significantly lower than that of conventional Si solar cells and thin film solar cells. To date, many efforts have been made to optimize the configuration of the QDSC towards expected PCE, such as the adapted polysulfide electrolyte,¹⁶ new type counter electrode,¹⁷ different morphology of mesoporous photoanode films,¹⁸ and QDs engineering by absorption extension, element doping, and surface modification.^{19–21}

In nanometer-sized QDs, the surface to interior atom ratio is high. The surface atoms have lower coordination number than the corresponding volume atoms leading to high probability that they act as the electrons or holes traps.²² In addition to such surface defects, the surface facets and chemistry of QDs may also affect the conformal coating and adhesion of QDs. Many efforts have been focused on the surface modification of QDs to enhance the efficiency of QDSCs. CdSe QDs can be modified by coating them with ZnS shell for improving the fluorescence quantum yield of QDs²³ and performance of QDSCs.²⁴ For QDSCs, ZnS coating layer can overcome the recombination losses leading to the higher photocurrents.²⁵ Recently, Pan *et al.*²⁶ achieved effective surface passivation of the ternary CuInS₂ (CIS) QDs using ZnS to form core/shell CIS/ZnS (CIS-Z) QDs. The QDSCs based on CIS-Z QDs show a very high PCE of 7.04% and a certified efficiency of 6.66%. Zhao *et al.*²⁷ boosted the efficiency of QDSCs beyond 8% by introducing a novel sequential inorganic ZnS/SiO₂ double layer to reduce

recombination processes. Zhang *et al.*²⁸ increased the stability and prolonged hot carrier lifetime in QDSCs using the halide treatment. Clearly, the interface modification is recognized as an effective approach for improving the performance of QDSC.

Here, a p-type semiconductor interfacial layer of Cu_xS was deposited on the surface of CdS QDs layer using an *in-situ* cationic-exchange method as shown in Scheme 1. CdS QDs were first directly grown on the mesoporous TiO₂ film using successive ionic layer absorption and reaction (SILAR) method.²⁹ Thereafter, CdS photoanodes were immersed in 1.0 mM copper chloride solution for 3 s and then rinsed with methanol and dried with air. The Cd²⁺ ions of CdS QDs were replaced by Cu²⁺ ions to form Cu_xS shell. (For the optimization of the device fabrication, see Figure S1 of supplementary material.³⁰) The cationic exchange reaction takes place at the surface of CdS QDs. As a result, a portion of surface Cd atoms is replaced by Cu atoms. The energy-dispersive X-ray spectroscopy (EDX) was conducted to monitor the elemental compositions of the CdS and CdS/Cu_xS QD sensitized TiO₂ photoanodes (see Figure S1 of supplementary material³⁰). The amount of the Cu element in the CdS/Cu_xS sensitized photoanodes increases as copper precursor solution concentration increases. The amount of the Cd element in the CdS/Cu_xS sensitized photoanodes films decreases accordingly. The X-ray diffraction patterns (XRD) of the CdS sensitized photoanodes with and without Cu_xS modification (see Figure S2 of supplementary material³⁰) further confirm the presence of Cu_xS in photoanodes. Additional diffraction peaks at $2\theta = 27.6^\circ$, 36.4° , 41.3° , and 55.2° assigned to copper sulphide are observed in CdS/Cu_xS sensitized photoanode compared with the neat CdS photoanode. However, the peaks match neither CuS phase nor Cu₂S phase. Therefore, the reaction product is called Cu_xS in this work.

Scheme 1(b) illustrates the role of p-type semiconductor Cu_xS layer in the functioning of CdS QDSCs. Upon illumination of light, CdS/Cu_xS QDs can absorb photon to excite electron-hole pairs. The hole transfer to electrolyte is mediated by the Cu_xS layer, while electron injection can only

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SCHEME 1. (a) Schematic illustration of *in-situ* cationic exchange from CdS to Cu_xS and (b) Cu_xS as a hole transport layer for charge separation from CdS QDs, (c) Energy band structure of TiO₂/CdS/Cu₂S/CuS,³¹ and (d) TEM images of TiO₂ films loaded with CdS/Cu_xS.

proceed from CdS directly to TiO₂. In this scenario, geminate recombination at the interface between QDs and electrolyte is expected to be blocked by the Cu_xS layer. Scheme 1(c) shows the values of the conduction bands (CB) of TiO₂/CdS/Cu₂S/CuS. The values of the valence bands (CB) for copper sulfide would be like that Cu₂S < Cu_xS < CuS. Because of the suited band gap structure between TiO₂/CdS and Cu_xS, Cu_xS would be a good hole mediator. Under the operating conditions, electron-hole pairs are rapidly separated, and the holes are reduced by redox couples ($\text{S}^{2-}/\text{S}_n^{2-}$) through Cu_xS. The layer suppresses recombination of electrons with holes in the electrolyte.³² Scheme 1(d) displays the TEM image of the TiO₂ films loaded with CdS/Cu_xS, showing the existence of Cu_xS on the surface of CdS that is

1–3 nm in thickness (the yellow dash lines). Combined with XRD analysis, the copper sulfide is similar to Cu_{1.96}S. The 10 nm-sized CdS QDs may be attributed to the fact that the small QDs became aggregated. In this work, UV-visible absorbance, photoluminescence (PL), electrochemical spectra, and photo-electric measurements were carried out to prove the effect of Cu_xS layer on the enhancement of charge separation and electron collection in QDSCs.

Absorption spectra of CdS and CdS/Cu_xS sensitized TiO₂ photoanodes are shown in Figure 1(a). The absorbance of CdS/Cu_xS sensitized photoanode is much higher than that of the neat CdS indicating better capability of photon absorption. In addition, the absorption onset of photoanode is redshift by introducing Cu_xS layer on the surface of CdS

FIG. 1. (a) UV-vis absorption spectra, (inset shows the pictures of the CdS and CdS/Cu_xS sensitized photoanodes), (b) Tauc-plots showing the optical band-gap of two samples, (c) light harvesting efficiency (LHE), and (d) Photoluminescence (PL) of the CdS sensitized photoanodes with and without Cu_xS surface layer (Excitation wavelength 325 nm).

FIG. 2. (a) Electron transport time and lifetime and (b) effective charge collection efficiency of the CdS based QDSCs with and without Cu_xS-surface layer.

QDs (see Figure 1(b)). Cu_xS is a narrow band-gap (1.2 eV) p-type semiconductor,³³ with a wide absorption range (~up to 850 nm). The inset pictures display that the colour of CdS/Cu_xS sensitized photoanode is much darker than that of the CdS sensitized photoanode. We can also evaluate the optical band gap by the Tauc plots $((Ah\nu)^{1/2} \sim h\nu)$ of the absorption spectra as shown in Figure 1(b), where A is the absorbance, h is the Plank's constant, and ν is the photon frequency. The E_g (band-gap) can then be calculated³⁴ to be 2.19 eV for CdS/Cu_xS, which is lower than the E_g (2.22 eV) of CdS. Such narrowing of E_g can be attributed to the lowering band-gap of Cu_xS (1.2 eV),^{33,35,36} compared with that of CdS. The light harvesting efficiency (LHE) of CdS/Cu_xS is also observed to be higher than QDSCs without Cu_xS layer as shown in Figure 1(c), which is consistent with the absorption spectra.

The role of Cu_xS layer in charge separation process could be studied by the steady-state photoluminescence (PL). As shown in Figure 1(d), PL intensity of the photoanode is reduced by adding Cu_xS layer on the surface of CdS QDs. One possible reason for such PL quenching would be the enhanced hole injection through Cu_xS layer which diminishes the radiative recombination between electrons and holes in the initial excited states. Other possibility such as interfacial trapping can be excluded here, as the decreased PL band width indicates the reduction of interfacial trapping state concentration if the Cu_xS layer is present in QDs.^{37,38} Moreover, the charge carrier dynamics and solar cell performance studies in the following part do confirm the improvement of the charge separation by Cu_xS layer coating in our system.

The electron transit and charge collection processes in the QDSC with and without Cu_xS modification were further characterized by intensity modulated photocurrent

spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS) as shown in Figure 2(a). From the figure, we can compare the dependence of the time constants, the transit time (τ_d) and electron lifetime (τ_r), which can be measured by following equations:³⁴

$$\tau_d = \frac{1}{2} \pi f_d, \quad (1)$$

$$\tau_r = \frac{1}{2} \pi f_r, \quad (2)$$

where f_d and f_r are the frequency of the minimum of the semicircle, i.e., the frequency of the lowest imaginary component in the IMPS and IMVS plots, respectively. As shown in Figure 2(a), the CdS/Cu_xS based QDSC shows longer τ_r and shorter τ_d than those of CdS counterpart, which corresponds to longer electron life time and faster electron transit, respectively. These results manifest the more efficient charge separation and transit facilitated by Cu_xS layer, consistent with previous conclusion from PL measurement. The charge-collection efficiency (η_{cc}) can also be calculated by τ_d and τ_r as^{39,40}

$$\eta_{cc} = 1 - \frac{\tau_d}{\tau_r}. \quad (3)$$

The η_{cc} of CdS/Cu_xS solar cell is 92%, which is higher than that of CdS solar cell (80%).

The enhanced charge separation by Cu_xS modification does result in better solar cell performance as illustrated below. Figure 3(a) shows incident photon-to-current conversion efficiency (IPCE) spectra of the solar cells. The maximum IPCE value of the CdS/Cu_xS based solar cell (65%) is higher than that of the CdS based device (50%). IPCE value can be expressed as multiplication of LHE, η_{cc} , and the charge injection efficiency (ϕ_{inj})⁴¹

FIG. 3. (a) Incident photon to charge carrier efficiency (IPCE) curves and (b) J - V curves of QDSCs with and without Cu_xS modification measured under AM 1.5 G, at 1 sun light intensity.

TABLE I. Photovoltaic properties obtained from the J - V curves. The standard deviation of the properties is based on the data of four cells in parallel.

Samples	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η (%)
CdS	0.53	3.95	0.58	1.21 ± 0.13
CdS/Cu _x S	0.56	8.53	0.59	2.78 ± 0.22

$$IPCE = LHE \times \phi_{inj} \times \eta_{cc}. \quad (4)$$

It is clear that the enhanced LHE and η_{cc} by Cu_xS modification account for the improvement of IPCE in real device, while ϕ_{inj} is probably not affected.

Figure 3(b) shows the photocurrent density-voltage (J - V) curves of the QDSCs under simulated solar illumination (100 mW/cm², AM 1.5 G). The photovoltaic properties of the devices are summarized in Table I. Under the illumination, the properties of CdS/Cu_xS sensitized solar cells are 0.56 V of open-circuit voltage (V_{oc}), 8.53 mA/cm² of short current density (J_{sc}), and 59% of fill factor (FF). All these photovoltaic parameters are improved compared to the neat CdS sensitized solar cell. The improvement of J_{sc} is related to the IPCE spectrum,^{42,43} which is caused by the enhancement of light absorption and η_{cc} . The increase of V_{oc} ⁴⁴ and FF⁴⁵ is attributed to the reduced surface charge recombination and prolonged electron lifetime. As a result, the PCE of CdS/Cu_xS based device is more than two times higher (from 1.21% to 2.78%), compared with the CdS based device.

In summary, *in situ* cationic exchange method was introduced to prepare a Cu_xS layer on the surface of CdS QDs to improve the electron collection efficiency of QDSCs. The layer of Cu_xS is considered as hole transporter to boost the hole transfer from CdS QDs to electrolyte with corresponding reduction of the charge recombination and increase of the electron collection efficiency. In addition, Cu_xS has a narrower band-gap (1.2 eV) that improves the light absorbance and extends the absorption range. As a result, both the electron collection efficiency and PCE of the solar cell are increased from 80% to 92% and from 1.21% to 2.78%, respectively.

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³⁰See supplementary material at <http://dx.doi.org/10.1063/1.4952435> for the details of materials, device fabrication and characterization.

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