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Influence of Deposition Strategies on CdSe Quantum Dot-Sensitized Solar Cells: A Comparison between Successive Ionic Layer Adsorption and Reaction and Chemical Bath Deposition

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Abstract: Deposition and synthesis strategy of quantum dots (QDs) exerts appreciable influences on the photovoltaic properties of quantum dot-sensitized solar cells (QDSCs). In this paper, a systematic characterization of morphology, optical and electrochemical properties has been carried out to correlate the assembling of QDs with the performance of the resultant QDSCs. CdSe sensitized TiO₂ solar cells were investigated focusing on influences of two commonly used in-situ QD deposition methods, i.e., successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD). By applying a pre-assembled CdS seed layer prior to CdSe deposition, a power conversion efficiency up to 4.85% has been achieved for CdS/CBD–CdSe cells, which is appreciably higher than 3.89% for CdS/SILAR–CdSe cell. TEM images revealed that CdS seeded SILAR is only capable of less than full coverage, in contrast, CdS seeded CBD technique secures full conformal coverage of QDs on TiO₂. The full conformal coverage of QDs offers two benefits, (1) high loading of QDs for efficient photon capturing, contributing to the increase of photocurrent, and (2) suppression of interfacial charge recombination, resulting in high open-circuit voltage and large fill factor. Our success in achieving the perfect coverage of QDs based on CdS seeded CBD highlights the strong implications for the performance optimization of QDSCs.

Keywords: *quantum dot-sensitized solar cells, deposition of CdSe, SILAR, CBD*

1. Introduction

The development of cost-effective and high-performance solar devices for clean and sustainable energy partially to replace fossil fuels has been an urgent matter all over the world.^{1,2} Inorganic quantum dots (QDs) have attracted considerable attention for novel quantum functional device application over the past couple of years.³⁻⁶ As a promising derivative of dye-sensitized solar cell (DSC), quantum dot-sensitized solar cell (QDSC), which employs semiconductor QDs as the photo-sensitizer instead of organic dyes, has demonstrated a hopeful development for future generation solar devices in view of the extraordinary optical and electrical properties, such as tunable band gap across a wide energy range by facilely changing the size, shape and composition, large extinction coefficient, high stability toward water and oxygen, and generation of multiple excitons with single-photon absorption.⁷⁻¹⁷ Another conceptual advantage of such nano-composite solar cells over most other types, like conventional p-n junction cells, is the high interfacial area between the absorbers and the electron and hole conductors, which makes the generation of electron-hole pairs always being close to the charge separating interface.¹⁸ Under such circumstance, carrier diffusion length requirements are relatively relaxed in contrast to the case for p-n junction cells. A high theoretical power conversion efficiency (PCE) up to 44%, beyond the traditional Shockley and Queisser limit of 32% for semiconductor solar cells, has encouraged people to develop QDSCs with the use of a variety of QDs as sensitizers for light harvesting.^{8,10,11,19-25} Although the utilization of narrow band gap QDs including PbS and Ag₂S lead to broad absorption spectra, the electron injection

efficiency from QDs to oxide semiconductor (TiO_2 , ZnO , etc) has remained relatively low, which severely hinders the promotion of PCE.^{23–25} The most possible reason is the low conduction band (CB) of QDs which reduces the driving force that injects the photo-excited electron. Among kinds of QDs developed, CdSe and CdS/CdSe as conventional components for sensitizers in QDSCs have been excellent ones showing prominent PCEs till now, especially for the co-sensitization system, which has been reported to push up efficiency over 5% employing mesoporous TiO_2 films.^{8,26,27}

However, the PCEs of QDSCs, employing liquid hole conductors, remain lower compared to that of DSCs exceeding 13%,²⁸ though a faster progress has been developed for QDSCs during the past years. Although the short-circuit photocurrent (J_{sc}) of QDSCs has already been comparable to that of DSCs, two other key parameters, open-circuit voltage (V_{oc}) and fill factor (FF) are still too low. This might partially arise from the serious charge recombination caused by the imperfect assembly of QDs on the TiO_2 surfaces which could generate dark current and lead directly to poor V_{oc} and FF.^{16,29} Therefore, to further improve the performance of QDSCs, one of the urgent issues is to determine the difficulty of assembling QDs effectively to obtain a perfectly covered layer of QDs onto TiO_2 or ZnO , so as to suppress and block the charge recombination.

Two categories of deposition strategies have been widely employed and extensively studied for the assembly of QDs. One is in-situ growth of QDs onto mesoporous oxide films, including successive ionic layer adsorption and reaction (SILAR)^{8–10,16,19,22–26} and chemical bath deposition (CBD).^{13–15,18,27,29} The other is

self-assembled binding of pre-synthesized colloidal QDs onto the surface of an oxide through the link of bi-functional molecules typically having a carboxylate or phosphonate group on terminal and a thiol group on the other to attach QDs to the TiO₂ surface, for instance, 3-mercaptopropionic acid (MPA).^{20,21,30,31} Although the self-assembled technique has the advantage of being able to precisely control the size of QDs, it is difficult to achieve uniform and sufficient coverage of QDs onto the oxide film.³⁰⁻³² In contrast to colloidal QDs, lower crystallinity QDs are grown in-situ on nanostructured films, with a relatively broad distribution of particle sizes together with the development of grain boundaries;³³ however, the lower control over the QD growth conditions is partially balanced by the advantage of higher QD loading. To date, SILAR and CBD have been the methods most commonly employed for the fabrication and study of QDSCs with high performance.^{8,25-27} Both of SILAR and CBD methods are based on low-cost solution processes, ideal for up-scaling and fabrication of high efficiency photovoltaic devices. It has been recognized that the deposition methods and growth conditions dramatically affect the assembling of QDs and the corresponding photovoltaic performance when in-situ grown QDs are employed.^{29,33} Understanding an effective and reliable strategy to achieve a full conformal coverage of QDs onto a mesoporous TiO₂ network in a large scale is a crucial stride in the development of high performance QDSCs.

This paper reports the systematic study of the influences of QD deposition strategies on the photovoltaic behaviors of the resultant CdSe QDSCs based on SILAR and CBD. The corresponding photovoltaic characteristics were found to vary

considerably with deposition strategies and parameters. A careful examination of SILAR- and CBD-grown CdSe QD absorber layers in QDSCs was conducted for a better understanding of physical and chemical processes occurring at $\text{TiO}_2/\text{QDs}/\text{electrolyte}$ interfaces. On the basis of the TiO_2/CdS -seeded CBD-CdSe photoanode coupled with a Cu_2S counter electrode and a polysulfide electrolyte, a PCE up to 4.85% has been achieved, as compared to 3.89% for QDSC prepared by CdS seeded SILAR. Possible mechanisms resulting in such an appreciable difference in PCE have been discussed.

2. Experimental

2.1 Materials

Titanium oxide (TiO_2 , Degussa, P25), α -terpineol ($\text{C}_{10}\text{H}_{18}\text{O}$, 96%, Sigma Aldrich), ethyl cellulose ($[\text{C}_6\text{H}_7\text{O}_2(\text{OC}_2\text{H}_5)_3]_n$, 48.0–49.5% (w/w) as ethoxyl, Sigma Aldrich), cadmium acetate dihydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 98%, Sigma Aldrich), sodium sulfide Nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, $\geq 98.0\%$, Sigma Aldrich), sulfur (S, purified by sublimation, Sigma Aldrich), sodium sulfide anhydrous (Na_2SO_3 , 99.1%, Italy), trisodium salt of nitrilotriacetic acid ($\text{N}(\text{CH}_2\text{COONa})_3$, $\geq 98.0\%$, Aldrich), zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\geq 99.0\%$, Aldrich), selenium powder (Se, 99.5%, Alfa Aesar), sodium borohydride (NaBH_4 , 98%, Alfa Aesar), brass foil (alloy 260, 0.3 mm thick, Alfa Aesar), hydrochloric acid (HCl, 37%, USA), methanol (CH_3OH , $\geq 99.5\%$, Sigma Aldrich), and ethanol (CH_3COOH , $\geq 99.5\%$, Decon) were all used as received.

2.2 Preparation of Mesoporous TiO₂ Films

Commercially available F-doped tin oxide (FTO) glass was used as transparent conducting substrates to prepare TiO₂ photoanodes. To prepare TiO₂ paste, 0.5 g Degussa P25 mixed with 0.25 g ethyl cellulose and 1.75 g α -terpineol were first dispersed into 5.0 mL ethanol, and then sonicated for 30 min to form a slurry after removing the ethanol under stirring. Mesoporous TiO₂ films were prepared by doctor blading of TiO₂ paste on the clean FTO substrate, followed by sintered at 500 °C for 30 min in air with a heating rate of 5 °C/min. The thickness of the TiO₂ film, measured from the cross sectional image of SEM, was ca. 16 μ m. The active area of the TiO₂ films was approximately 0.36 cm² (0.6 cm \times 0.6 cm square).

2.3 In Situ QDs Assembling by SILAR and CBD

Typical procedures for SILAR and CBD to deposit CdSe QDs were illustrated in Scheme S1a, b. In both cases, the films were immersed into the as-prepared precursor solutions to allow the ions of the reactants to penetrate into the mesoporous film and incorporate into the interior of mesopores, leading to the formation of one layer of semiconductor QDs. Specifically, the SILAR processes for CdSe deposition were all conducted inside a glove box under N₂ atmosphere. TiO₂ films were first dipped into 0.1 M Cd(CH₃COO)₂ \cdot 2H₂O methanol solution for 1 min, rinsed with methanol and dried under N₂ atmosphere for several minutes. Subsequently, the dried films were then dipped into a solution containing 0.1 M Se²⁻ for another 1 min to allow Se²⁻ to react with the pre-adsorbed Cd²⁺, leading to the formation of desired CdSe QDs. Se²⁻ solution was prepared by mixing Se powder and excess NaBH₄ in ethanol under

vigorous stirring. One deposition cycle was completed by further rinsing and drying. The two-step dipping procedure is termed as one SILAR cycle. A certain number of SILAR cycles (2, 4, 6, 8 or 10) were employed to obtain a desired amount of CdSe loading on the TiO₂ films. As follows is a brief description of CBD procedure to CdSe deposition: 0.1 M Na₂SeSO₃, 0.1 M Cd(CH₃COO)₂, and 0.2 M N(CH₂COONa)₃ aqueous solution were mixed together with a volume ratio of 1:1:1, and then the TiO₂ films were vertically immersed into the solution for the assembly of a CdSe layer under dark condition at 24 °C for a certain amount of time (3, 5, 7 or 9 hours). Na₂SeSO₃ solution was prepared by dissolving Se powder in an aqueous solution of Na₂SO₃ at 70 °C for ca. 1 h under vigorous stirring. Prior to the assembling of CdSe, SILAR was employed to deposit CdS serving as a seed layer to facilitate the subsequent SILAR or CBD growth. Briefly, a 0.1 M Cd(CH₃COO)₂ in methanol was used as a cation source and 0.1 Na₂S in a mixture of methanol and water (1:1, volume ratio) as anion source, and the SILAR procedure was conducted in air. Finally, all the photoanodes were coated with 2 SILAR cycles of ZnS passivation layer, by dipping alternatively into 0.1 M Zn(CH₃COO)₂ and 0.1 M Na₂S solutions for 1 min/dip. The deposition of ZnS serves as a tunnel barrier for back charge transfer at the absorber and TiO₂ interface, which improves the performance and stability of the solar devices.

2.4 Solar Cell Fabrication

Solar device was assembled by sandwiching the as-prepared photoanode and Cu₂S counter electrode using a scotch tape spacer (ca. 50 μm thick) and permeating the assembly with the polysulfide electrolyte. The polysulfide electrolyte employed in

this study was composed of 1 M S and 1 M Na₂S in deionized water. The counter electrode was a Cu₂S film fabricated on a brass foil and the preparation procedure can be described briefly as follows: brass foil was immersed into 37% HCl solution at about 70 °C for 30 min, then rinsed with water and dried in air; the etched brass foil was then dipped into the as-prepared polysulfide electrolyte for about 5 min, resulting in a black Cu₂S layer forming on the foil.

2.5 Characterization

Morphologies of the film samples were directly characterized by a JEOL JSM 7000 scanning electron microscope (SEM) equipped with an energy dispersion X-ray (EDX) spectrometer to analyze the element content and distribution. Transmission electron microscope (TEM) and high-resolution TEM observations were performed on a Tecnai G2 F20 microscope. Optical absorption spectra were measured on a thermal scientific UV-vis-NIR spectrophotometer (Evolution 300 PC) fitted with an integrating sphere accessory. Photovoltaic properties were measured using an HP 4155A programmable semiconductor parameter analyzer under AM 1.5 simulated sunlight with the power density of 100 mW/cm². *J-V* characteristics were recorded using a Keithley 2400 source meter with a 0.36 cm² active cell area. Electrochemical impedance spectroscopy (EIS) measurements were carried out under dark condition using a Solartron 1287A coupled with a Solartron 1260 FRA/impedance analyzer to investigate the resistance distributions and charge recombination processes in QDSCs.

3. Results and discussion

Fig. 1a,b shows the UV-vis absorption spectra of CdSe QDs sensitized TiO₂ mesoporous films prepared by SILAR for various cycle numbers and CBD for different deposition hours, respectively. Apparently, for both of SILAR- and CBD-CdSe, the successive deposition of CdSe QDs over mesoporous TiO₂ was accompanied by deepening of the color visible to the naked eye along with the increasing SILAR cycle and CBD time, implying the increased amount of CdSe QDs as well as the grown particle size. Furthermore, as demonstrated in Fig. S1, the effective band gap of CdSe QDs can be estimated by extrapolating the linear portion of the $(Ah\nu)^2$ versus $h\nu$ plots at $A = 0$, according to the following equation, which expresses the relationship between the optical band gap (E_g) for direct interband transition and the absorption coefficient (A) near the absorption edge,^{16,34,35}

$$(Ah\nu)^2 = c(h\nu - E_g) \quad (1)$$

where c is a constant, ν is the frequency and h is Planck constant. The obtained values of effective band gaps and absorption onsets, depending on SILAR cycle number and CBD time, are summarized in Table S1 and plotted in Fig. 1c,d. As expected, the calculated band gaps of the CdSe QDs are considerably larger than the band gap of bulk CdSe (1.74 eV) as a result of quantum confinement effect. As the SILAR cycle number or CBD time increased, the effective band gap of QDs became increasingly smaller, correlated with the more and more pronounced red shift of absorption edge. Therefore, deposits from SILAR and CBD vary considerably depending on the deposition parameters.

The light harvesting capability, as one of the key functional properties of a

QD-sensitized film, can be evaluated using the UV-vis absorption spectrum, which highlights two important features: (1) the particle size of QDs reflected by the absorption range, and (2) the amount of QDs loaded determined by the absorbance. Through the careful examination of the absorption spectra of SILAR- and CBD-CdSe films, the clear differences need to be elaborated here. Firstly, it was more facile for SILAR-CdSe films to exhibit pronounced absorption red shift compared to CBD-CdSe films, which suggested the larger crystalline size for QDs prepared by SILAR. Secondly, comparatively stronger absorbances were more likely to be reached for CBD-CdSe films in comparison with SILAR-CdSe films, indicating a relatively higher QD loading delivered by CBD.

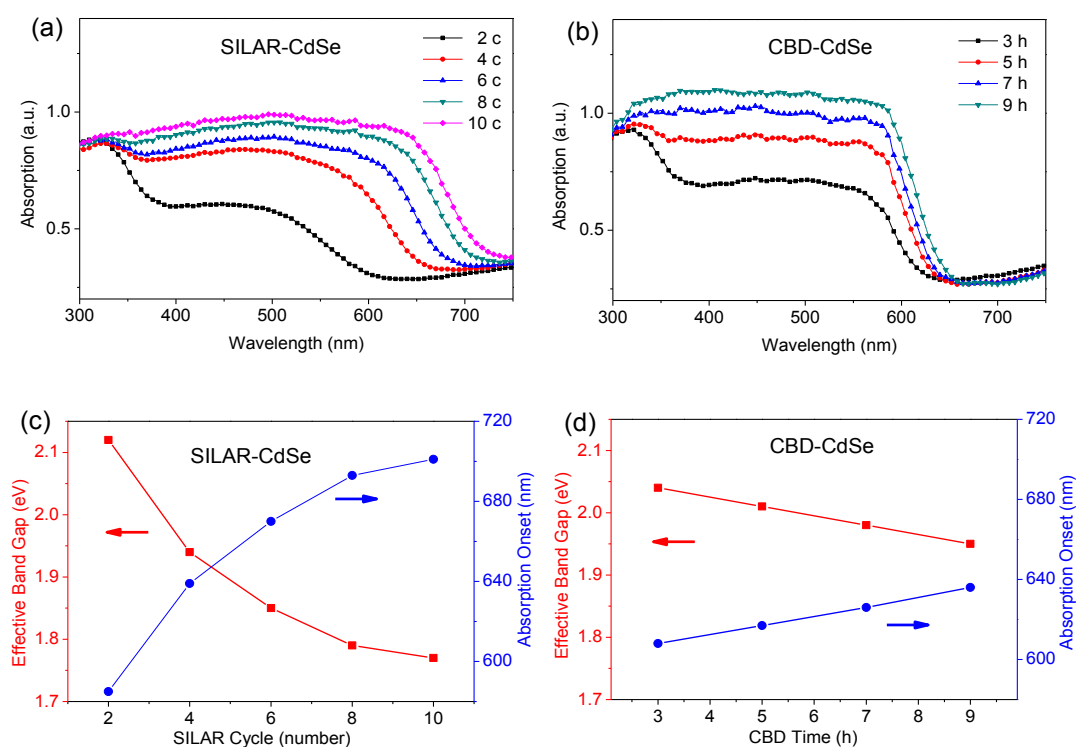


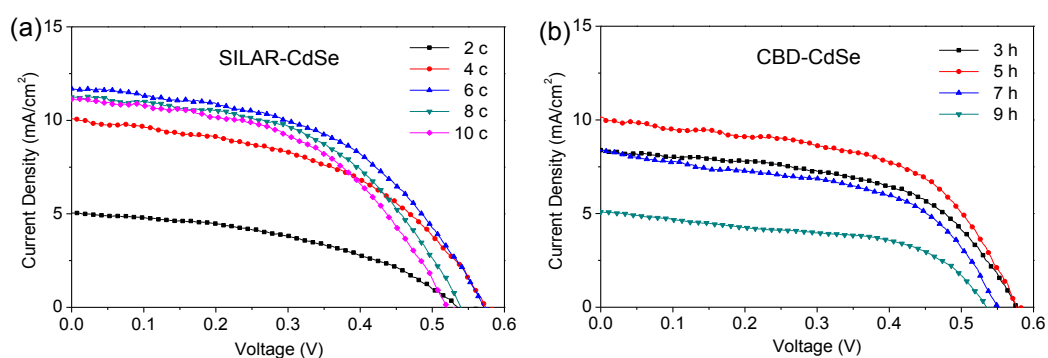
Fig. 1 UV-vis absorption spectra of CdSe QDs sensitized TiO₂ mesoporous films prepared by (a) SILAR for various cycles and (b) CBD for different time, respectively, and the estimated effective band gaps and absorption onsets depending on (c) SILAR

cycle and (d) CBD time, determined by the corresponding UV–vis absorption spectra.

The photovoltaic properties of CdSe QDSCs based on SILAR and CBD are carefully examined, and the corresponding J – V characteristics under the illumination of one sun (AM 1.5, 100 mW/cm²) are presented in panels a and b of Fig. 2 for SILAR– and CBD–CdSe QDSCs, respectively. For clear illustration, photovoltaic parameters (i.e., PCE, J_{sc} , V_{oc} and FF) depending on SILAR cycle and CBD time are plotted in Fig. 2 c,d. It is noteworthy that, for each device studied in this paper, at least three identical samples have been fabricated to check the reproducibility of cell performance. As shown in the plotted histograms, the performance of a QDSC was very much dependent on the deposition parameters for both strategies, and the PCE firstly increased and then decreased with the increasing SILAR cycle and CBD time to deposit CdSe QDs. Specifically, it is easy to understand that a small amount of QDs incorporated on the TiO₂ film would result in a small photocurrent density, along with a low PCE. However, an overload of QDs might also lead to a poor cell performance, possibly for the reason of blocking of the mesopores, which gave rise to a decrease of the QDs/electrolyte contact area and unfavorable electron transport at the TiO₂/QDs/electrolyte interface.^{16,36} This explains the fact that, although the QD loading would further increase, the cell performance deteriorated along with the overextended SILAR cycle (>6) or CBD time (>5 h).

Optimized PCEs of 3.31% and 3.16% were achieved for SILAR– and CBD–CdSe QDSCs, respectively. In order to carefully compare the differences of two deposition techniques, we take a look at each photovoltaic parameter separately. On

one band, as for J_{sc} , a highest value of 11.64 mW/cm^2 could be obtained for SILAR–CdSe cell (SILAR cycle = 6), a little larger than that of the highest one of 10.05 mW/cm^2 for CBD–CdSe cell (CBD time = 5 h). Evidently, as the photocurrent was proportional to the amount of photons captured, the slightly larger J_{sc} should be directly associated with the broader light absorption range of QDs for SILAR–CdSe cell, compared to that of CBD–CdSe cell, although the amount of QD loading might be comparatively smaller. On the other hand, higher V_{oc} and FF values were systematically observed for CBD–CdSe cells compared to SILAR–CdSe cells, taking into consideration the value variation depending on the deposition parameters. For instance, the FF of CBD–CdSe cells lay between 0.52 and 0.55, higher than the values distributed in the range of 0.44 to 0.50 for SILAR–CdSe cells. As the identical TiO_2 mesoporous film, electrolyte and counter electrode were employed for cell fabrication, the obvious differences in photovoltaic behavior of SILAR– and CBD–CdSe cells unequivocally resulted from the different deposition techniques.



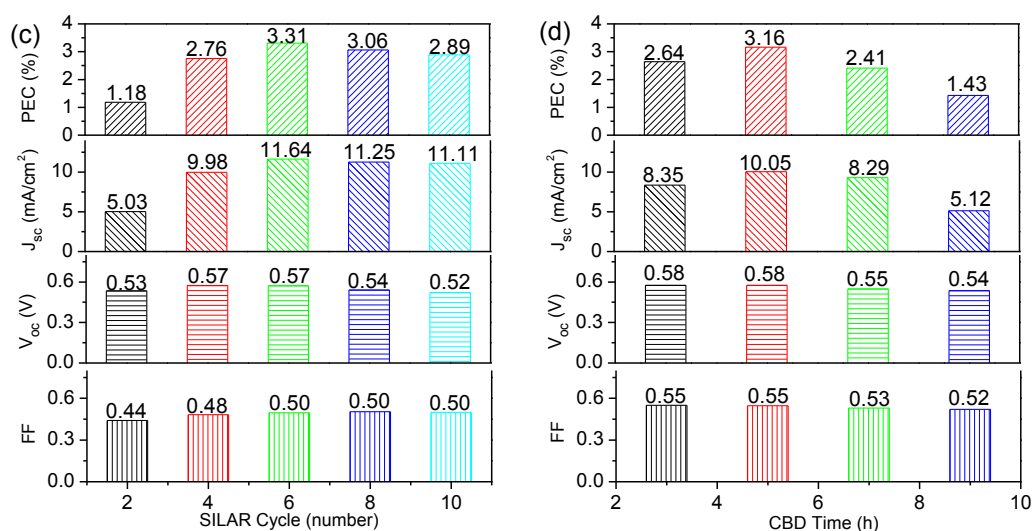


Fig. 2 J - V characteristics of CdSe QDSCs prepared by (a) SILAR and (b) CBD, and photovoltaic parameters (PCE, J_{sc} , V_{oc} and FF) depending on (c) SILAR cycle and (d) CBD time, respectively, measured under the illumination of one sun (AM 1.5, 100 mW/cm²).

A pre-assembled seed layer of CdS QDs prior to CdSe deposition has been extensively reported to improve the cell performance.^{8,10,18} Several possibilities have been proposed to explain the complementary effect in the literatures, including the passivation effect of CdS on the TiO₂ surface, the growth of different nature of CdSe (or TiO₂/CdSe junction), the formation of stepwise band-edge levels facilitating the electron injection and so forth.^{10,18,37} Here, we will not belabor the particular effects of the CdS seed layer too much, as they are beyond the research scope of this study. CdS QDs seed layer prepared by SILAR for 4 cycles was employed in this work and verified to improve the cell performance.

Fig. 3a presents the UV-vis absorption spectra of CdS seeded SILAR-CdSe (SILAR cycle = 6) and CBD-CdSe (CBD time = 3 h) films, denoted as

CdS/SILAR–CdSe and CdS/CBD–CdSe, respectively. At the presence of a SILAR–CdS seed layer, the growth of CdSe was greatly enhanced as demonstrated by the higher absorbances, compared to those of the corresponding pure CdSe QDs sensitized films. Moreover, the CdS/SILAR–CdSe film exhibited broader absorption range with an absorption onset at the wavelength of ca. 667 nm, longer than that of ca. 636 nm for CdS/CBD–CdSe film (as illustrated in Fig. S1c), while the absorbance of CdS/CBD–CdSe film was higher than that of CdS/SILAR–CdSe film, implying the larger amount of QD loading, similar to the case for pure CdSe sensitized films as demonstrated in Fig. 1a,b. Another point of particular interest is the CB lineup affected by the QD size. In consideration of the smaller QD size of CdS/CBD–CdSe suggested by the shorter wavelength of the absorption onset in comparison with CdS/SILAR–CdSe, the facilitated electron injection from the CB of QDs to CB of TiO₂ and the reduced back charge transfer might be achieved, arising from its higher CB edge, as illustrated in Scheme S2. Although the exact CB lineups of QDs are not very clear in our case because of the high pH of polysulfide electrolyte, which has been reported to make the TiO₂ bands shift negative to a greater extent than the corresponding shifts of CdS or CdSe QDs,¹⁸ it can be inferred that a larger offset of CB of CdSe with respect to CB of TiO₂ will render the electron injection rather facile, while a smaller offset probably lead to the recombination of photo-generated carriers.

The photovoltaic characteristics of CdS seeded SILAR– and CBD–CdSe QDSCs measured under the illumination of one sun (AM 1.5, 100 mW/cm²) are compared in Fig. 3b and the extracted parameters (i.e., J_{sc} , V_{oc} , FF and PCE) are tabularized in

Table 1. As shown, J_{sc} of 13.64 mV/cm^2 , V_{oc} of 0.56, FF of 0.51, and a PCE of 3.89% were achieved for CdS/SILAR–CdSe cell, while CdS/CBD–CdSe cell delivered J_{sc} of 14.98 mV/cm^2 , V_{oc} of 0.60, and FF of 0.54, leading to a PCE of 4.85%. Two performance features are worth mentioning here. Firstly, a relatively larger J_{sc} was reached for CdS seeded CBD cell than that of CdS seeded SILAR cell. It is well known that J_{sc} not only relies on photocarrier generation process based on light harvest capability but also a process after photocarrier generation, i.e., electron injection. On one hand, as presented in the absorption spectra, CdS/CBD–CdSe film exhibited much more efficient photon capturing than that of CdS/SILAR–CdSe film, although the red-shifted absorption edge of CdS/SILAR–CdSe film could make up for a somewhat weaker light harvest capability. The stronger absorbance of CdS/CBD–CdSe film indicated a higher QD loading delivered by CdS seeded CBD. On the other hand, a more facile electron injection achieved in view of the higher CB edge of CdS/CBD–CdSe QDs, compared to that of CdS/SILAR–CdSe QDs, would result in a more efficient photon to electron quantum yield. Therefore, CdS/CBD–CdSe cells delivered a larger J_{sc} than that of CdS/SILAR–CdSe cells. Secondly, particular attention is given to V_{oc} and FF. Compared to CdS seeded SILAR, the CdS seeded CBD consistently delivered higher and more reproducible V_{oc} and FF. As V_{oc} and FF are systematically correlated to the charge recombination processes in the solar device,^{29,38} it might be inferred that, lower charge recombination would occur for CdS/CBD–CdSe cell in comparison with CdS/SILAR–CdSe cell, which might resulted from the well-distributed CBD grown CdSe QDs. In order to validate

our conjecture on the different photovoltaic features for CdS seeded SILAR- and CBD-CdSe cells, we resorted to microscopic examinations for further reasonable explanations below.

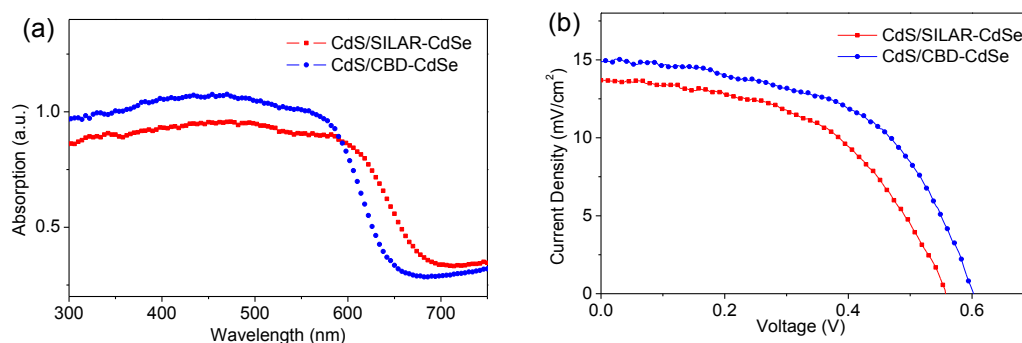


Fig. 3 (a) UV-vis absorption spectra of CdS seeded SILAR- and CBD-CdSe electrodes, and (b) J - V characteristics of CdS seeded SILAR- and CBD-CdSe QDSCs measured under the illumination of one sun (AM 1.5, 100 mW/cm²).

Table 1 Solar cell parameters of CdS seeded SILAR- and CBD-CdSe QDSCs measured under the illumination of one sun (AM 1.5, 100 mW/cm²)^a

| cell | J_{sc} (mA/cm ²) | V_{oc} (V) | FF | PCE (%) |
|----------------|--------------------------------|---------------------|---------------------|---------------------|
| CdS/SILAR-CdSe | 13.64 (± 0.20) | 0.56 (± 0.01) | 0.51 (± 0.01) | 3.89 (± 0.20) |
| CdS/CBD-CdSe | 14.98 (± 0.20) | 0.60 (± 0.01) | 0.54 (± 0.01) | 4.85 (± 0.20) |

^aThe standard deviation of the photovoltaic characteristics is based on the data of three cells.

The mesoporous structure of TiO₂ films, shown in Fig. 4a, favors the penetration of the precursor solutions. As is well-known, for absorber (i.e., dye or QD) deposition, it is important that the absorber is deposited throughout the porous oxide layer, which is ca. 16 μ m as revealed by the cross sectional view (Fig. 4b) in this case. Therefore, a method that allows the infiltration of the reactants into the film pores is preferentially

required. Solution deposition methods, such as SILAR and CBD, are supposed to be ideal for this purpose. Fig. 4c compares the EDX spectra based on the film surfaces for CdS seeded SILAR–CdSe and CBD–CdSe electrodes, which confirms the successful deposition of CdS and CdSe. The atom ratios of the elements, listed in the inset of each spectrum, revealed that compared to SILAR, CBD led to a larger amount of QDs loaded, consistent with the results obtained from absorption spectra (Fig. 3a) and XPS analysis (Fig. S2). For microscopically tracing the spatial distribution of CdS and CdSe in the mesoporous film, the elementary mapping technique was employed. The cross-sectional mapping images as presented in Fig. 4d demonstrated that the element distributions of Cd, S and Se were indeed essentially homogeneous throughout the thickness of the mesoporous TiO₂ film for both of CdS seeded SILAR and CBD, as we had expected.

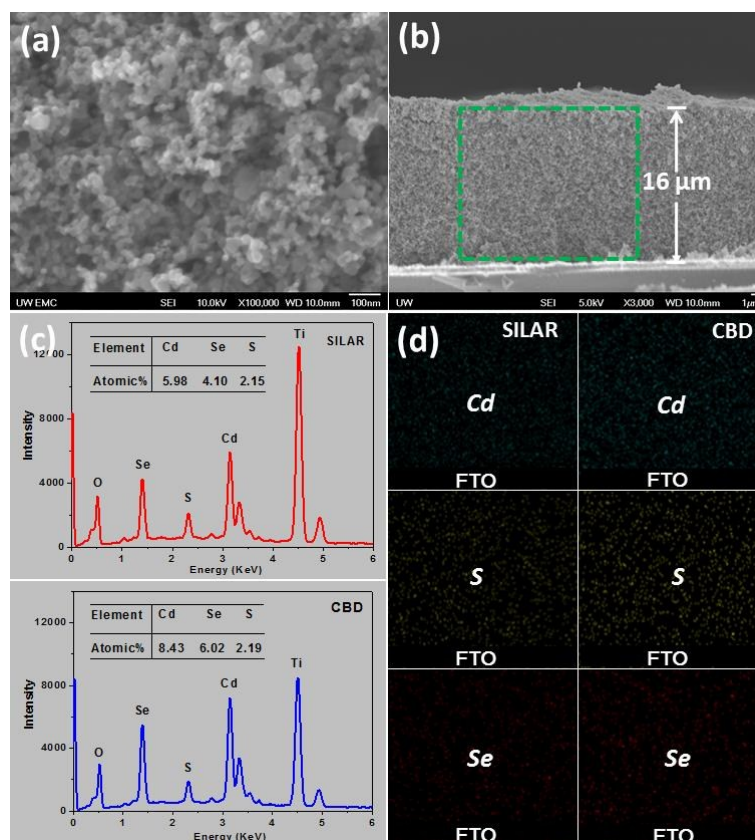


Fig. 4 SEM images of (a) top view and (b) cross sectional view of a bare TiO₂ mesoporous film, (c) EDX spectra based on the film surface and (d) element distribution maps of Cd, S and Se along the cross-section for CdS seeded SILAR–CdSe and CBD–CdSe films.

The deposition status of QDs onto TiO₂ films can be microscopically revealed by TEM images as shown in Fig. 5. Compared to the image of pure TiO₂ nanoparticles (Fig. 5a,d), the images of TiO₂ nanoparticles loaded with QDs (Fig. 5b,c) clearly indicated the successful deposition of QDs, which could be further confirmed as TiO₂/CdS/CdSe structures by HRTEM images (Fig. 5e,f). It is apparent that the deposition status of CdS/SILAR–CdSe on the TiO₂ surface differs from that of CdS/CBD–CdSe. The observations manifest that CBD can ensure the preferential growth of QDs on the TiO₂ surface, forming a full conformal coverage of “thin QD layer” coated continuously on the surface of TiO₂, while SILAR produces separated “small QD particles” distributed on TiO₂, as has also been previously reported in the literatures.^{23,25,39,40} Presumably, the success in achieving a full conformal coverage and high loading of QDs for CdS/CBD–CdSe electrode would lead to an interfacial structure with superior ability in inhibiting the charge recombination at the TiO₂/electrolyte interface, and thus contribute for the improvements of V_{oc} and FF of the corresponding solar cells. On the contrary, although it was also easy for CdS/SILAR–CdSe electrode to load a certain amount of QDs on TiO₂ judging from the color change, the discontinuous distribution and imperfect anchorage of QDs might give rise to interface charge recombination, which would inevitably worsen the

cell performance. The explanations coincide with the photovoltaic behaviors of CdS seeded SILAR- and CBD-CdSe cells.

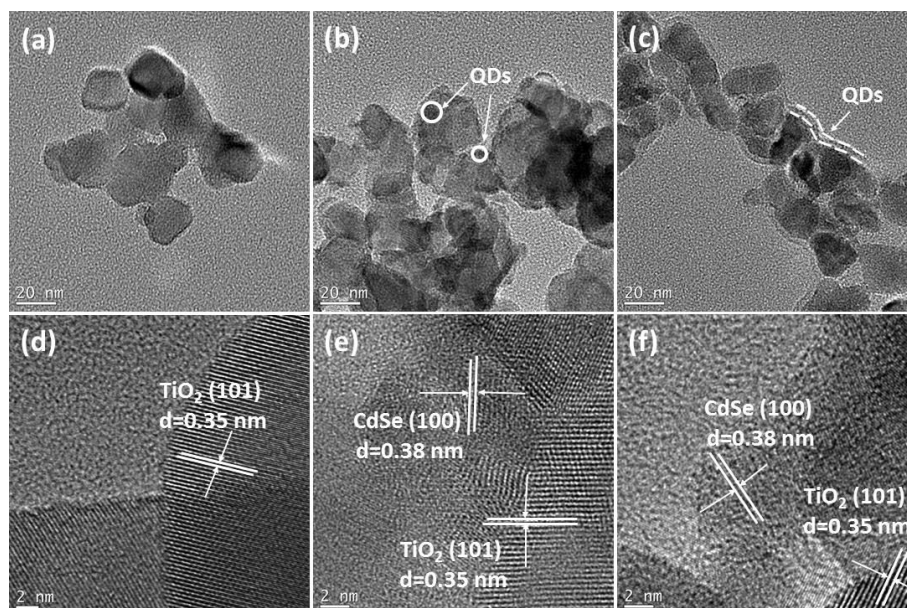


Fig. 5 TEM and HRTEM images of TiO₂ nanoparticles (a, d) before QDs deposition, and after CdSe QDs deposited by CdS seeded (b, e) SILAR and (c, f) CBD.

The significant influences of QD deposition status on the interfacial charge transfer and recombination are illustrated in Fig. 6. As demonstrated in panel a, under the illumination, photons are harvested by the QD absorbers, generating electron-hole pairs that are quickly separated. The electrons excited to the CB of QDs inject into the CB of TiO₂, and then are collected by the FTO substrate, while the holes left in the QDs are reduced by S^{2-} ions in the electrolyte. Particularly, besides the charge transfer processes, there also exist some charge recombination pathways as marked in the schematic diagram:^{14,41} k_b and k_r represent the back reaction of the injected electrons in the CB of QDs and TiO₂ with S_n^{2-} ions in the electrolyte and the recombination of these electrons with holes remained in the VB of QDs, respectively. Among all these

pathways, the back electron injection from TiO_2 to the electrolyte dominates the recombination processes in view of the highly efficient charge separation of QDs.^{14,42} A full conformal coverage of QD layer onto TiO_2 will be effective in preventing back reaction of electrons in the CB of TiO_2 with S_n^{2-} . Schematic diagrams shown in panel b highlight the differences of CdSe QDs deposition between CdS seeded SILAR and CBD, on the basis of TEM observations. Apparently, in comparison with CdS/SILAR–CdSe, CdS/CBD–CdSe electrode provides better blockage of electron re-injection from TiO_2 back into the electrolyte, which will undoubtedly suppress the charge recombination. In addition, it is worth mentioning that QDs layer play an active role on the charge transfer and recombination processes in QDSCs, perhaps by forming an electron transport channel along QDs, a situation that is different from that in typical DSCs.^{29,43} S. Yang Group has also reported that, even for the same TiO_2 mesoporous films employed, the compact QD layer not only helps to suppress recombination but also gives rise to the enhanced charge transport in a solar device.²⁹

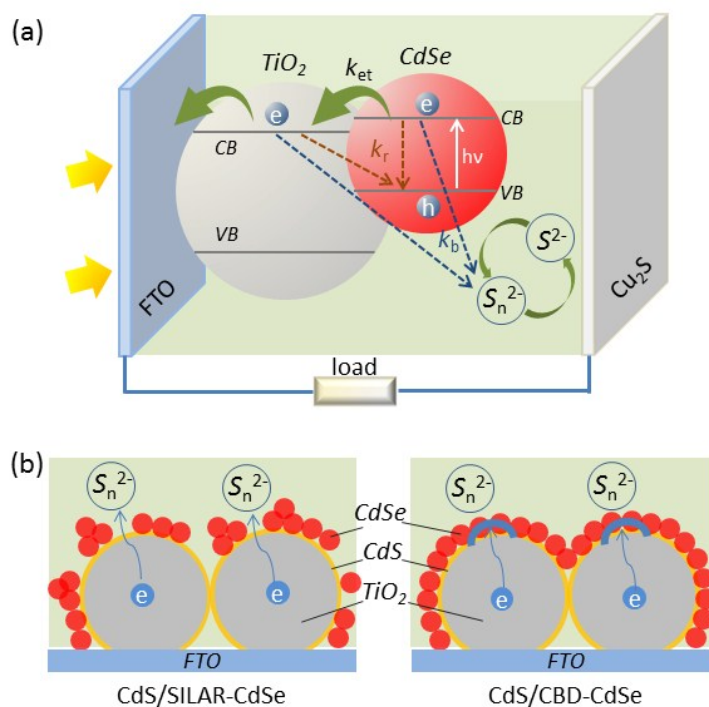


Fig. 6 Schematic diagrams (a) illustrating the electron transfer (k_{et}) from CdSe into TiO_2 nanoparticles. k_b and k_r represent the back reaction of the injected electrons in the CB of QDs and TiO_2 with S_n^{2-} ions in the electrolyte and the recombination of these electrons with holes remained in the VB of QDs, respectively; (b) highlighting the differences of CdSe QDs deposition between CdS seeded SILAR and CBD.

To evaluate the resistance distributions and charge recombination processes in the solar device, especially at interfaces, EIS measurements have been carried out. Fig.7 a,b shows the impedance spectra of CdS seeded SILAR– and CBD–CdSe cells recorded under dark at an applied forward bias of -0.6 V. The EIS curves were fitted in terms of the equivalent circuit depicted in the inset of Fig. 7a. R_s accounts for the sheet resistance of FTO and the contact resistance between FTO and TiO_2 , and two typical semicircles in the Nyquist plot of QDSCs corresponded to the redox reaction

at the counter electrode/electrolyte interface at high frequencies (R_1 , smaller semicircle), and the electron transfer at the $\text{TiO}_2/\text{QDs}/\text{electrolyte}$ interface at medium frequencies (R_2 , bigger semicircle), respectively.^{29,42,44,45} The fitting results of R_s , R_1 and R_2 for QDSCs based on EIS measurements are presented in Table 2. In consideration of the same counter electrode and electrolyte employed in our experiments, R_1 exhibits no apparent differences for CdS seeded SILAR- and CBD-CdSe cells as shown in Fig. 7a; while for our interest, we would like to draw attention to the most conspicuous difference between the two cells, i.e., R_2 , which reflects the charge recombination corresponding to the k_b and k_r processes illustrated in Fig. 6a. The R_2 of CdS/CBD-CdSe cell is 93.3 Ω , which is more than twice that of CdS/SILAR-CdSe cell (40.2 Ω). The fact revealed that, compared to CdS/SILAR-CdSe, electrons in CdS/CBD-CdSe photoanode are more difficult to recombine with the electrolyte redox couple (S^{2-}/S_n^{2-}) in view of the higher R_2 value. As the same counter electrode, electrolyte and TiO_2 film were employed in both cells, the value difference of R_2 should be closely associated with the deposition status of QDs onto the TiO_2 surface, which could give rise to different charge transport and recombination characteristics. Evidently, the full conformal coverage of QDs on TiO_2 achieved by CdS seeded CBD technique attributes to the reduction of the contact area of TiO_2 with the electrolyte and thus leads to the suppressed charge recombination and enhanced electron transport in the device. Fig. 7b gives the bode plots of the impedance spectra. The electron lifetime (τ_n) in the TiO_2 can be evaluated by the peak frequency at the minimum phase angle in the Bode plot based on the following

equation:^{45–47}

$$\tau_n = \frac{1}{\omega_{\text{peak}}} = \frac{1}{2\pi f_{\text{peak}}} \quad (2)$$

The estimated electron lifetime of CdS/CBD–CdSe cell is up to 79.6 ms, much longer than that of 50.4 ms for CdS/SILAR–CdSe cell. Apparently, the long-lived charge carrier implies a suppressed charge recombination, and ensures the efficient collection of electrons at the FTO substrate.

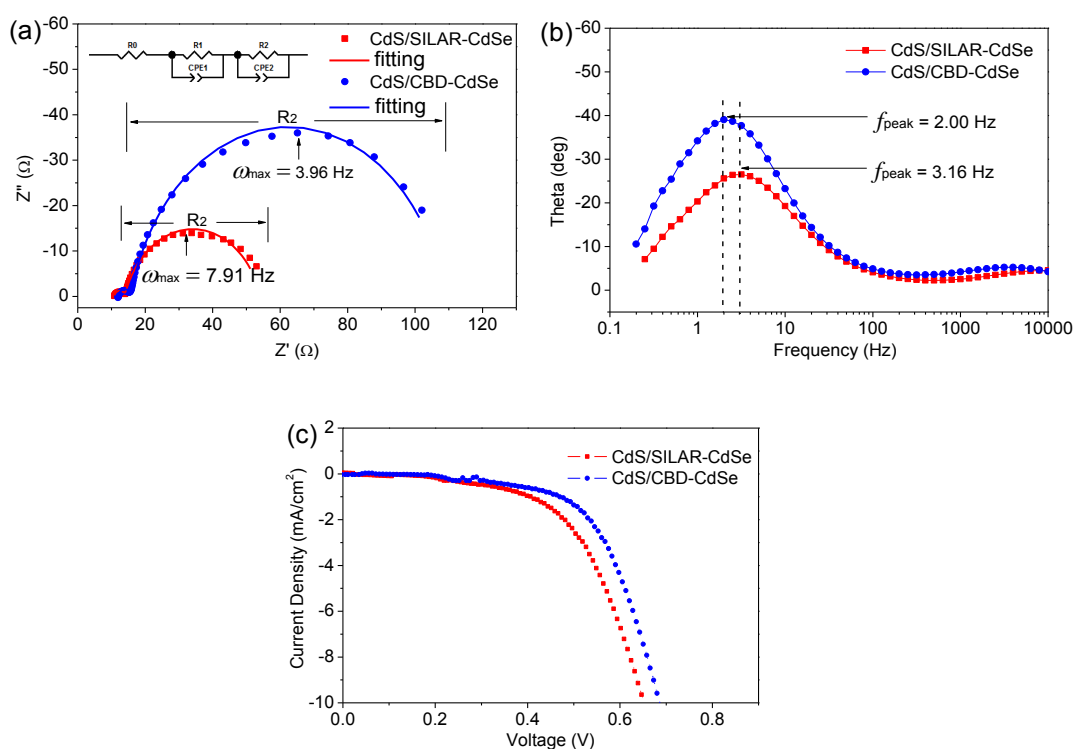


Fig. 7 (a) Nyquist plots and (b) Bode plots of EIS spectra of CdS seeded SILAR– and CBD–CdSe cells recorded under dark at an applied forward bias of -0.6 V, and (c) J – V characteristics of CdS seeded SILAR– and CBD–CdSe QDSCs measured under dark condition.

Table 2 Electrochemical impedance results of CdS seeded SILAR- and CBD-CdSe QDSCs under dark at an applied forward bias of -0.6 V

| sample | R_s (Ω) | R_1 (Ω) | R_2 (Ω) | τ_n (ms) |
|----------------|--------------------|--------------------|--------------------|---------------|
| CdS/SILAR-CdSe | 11.26 | 3.2 | 40.2 | 50.4 |
| CdS/CBD-CdSe | 11.92 | 3.9 | 93.3 | 79.6 |

Based on the discussions above, it is concluded that CdS/CBD-CdSe delivers a superior ability, compared to that of CdS/SILAR-CdSe, in inhibiting the charge recombination from TiO_2 back to the redox couple (S^{2-}/S_n^{2-}) in the electrolyte, arising from the full conformal coverage of QDs onto the TiO_2 surface. The suppression of interfacial charge recombination results in high V_{oc} and large FF. Moreover, the inference is further supported by the $J-V$ characteristics measured under dark condition (shown in Fig. 7c), which shows a smaller dark current for the CdS/CBD-CdSe cell than that of CdS/SILAR-CdSe cell.

4. Conclusions

The present work has demonstrated the appreciable influences of deposition strategies, i.e., SILAR and CBD, on the assembly of QDs on mesoporous films and the performance of the resultant QDSCs. The photovoltaic characteristics of CdSe sensitized TiO_2 solar cells vary considerably depending on the synthesis strategy and deposition parameters. Optical measurement and microscopic examination of the QDs-deposited films revealed that, compared to CdS seeded SILAR only capable of less than full coverage, CdS seeded CBD could deliver a high loading and full

conformal coverage of CdSe QDs onto the TiO₂, which contributed to the improvement of cell performance. On one hand, high loading of QDs secures efficient photon capturing, benefitting for the increase of J_{sc} ; on the other hand, the full conformal coverage of QDs suppresses the interfacial charge recombination, so as to enhance V_{oc} and FF. Eventually, an overall PCE of 4.85% has been reached for CdS/CBD–CdSe cells, which remarkably outperformed that of CdS/SILAR–CdSe cells (PCE = 3.89%). This work emphasizes the importance of the interface engineering in QDSCs and performance improvements are promisingly expected through further optimization and development of manufacturing procedures of solar devices.

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Supporting information

Schematic illustrations of the typical procedures for SILAR and CBD processes to deposit CdSe QDs. $(Ah\nu)^2$ vs $h\nu$ plots for determining the absorption onsets, effective band gap and band gap shift of CdSe QDs obtained. Scheme illustrating the

dependence of energy difference between the CB on QD size for CdS seeded SILAR–CdSe and CBD–CdSe, and the electron transfer from the CdSe QDs with different sizes into TiO₂. Experimental details and typical survey of XPS measurements, and surface compositions of CdS/SILAR–CdSe and CdS/CBD–CdSe sensitized TiO₂ electrode obtained from XPS analysis. This material is available free of charge via the Internet at <http://pubs.rsc.org>.

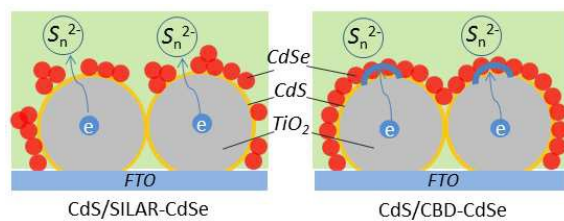
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