

# CdSe quantum dots as co-sensitizers of organic dyes in solar cells for red-shifted light harvesting

S.-Q. FAN\*, R.-J. CAO, Y.-X. XI, M. GAO, M.-D. WANG, D.-H. KIM<sup>a</sup>, C.-W. KIM<sup>a</sup>, J.-J. KO<sup>a</sup>

*Department of Applied Chemistry, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, P.R.China*

*<sup>a</sup>Department of Chemistry, Korea University, Jochiwon, Seochang 208, Chungnam 339-700, Republic of Korea*

We first demonstrated an application of CdSe quantum dots (QDs) as co-sensitizers of organic dyes in solar cells with a polysulfide electrolyte for obtaining red-shifted light-harvesting. Firstly, the loading of QDs on the co-sensitized electrodes was found to have little influence on the electron transport properties, which mainly depended on the organic dye adsorption. IPCE spectra of the co-sensitized solar cells extended from 570 nm, the organic dye (JK24 and JK28) absorption threshold, to 650 nm due to the adsorption of 4.2 nm diameter CdSe QDs. Secondly, the photovoltaic performance of co-sensitized solar cells correlated significantly with the electrode architecture. With a spatially-organized electrode, on which QDs were mainly located on the back side of TiO<sub>2</sub> film and organic dye molecules covered on the front side, the co-sensitized solar cells can maintain IPCE values as high as those obtained from the singly dye sensitized solar cells at short wavelengths of the organic dye photoresponsive region. As the result of the IPCE extension to longer wavelengths and retention at short wavelengths, the co-sensitized solar cells with QDs presented dramatically improved photocurrent and power conversion efficiency. The open-circuit voltage of co-sensitized solar cells was also improved due to an enhanced retardation of charge recombination. Although the photovoltaic performance in our system is still inferior to the best dye-sensitized solar cell system, the success in utilizing QDs as co-sensitizers open up an alternative way to the design of next-generation solar cells.

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*Keywords:* CdSe; Quantum dot; co-sensitizer; solar cell

## 1. Introduction

Dye-sensitized solar cells (DSSCs) are considered to be a promising alternative to conventional solid-state junction solar cells due to their low-cost, environmental friendly and high power conversion efficiency [1-2]. Ruthenium complexes have reached the best efficiencies of ~11% so far, but they show poor response in near infrared (IR) region. Metal-free organic dyes, having high molar extinction coefficient, are also employed as the sensitizers [3-4], with which a high incident photon-to-current conversion efficiency (IPCE) of up to 90% has been obtained [3]. However, the sharp, narrow absorption bands of organic dyes impair their panchromatic light-harvesting capacity. For obtaining wide photoresponse, several groups have successfully developed co-sensitized solar cells employing blue and red absorbing organic dyes homogeneously loading on TiO<sub>2</sub> electrodes [5-6] or spatially separated by a layer of Al<sub>2</sub>O<sub>3</sub> [7]. But their photo-response at 700-1000 nm was still inappreciable.

Quantum-dot (QD) chalcogenide semiconductors such as CdS[8-13], PbS[14], CdSe[15-20], and PbSe[21] can also serve as sensitizers because they can transfer electrons to TiO<sub>2</sub> under visible light excitation.

Development of QD-sensitized solar cells has become of particular interest because of two advantages. Firstly, these QDs open new way to utilize hot electrons or generate multiple electron-hole pairs with one single photon through the impact ionization effect [22]. Secondly, QD band energy and the photo-response can be tuned by simply varying the QD size [23-24]. For CdSe QDs, the absorption band extends to more than 600 nm when the size is up to 3.0 nm [24]. Most importantly, some QDs such as PbS have shown an impressive photo-response in the near IR region [25]. The present problem existed in QD-sensitized solar cell is its low IPCE level of no more than 60% [16].

For DSSCs, their photo-response in near IR region should be further improved to obtain more efficient devices for their practical applications. Because of the challenging task in developing panchromatic organic dyes, a combination of near IR adsorbing QDs with these organic dyes might be a practical solution. In this study, we made a first attempt toward this purpose. Our preliminary strategy employs red-absorbing CdSe QDs as co-sensitizers of blue-absorbing organic dyes, as depicted in Fig. 1 (a). Organic dye molecules and CdSe QDs adsorb on one TiO<sub>2</sub> film homogeneously by employing a sequential adsorption process: firstly

dipping in QD solutions and subsequently dipping in dye solutions. The obtained homogenous electrode is denoted as  $\text{TiO}_2/(\text{Dye-QDs})$  (Fig. 1a). According to previous work on two organic dyes sensitized solar cells, a problem might occur for the  $\text{TiO}_2/(\text{Dye-QDs})$  electrode is that CdSe QDs, whose adsorption spectra overlap with organic dyes at short wavelengths, can share the incident photons in this wavelength region, resulting in a decrease in IPCE values due to the low efficiency of QDs in photo-to-electron conversion. In order to avoid this possibility, we meanwhile designed a distinct electrode on which CdSe QDs and organic dye molecules are spatially organized. As illustrated in Fig. 1 (b), for the

fabrication of this electrode, QDs are firstly loaded mainly on the back side of the film (farther from FTO glass) by controlling  $\text{TiO}_2$  film architecture or dipping process. With this asymmetry  $\text{TiO}_2/\text{QDs}$  electrode, organic dye molecules cover on the front side after a long time dipping in dye solutions. The final electrodes are termed as  $\text{TiO}_2/\text{Dye}/\text{QDs}$ . We expect, under illumination, shorter-wavelength photons are only absorbed by dye molecules on the front side to get high IPCE values, while the longer-wavelength photons can transmit to the back side and be adsorbed by QDs for extending photo-responsive region.

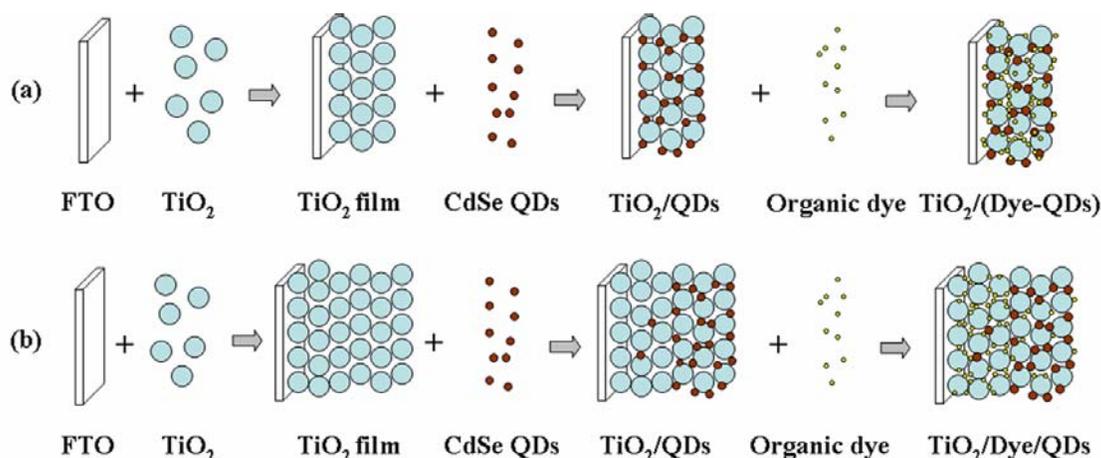


Fig. 1. Scheme of the fabrication of homogenous  $\text{TiO}_2/(\text{Dye-QDs})$  electrode (a) and spatially organized  $\text{TiO}_2/\text{Dye}/\text{QDs}$  electrode (b).

In this study, we employed 4.2 nm diameter CdSe QDs and two organic dyes, 2-cyano-3-(5-(9-(9,9-dimethylfluoren-2-yl)-carbazol-6-yl)thiophen-2-yl)acrylic acid (JK24) and 2-cyano-3-(5-(9-(4-(2,2-diphenylvinyl)phenyl)carbazol-6-yl)thiophen-2-yl)acrylic acid (JK28), whose molecule structures were shown in Fig. 2, to prepare co-sensitized  $\text{TiO}_2/(\text{Dye-QDs})$  and  $\text{TiO}_2/\text{Dye}/\text{QDs}$  electrodes, and investigate the electron transport properties and the photovoltaic performance of their solar cells.

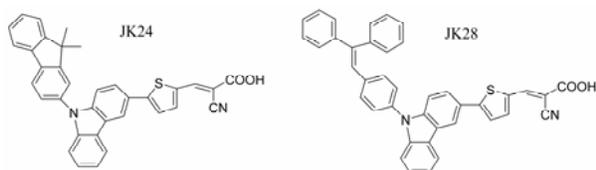


Fig. 2. Molecular structure for JK24 and JK28 dyes.

Two kinds of electrodes were prepared by controlling the  $\text{TiO}_2$  film thickness, as described detailedly below. As we desired, with the spatially organized  $\text{TiO}_2/\text{Dye}/\text{QDs}$  electrodes, the solar cells not only presented a wider IPCE spectrum than singly dye solar cells due to the QDs

absorption, but also maintained high IPCE values at short wavelengths by avoiding the QDs sharing photons in this wavelength region.

## 2. Experimental section

### 2.1 Preparation of CdSe QDs

A one-pot synthesis was used to create colloidal CdSe QDs [15]. In particular, 0.05 g (~0.39 mmol) of cadmium oxide (CdO, Sigma-Aldrich, 99.99+%) and 0.30 g (~1.1 mmol) of tetradecylphosphonic acid (TDPA, Alfa, 98%) were mixed with 4.0 g of trioctylphosphine oxide (TOPO, Sigma-Aldrich, 99%). The mixture was heated under nitrogen at 320 °C to coordinate Cd ions with the phosphonic acid. Upon completion, the temperature was lowered to 270 °C, and 5 mL (0.25 M) TOPSe, which was prepared by dissolving selenium (Aldrich, 99.5+%) in trioctylphosphine (TOP, Aldrich, 90%), was injected into the mixture. This caused the solution temperature to drop to ~240-250 °C. Subsequent growth was carried out at 270 °C. On reaching the desired QD size, as determined through UV/visible spectroscopy, the temperature was lowered, stopping the reaction.

## 2.2 Fabrication of TiO<sub>2</sub> electrodes and solar cells

TiO<sub>2</sub> films with thickness of 1-15 μm were fabricated by doctor blade printing TiO<sub>2</sub> paste (Solaronix, 13 nm anatase) on FTO (Pilkington, 8 Ω) glass plates, as reported elsewhere [2]. After thermal-annealed at 500 °C for 30 min, a second scattering layer of 4 μm thickness was coated using a paste with 400 nm diameter TiO<sub>2</sub> particles (CCIC, PST-400C) and then subject to another annealing process. Finally, the electrodes were immersed in 40 mM TiCl<sub>4</sub> aqueous solution at 70 °C for 30 minutes and sintered again.

When the electrodes were cooled to 80 °C, they were left in the CdSe QDs solution of toluene for 24 hours to load the QDs. Subsequently, they were soaked in organic dye solution in ethanol to obtain co-sensitized electrodes. Dye solutions employed in this study contained 0.3 mM dye (JK24 or JK28) and 10 mM 3a,7a-dihydroxy-5b-cholic acid (Cheno). The JK24 and JK28 dyes were synthesized according to the procedures described elsewhere [26]. For reference, TiO<sub>2</sub> electrodes loaded only with organic dye or with QDs were also prepared and were denoted as TiO<sub>2</sub>/JK24(or JK28) or TiO<sub>2</sub>/QDs.

The sensitized electrodes were employed to assemble sandwich-typed solar cells with Pt loaded counter electrodes using a 50-μm-thick hot-melt ionomer film (Surlyn) as a spacer between the electrodes. The electrolyte was polysulfide containing 0.5 M Na<sub>2</sub>S and 2 M S in methanol/H<sub>2</sub>O (7:3 in volume) [12].

## 2.3 Optical and photovoltaic measurements

The absorption spectra for CdSe QDs in toluene and on 5 μm-thick TiO<sub>2</sub> electrodes (without scattering layers) were recorded on a Shimadzu UV3101 UV-visible spectrometer using bare TiO<sub>2</sub> films as references. The dye adsorption amount was investigated by measuring the UV-visible spectrum of the dye-ethanol solution after desorbing from electrodes with 0.01 M tetrabutylammonium hydroxide in ethanol. The J-V curves of solar cells were measured under illumination (100mW/cm<sup>2</sup>) using 1000 W xenon light source, whose power of an AM 1.5 Oriel solar simulator was calibrated by using KG5 filtered Si reference solar cell. The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were measured on an IPCE measuring system (PV measurements). The ac impedance measurements were carried out under illumination (100 mW/cm<sup>2</sup>) using an impedance analyzer (Parstat 2273, Princeton).

## 3. Results and discussion

### 3.1 Structure and light absorption of co-sensitized TiO<sub>2</sub> electrodes

The absorption spectrum of CdSe QDs employed in

this study is shown in Fig. 3. By comparing the exciton transition at 590 nm to the absorption curve reported by Peng and coworkers [24], we can identify the particle size is 4.2 nm.

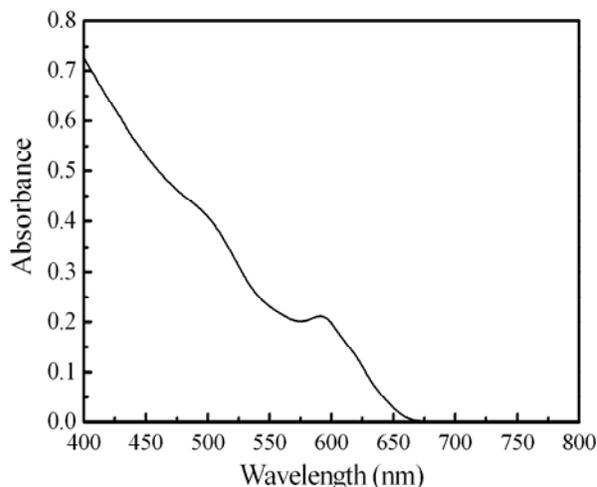


Fig. 3. Absorption spectrum of CdSe QDs in toluene.

TiO<sub>2</sub> films employed in this study have a mean pore size of ~15 nm and a porosity of ~60% [27]. Organic dye molecules like JK24 and JK28 can penetrate into 20-μm-thick such mesoporous films and adsorb on the TiO<sub>2</sub> surface in near homogeneity in the lateral direction (perpendicular to FTO surface) [28]. While for 4.2 nm diameter CdSe QDs, it is still unknown whether they can transport into the thick films. We measured the absorbance of different thickness TiO<sub>2</sub>/QDs electrodes at 590 nm (not shown). It is found that the absorbance was proportional to the electrode thickness in the range of no more than 5 μm. As thickness increased, the absorbance reached a constant value at 10 μm. It means that on the 5-μm-thick TiO<sub>2</sub>/QDs electrode, QDs had a homogeneous lateral distribution. While on 10-μm-thick electrodes, QDs distribution was not uniform in the lateral direction. They were located mainly on the back side of the film, and little can penetrate into the front side, where TiO<sub>2</sub> surface maintained uncolored as observed by naked eyes. Upon these findings, 5-μm-thick TiO<sub>2</sub> films were employed to fabricate homogenous TiO<sub>2</sub>/(Dye-QDs) electrodes (scheme 1a) and 10-μm-thick TiO<sub>2</sub> films were used to prepare spatially organized TiO<sub>2</sub>/Dye/QDs electrodes. It is estimated that for the 10-μm-thick TiO<sub>2</sub>/Dye/QDs electrode, the front 5 μm thickness (near FTO glass) was adsorbed mainly by organic dyes, and the back 5 μm thickness had a saturated QDs load amount. Additionally, the dye adsorption amount on 5 μm TiO<sub>2</sub> films was determined to be 9.8×10<sup>-8</sup> and 11.9×10<sup>-8</sup> mol/cm<sup>2</sup> for the TiO<sub>2</sub>/Dye and TiO<sub>2</sub>/Dye/QDs electrodes, respectively. It suggests that the dye molecules can be also adsorbed on the QD surface.

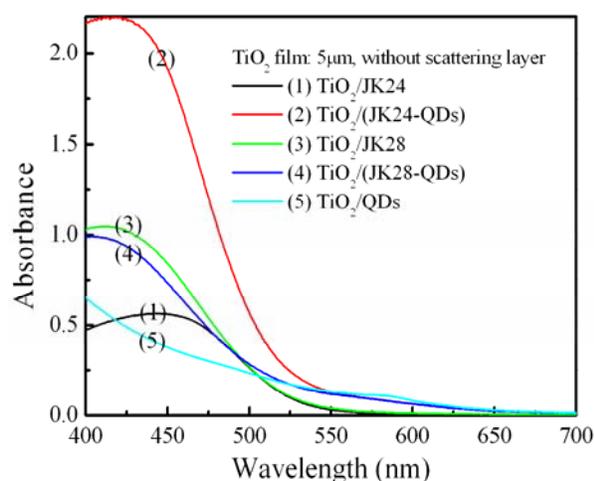


Fig. 4. Absorption spectra of  $\text{TiO}_2/\text{JK24}$ ,  $\text{TiO}_2/(\text{JK24-QDs})$ ,  $\text{TiO}_2/\text{JK28}$ ,  $\text{TiO}_2/(\text{JK28-QDs})$  and  $\text{TiO}_2/\text{QDs}$  electrodes employing 5- $\mu\text{m}$ -thick  $\text{TiO}_2$  films without scattering layers.

Fig. 4 compares absorption spectra of singly sensitizer electrodes of  $\text{TiO}_2/\text{QDs}$  and  $\text{TiO}_2/\text{Dye}$ , and co-sensitized  $\text{TiO}_2/(\text{Dye-QDs})$  electrodes.  $\text{TiO}_2/\text{QDs}$  electrode presented a wide visible absorption at 400-670 nm, which was similar to the solution absorption (Fig. 3). Both organic dyes, JK24 and JK28, had narrower but stronger visible absorptions below 550 nm. The absorption spectra of co-sensitized  $\text{TiO}_2/(\text{Dye-QDs})$  electrodes were evident to be the combination of those from QDs and organic dyes, suggesting the co-existence of these two kinds of sensitizers on the electrodes.

### 3.2 Electron transport properties

The adsorption of sensitizers is proved to affect electron transport properties of the  $\text{TiO}_2$  electrodes [29]. With different sensitizers, the electrodes possess diverse electron transport properties and thus result in different photovoltaic performance for the solar cells. Electrochemical impedance spectroscopy has been employed to investigate electronic process in dye-sensitized solar cells [30]. In order to examine the effect of QDs adsorption on the transport properties of the electrodes, we measured the impedance spectra of the  $\text{TiO}_2/\text{QDs}$ ,  $\text{TiO}_2/\text{JK24}$  and  $\text{TiO}_2/(\text{JK24-QDs})$  solar cells under illumination ( $100\text{mW}/\text{cm}^2$ ) at their open-circuit voltage. The Nyquist plots of the impedance data are shown in Fig.5. Bisquert and co-workers [31-32] have proposed a diffusion-recombination model to analyze the impedance data obtained from dye-sensitized nanocrystalline  $\text{TiO}_2$  solar cells,

$$Z = \left( \frac{R_t R_r}{1 + i\omega / \omega_k} \right)^{\frac{1}{2}} \coth \left[ (\omega_r / \omega_d)^{\frac{1}{2}} (1 + i\omega / \omega_r)^{\frac{1}{2}} \right] \quad (1)$$

where,  $Z$ ,  $R_t$ ,  $R_r$ , and  $\omega$  represent the impedance, electron transport resistance on  $\text{TiO}_2$ , charge-recombination resistance and angular frequency, respectively, while  $\omega_d = D_e/L^2$  ( $D_e$  is electron diffusion coefficient on  $\text{TiO}_2$  and  $L$  is  $\text{TiO}_2$  film thickness). By fitting the impedance data in the medium frequency semi-circle region shown in Fig. 5 to the equation (1), the parameter  $D_e$  can be determined. The  $D_e$  values for the  $\text{TiO}_2/\text{QDs}$ ,  $\text{TiO}_2/\text{JK24}$ , and  $\text{TiO}_2/(\text{JK24-QDs})$  electrodes were estimated to be  $2.4 \times 10^{-5} \text{ cm}^2/\text{s}$ ,  $9.4 \times 10^{-5} \text{ cm}^2/\text{s}$ ,  $8.6 \times 10^{-5} \text{ cm}^2/\text{s}$ , respectively.

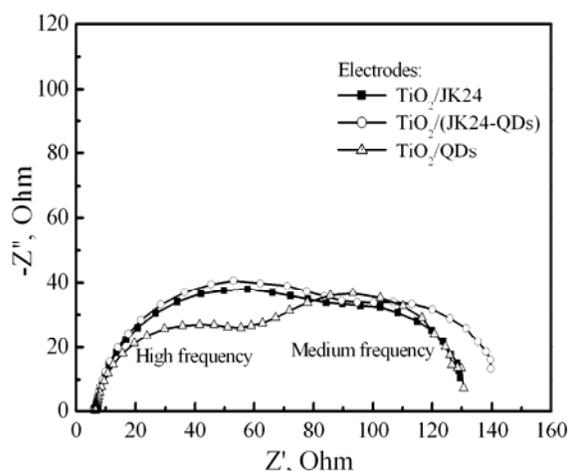


Fig. 5. Electrochemical impedance spectra measured under illumination ( $100\text{mW}/\text{cm}^2$ ) and at the open-circuit voltage for the  $\text{TiO}_2/\text{JK24}$ ,  $\text{TiO}_2/(\text{JK24-QDs})$ , and  $\text{TiO}_2/\text{QDs}$  solar cells.

It is clear that the  $D_e$  of QD-sensitized electrode was only one quarter of that obtained from organic dye-sensitized electrode. As proved in the literature [33], protons in organic dye molecules can couple on  $\text{TiO}_2$  surface during adsorption and facilitate electron diffusion on the electrode. While for CdSe QDs, lack of protons let them have no contribution to the electron diffusion. But when comparing  $\text{TiO}_2/(\text{JK24-QDs})$  electrode with  $\text{TiO}_2/\text{JK24}$  electrode, their  $D_e$  were almost the same. It demonstrated that the  $D_e$  of the co-sensitized electrodes mainly depended on the organic dye, and the QD's coadsorbing on the electrode had no impairment on the electron transport.

### 3.3 Photovoltaic performance

The photovoltaic response of the solar cells to monochromatic light irradiation was analyzed in terms of IPCE. The IPCE action spectra for  $\text{TiO}_2/\text{QDs}$ ,  $\text{TiO}_2/\text{Dye}$ ,  $\text{TiO}_2/\text{Dye/QDs}$  and  $\text{TiO}_2/(\text{Dye-QDs})$  are presented in Fig. 6. Fig. 6 (a) compares the difference between the singly sensitized  $\text{TiO}_2/\text{Dye}$  solar cell and the co-sensitized  $\text{TiO}_2/(\text{Dye-QDs})$  solar cell with 5- $\mu\text{m}$ -thick films. As can be seen, with organic dye (JK24 or JK28) sensitization,

the IPCE spectra in the visible region was at 400-570 nm. While when the dye was co-sensitized with 4.2 nm diameter CdSe QDs, the prepared TiO<sub>2</sub>/(JK24-QDs) and TiO<sub>2</sub>/(JK28-QDs) solar cells extended their IPCE spectra to 650 nm, corresponding to the QDs absorption upper limit. However, at short wavelengths, the co-sensitizing with QDs lead to a decrease in IPCE values. For JK24 dye, IPCE decreased at 400-550 nm by almost 20% averagely. For JK28 dye, IPCE decreased at 400-500 nm. This might be due to the light absorption by the dye molecules on the QDs surface. It is found that the organic dye molecules with carboxylic acid (-COOH) as anchoring groups might not inject electrons to the CdSe QDs (although needs further evidences), even though the LUMO level (-1.05 V vs NHE) of the dye is higher than the conduction band level (-0.5 V ~ -1.0 V vs NHE) of CdSe QDs [26]. Another factor causing the IPCE decline may be ascribed to a 'dilution effect' from QDs [34]. As we can see from Fig. 6 (a), the QDs solar cell TiO<sub>2</sub>/QDs had a much lower IPCE than dye solar cells, TiO<sub>2</sub>/JK24 and TiO<sub>2</sub>/JK28 at 400-500 nm. It means, in this wavelength region, QDs are low efficient and organic dye JK24 and JK28 are high efficient. When QDs and organic dye co-loaded homogenously on TiO<sub>2</sub> films, upon illumination, QDs can share incident photons with organic dyes, but produced less electrons than organic dyes. It is just like an effect of dilution the photons, thus causing the IPCE decrease.

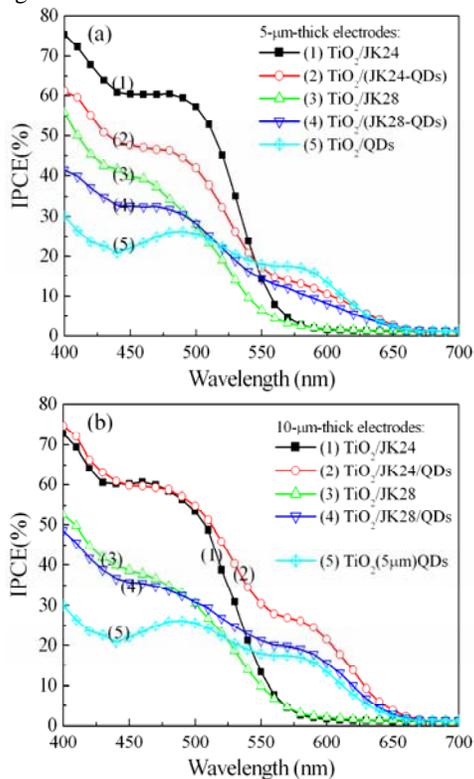


Fig. 6. IPCE spectra of solar cells with 5- $\mu\text{m}$ -thick (a) and 10- $\mu\text{m}$ -thick (b) electrodes.

A possible method to avoid this 'dilution effect' is to arrange QDs on the back side of the TiO<sub>2</sub> film and the organic dye molecules on the front side, so that the QDs only adsorb the transmitted light from dye layer. As we have already prepared, for 10- $\mu\text{m}$ -thick TiO<sub>2</sub> films, QDs were located mainly on the back 5  $\mu\text{m}$  thickness and organic dyes covered the front 5  $\mu\text{m}$  thickness. With these spatially organized electrodes, IPCE spectra of the solar cells are shown in Fig.6b. As we desired, the IPCE of the co-sensitized TiO<sub>2</sub>/JK28/QDs solar cell at 400-550 nm had a marginal decrease compared with that of the singly JK28 solar cell. As for the JK24 based solar cells, the IPCE values of TiO<sub>2</sub>/JK24/QDs at 400-550 nm even maintained the same level as those of TiO<sub>2</sub>/JK24.

An interesting result worthwhile to note was the higher IPCE values at 570-650 nm for the spatially organized TiO<sub>2</sub>/Dye/QDs solar cells (Fig. 6 (b)) than those for TiO<sub>2</sub>/(Dye-QDs) solar cells (Fig. 6 (a)). The photoresponse at 570-650 nm was mainly ascribed to the QDs absorption as shown in Fig. 4 and Fig. 6. So the IPCE increase in this wavelength region should be explained from the QDs aspect. Higher QDs load amount on the 10- $\mu\text{m}$ -thick TiO<sub>2</sub>/Dye/QDs electrodes due to the thicker film might be one important reason. The detailed is still under investigation in our group.

The J-V curves measured under illumination (100mW/cm<sup>2</sup>) for solar cells are shown in Fig. 7. The photocurrent ( $J_{\text{SC}}$ ), open-circuit voltage ( $V_{\text{OC}}$ ), fill factor (FF) and power conversion efficiency ( $\eta$ ) are listed in Table 1. As for the cells with 5- $\mu\text{m}$ -thick TiO<sub>2</sub> films (Fig. 6 (a)), the co-sensitized one with JK24 and QDs, TiO<sub>2</sub>/(JK24-QDs), presented a higher  $\eta$  than TiO<sub>2</sub>/JK24 because of the increase in  $V_{\text{OC}}$  and FF. But the  $J_{\text{SC}}$  declined, which was caused by the dramatic decrease in IPCE at 400-550 nm (Fig. 6 (a)). For the cells with JK28 dye, after co-sensitized with QDs, they displayed a slightly increased  $J_{\text{SC}}$  because the extended IPCE at 570-650 nm can offset the decrease at 400-450 nm. Furthermore, their  $V_{\text{OC}}$  and FF were also enhanced, thus resulting in a well increased  $\eta$ .

As we have known above (Fig. 6 (b)), the co-sensitized solar cells based on 10- $\mu\text{m}$ -thick TiO<sub>2</sub> films, the TiO<sub>2</sub>/JK24/QDs and TiO<sub>2</sub>/JK28/QDs ones, retained high IPCE levels at short wavelengths, which was expected to have better performance than the cells based on 5- $\mu\text{m}$ -thick TiO<sub>2</sub> films. From Table 1 and Fig. 7 (b), it can be found that for the co-sensitized TiO<sub>2</sub>/(JK24-QDs) solar cells with 10- $\mu\text{m}$ -thick TiO<sub>2</sub> films,  $J_{\text{SC}}$  was 8.919 mA/cm<sup>2</sup>,  $V_{\text{OC}}$  was 0.4181V, FF was 33.17%, and  $\eta$  was 1.24%. These values were higher than that obtained from 5- $\mu\text{m}$ -thick TiO<sub>2</sub> electrodes. For the co-sensitized solar cells with JK28 dye and QDs, the one with 10- $\mu\text{m}$ -thick TiO<sub>2</sub> film also had much higher  $J_{\text{SC}}$  and  $\eta$  than the one with 5- $\mu\text{m}$ -thick TiO<sub>2</sub> film. This improvement was not ascribed to effect of film thickness on the organic dye load amount, because the singly JK28 sensitized solar cell with 10- $\mu\text{m}$ -thick TiO<sub>2</sub> film, TiO<sub>2</sub>(10 $\mu\text{m}$ )/JK28, exhibited the similar  $J_{\text{SC}}$  and  $\eta$  with the one composed of

5- $\mu\text{m}$ -thick  $\text{TiO}_2$  film. It is more reasonable to attribute this improvement to the spatially organized architecture for the QDs and organic dye on the 10- $\mu\text{m}$ -thick  $\text{TiO}_2$  electrodes.

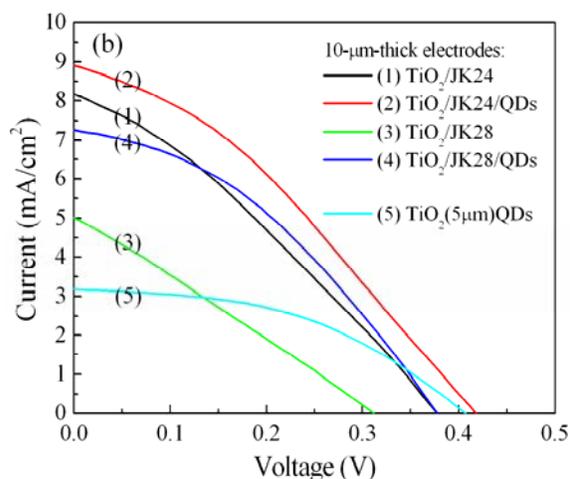
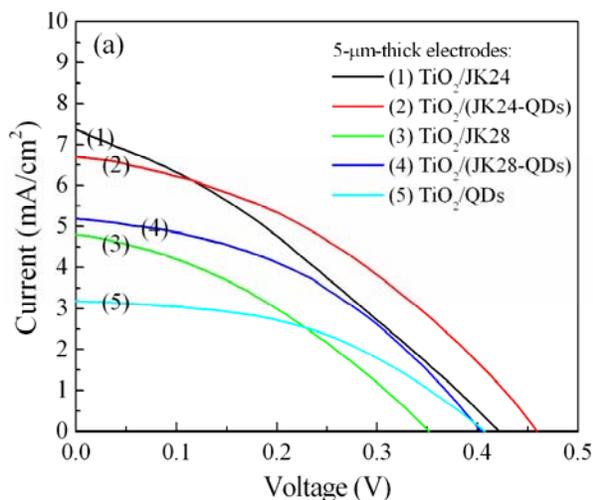


Fig. 7. *J-V* curves of the assembled solar cells with 5- $\mu\text{m}$ -thick (a) and 10- $\mu\text{m}$ -thick (b) electrodes.

In Table 1, the performance of singly QD-sensitized solar cells was also given as reference. With 5- $\mu\text{m}$ -thick electrode,  $J_{\text{SC}}$  was 3.181  $\text{mA}/\text{cm}^2$  and  $\eta$  was 0.59%. With 10- $\mu\text{m}$ -thick electrode,  $J_{\text{SC}}$  decreased to 1.045  $\text{mA}/\text{cm}^2$  because QDs were unable to penetrate inside. These values were quite lower than those from co-sensitized solar cells, suggesting the effectiveness of our design in co-sensitizing.

Table 1. Photovoltaic performance of solar cells.

Electrodes	$J_{\text{SC}}$ ( $\text{mA}/\text{cm}^2$ )	$V_{\text{OC}}$ (V)	FF(%)	$\eta$ (%)
5 $\mu\text{m}$ -thick- $\text{TiO}_2$ films:				
$\text{TiO}_2/\text{JK24}$	7.370	0.4213	30.97	0.96
$\text{TiO}_2/(\text{JK24-QDs})$	6.705	0.4589	38.25	1.18
$\text{TiO}_2/\text{JK28}$	4.800	0.3518	35.45	0.60
$\text{TiO}_2/(\text{JK28-QDs})$	5.182	0.4036	41.82	0.87
$\text{TiO}_2/\text{QDs}$	3.181	0.4071	45.60	0.59
10 $\mu\text{m}$ -thick- $\text{TiO}_2$ films:				
$\text{TiO}_2/\text{JK24}$	8.123	0.3775	30.51	0.94
$\text{TiO}_2/\text{JK24/QDs}$	8.919	0.4181	33.17	1.24
$\text{TiO}_2/\text{JK28}$	5.014	0.3117	26.19	0.41
$\text{TiO}_2/\text{JK28/QDs}$	7.265	0.3778	37.65	1.03
$\text{TiO}_2/\text{QDs}$	1.045	0.2437	35.73	0.09

In comparison with the best efficient solar cell system, the co-sensitized solar cell system established in this study is at a low level at present. But our initial effort is to demonstrate the effectiveness of QDs as co-sensitizers to improve photoresponse toward near IR region for the next generation solar cells. By optimizing

the cell configuration, including development of a non-aqueous electrolyte more effective than polysulfide both for organic dye and QDs, and an introduction of larger sized, or other type QDs besides CdSe which shift light absorption to the longer wavelength region up to 800-1000 nm, it should be possible to further improve

the performance of solar cell.

#### 4. Conclusions

In summary, CdSe QDs were firstly employed as co-sensitizers of organic dyes in solar cells to obtain a red-shifted light harvesting. Employing 5- $\mu\text{m}$ -thick  $\text{TiO}_2$  films on which QDs and organic dye molecules adsorbed homogeneously, IPCE of the electrodes extended to longer wavelengths, but decreased to a lower level at short wavelengths than those obtained from singly dye electrodes due to the QDs adsorption in this region and sharing photons with organic dye. By using 10- $\mu\text{m}$ -thick  $\text{TiO}_2$  films, QDs were mainly located on the back side of the film due to their unable penetration and organic dye molecules covered on the front side. With these spatially organized co-sensitized electrodes, the IPCE values maintained at high levels at short wavelengths, and extended toward long-wavelength region. As a result, the assembled solar cells presented significantly improved photocurrent and power conversion efficiency. Resulted from a retardation of charge recombination for the co-sensitized electrodes, the open-circuit voltage and FF was also improved. The success in utilizing QDs as co-sensitizers opens up a new way to the design of solar cells.

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\*Corresponding author: fsq@mail.xjtu.edu.cn