Efficiency Enhancement of Solid-State CuInS$_2$ Quantum Dot-Sensitized Solar Cells by Improving the Charge Recombination

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**Abstract**

Copper indium sulfide quantum dots (CuInS$_2$ QDs) were incorporated into a nanocrystalline TiO$_2$ film by using spin coating-assisted successive ionic layer adsorption and reaction process to fabricate CuInS$_2$ QD-sensitized TiO$_2$ photoelectrodes for the solid-state quantum dot-sensitized solar cell (QDSSC) applications. The result shows that the photovoltaic performance of solar cell is extremely dependent on the number of cycles, which has an appreciable impact on the coverage ratio of CuInS$_2$ on the surface of TiO$_2$ and the density of surface defect states. In the following high-temperature annealing process, it is found that annealing TiO$_2$/CuInS$_2$ photoelectrode at a suitable temperature would be beneficial for decreasing the charge recombination and accelerating the charge transport. After annealing at 400 °C, a significantly enhanced photovoltaic properties of solid-state CuInS$_2$ QDSSCs are obtained, achieving the power conversion efficiency (PCE) of 3.13%, along with an open-circuit voltage ($V_{oc}$) of 0.68 V, a short-circuit photocurrent density ($J_{sc}$) of 11.33 mA cm$^{-2}$, and a fill factor (FF) of 0.41. The enhancement in the performance of solar cells is mainly ascribed to the suppression of charge recombination and the promotion of the electron transfer after annealing.

**Keywords:** CuInS$_2$ quantum dots, Solar cells, Charge recombination, Electron transfer

**Background**

Owing to the merits of multiexciton generation and tunable band gap, quantum dot-sensitized solar cells (QDSSCs) have been considered as one of the ideal candidates for the new generation solar cells [1–4]. For the improvement of power conversion efficiency, it is essential to select a semiconductor material with the proper band gap. CuInS$_2$ (CIS) is a direct band gap I-III-VI$_2$ semiconductor compound with a near-optimal bulk band gap (1.5 eV) and has many advantageous features including the higher absorption coefficient (10$^5$ cm$^{-1}$), non-toxicity, and excellent stability [5–7]. To date, it has been demonstrated as a promising photosensitizer which has been successfully used in the field of QDSSCs [8–12].

The deposition process of QDs has a significant impact on the photovoltaic properties. As we have known, there are two major QD deposition approaches, i.e., the direct growth and post-synthesis assembly. Most of the researches are focused on the post-synthesis assembly method to fabricate solar cells [13–15]. For example, Wang et al. [16] controlled the Cu/In non-stoichiometric ratios of CIS QDs, achieving a PCE of 8.54%, which was a high efficiency for the CIS-based solar cells. Zhong’s group [17] explored an alloyed Zn-Cu-In-Se (ZCISe) QD sensitizer and deposited ZCISe and CdSe QDs on mesoporous TiO$_2$, which achieved a PCE of 12.75%. However, this method suffers from the small loading amount of QDs and the disadvantageous status of electronic coupling between QD and TiO$_2$. To increase the QD loading and enhance the ability of efficient electron transfer to TiO$_2$, QDs could be directly grown on mesoporous TiO$_2$ film by successive ionic layer adsorption and reaction (SILAR) [18–20]. Furthermore, developing a strategy to accelerate the charge transport and enhance the device stability could greatly enhance the photovoltaic performance and versatility of QD-sensitized TiO$_2$ electrodes. It has been realized that the solid-state cell device architecture is desirable to retard the deterioration of long-term stability associated with liquid electrolytes [21,
Despite the promise of solid-state cells, the efficiencies reported to date were lower. In the earlier reports, So and co-workers [23] fabricated a non-annealed heterojunction solar cell with a PCE of 1.16% by incorporating colloidal CIS nanocrystals into porous TiO$_2$ network. Zhou et al. [24] introduced In$_2$S$_3$ buffer layer into the solar cell based on CuInS$_2$, achieving a PCE of 1.06%. Chang et al. [25] developed the Cu$_2$S-CuInS$_2$-ZnS solid-state QDSSCs with a PCE of 2.52% through the SILAR process. The performance of such devices commonly gets worse due to the recombination between TiO$_2$ and hole conductor, which is faster than the analogous process in the devices with liquid electrolyte. A significant approach used to decrease recombination and increase efficiency is to modify the QDs absorber or TiO$_2$ photoanode, e.g., through increasing the loading amount of QDs, doping QDs to optimize the interfacial band alignment, or using of passivation layer.

In a previous study, we succeeded in fabricating solid-state devices using CuInS$_2$ quantum dot-sensitized TiO$_2$ photoanodes through SILAR method [26]. Herein, to further improve the efficiency of the device, we fabricated the solid-state solar cell by introducing CIS QDs into TiO$_2$ mesoporous layer through spin coating-assisted SILAR process, completely filling QDs in the pores of TiO$_2$ mesoporous layer. Through optimization of QD-sensitized TiO$_2$ films by using the precise deposition based on SILAR, together with the annealing treatment for the photoelectrodes, the solar cell consequently exhibits a PCE of 3.13%. As far as we know, this result is one of the best performances of CIS-based solid-state QDSSCs.

**Methods**

**Materials**

Indium acetate (In(OAc)$_3$, 99.99%) was purchased from Alfa Aesar. Copper(II) chloride dihydrate (CuCl$_2$·2H$_2$O, 99.99%), sodium sulfide nonahydrate (Na$_2$S·9H$_2$O, 99.9%), titanium isopropoxide (99.9%), hydrochloric acid (HCl, 37% in water), 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMe-TAD, 99.5%), chlorobenzene (anhydrous, 99.8%), 4-tert-Butylpyridine (tBP), bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI), and acetonitrile (anhydrous, 99.8%) were purchased from Sigma-Aldrich. TiO$_2$ paste (DSL 18NR-T) was obtained from Dyesol. All of the chemicals were utilized directly without further purification. Ultrapure deionized water was used for the preparation of aqueous solutions.

**Preparation**

A TiO$_2$ compact layer with a thickness of 70 nm was fabricated by spin-coating on the cleaned FTO glass at 4000 rpm for 30 seconds, using titanium isopropoxide (350 μL)
and HCl (35 μL) diluted in ethanol (5 mL) as the precursor solution. The film was then annealed in the air starting at room temperature with 100 °C increments, holding for 10 min at each increment. At 500 °C, the film was annealed for an hour and then allowed to cool naturally. Next, the TiO₂ mesoporous layer was fabricated by spin-coating the diluted 18NR-T paste on the compact layer at 800 rpm for 10 s, followed by a heat treatment to achieve a 2-μm thickness layer.

CIS QD-sensitized TiO₂ thin film was prepared by spin coating-assisted SILAR. 80 μL of a mixture of 25 mM CuCl₂ and 50 mM In(OAc)₃ was dropped on the TiO₂ mesoporous layer and then spin-coated at 800 rpm for 20 s. Subsequently, 80 μL of 100 mM Na₂S was dropped and followed by spin-coating at 800 rpm for 20 s. The two steps were denoted as one cycle. Between each step, the film should be rinsed with deionized water and dried by N₂. In order to enhance the crystallinity of CIS QDs, the photoelectrodes were annealed under nitrogen atmosphere at 200–500 °C for 30 min. Subsequently, the hole transport material (HTM) was spin-coated under N₂ atmosphere by using a solution with a proper concentration of 300 mg of spiro-OMeTAD, 2.91 μL of chlorobenzene, 28.77 μL of tBP, and 126 μL of Li-TFSI. Finally, gold was deposited by thermal evaporation as a counter electrode and the active area of 0.09 cm² was defined.

### Characterization

UV-vis absorption spectra were recorded on a UV-vis spectrophotometer (Perkin Elmer Lambda 950). Cross-sectional scanning electron microscopy (SEM) was characterized by FEI nova nano SEM450. The elemental mappings were characterized by an ORBIS energy dispersive spectroscopy (EDS), an accessory of the SEM. The current density-voltage (J-V) measurements for solar cells were carried out under the illumination of a solar simulator equipped with a 300 W xenon lamp (Model No. XES-10051, SAN-EL, Japan) under the standard test conditions (25 °C, AM1.5, 100 mW·cm⁻²). The incident photon-to-current conversion efficiency (IPCE) was measured by an Enlitech QER3011 system equipped with a 150 W xenon light source. Electrochemical impedance spectroscopy (EIS) was carried out on an electrochemical workstation (Zahner, Zennium) under dark conditions at different forward biases from −0.1 to −0.5 V, applying a 20-mV AC sinusoidal signal over the constantly applied bias with the frequency ranging from 1 to 0.1 Hz. Time-resolved photoluminescence (TRPL) was employed by PL Spectrometer (Edinburgh Instruments, FLS 900), excited with a picosecond pulsed diode laser (EPL 445) at a wavelength of 543 nm.

### Results and Discussion

A schematic of the device architecture is shown in Fig. 1, incorporating with the cross-sectional SEM image covered by false colors to distinguish the different layers prepared in the device. The uniform distribution of particles and superior contact between interfaces can improve the electrical conductivity of thin films that would enhance the charge carrier transfer [27–29]. The elemental mapping of CIS-sensitized TiO₂ mesoporous film electrode is also performed through energy dispersive X-ray (EDX) analysis, providing clear evidence to prove the uniform distribution of CIS throughout the film.

The procedure of fabricating CIS QD-sensitized TiO₂ photoelectrodes in our work is schematically illustrated...

![Fig. 3](image-url)  
**Fig. 3** a UV-vis absorption spectra of CIS QD-sensitized TiO₂ film prepared by spin coating-assisted SILAR with different cycles. The inset is the photographs of the corresponding photoelectrode films. b J-V curves of QDSSCs prepared at different cycles.
in Fig. 2. It is worth pointing out that the spin coating-assisted SILAR method adopted in this work can control the amount of QD depositions accurately. The amount of CIS QDs incorporated in the mesoporous TiO$_2$ layer was evaluated using the UV-vis absorption spectra. Figure 3a shows the variation of spectra with different spin coating-assisted SILAR cycles. After four cycles performed, only a much smaller amount of CIS QDs is deposited in TiO$_2$ film, as indicated by the lower absorbance of TiO$_2$/CIS photoelectrode. An increase in the number of cycles results in an increase of absorbance and a slight red shift of the absorption onset, corresponding to the color change of photoelectrodes from dark yellow to black, as shown in the inset of Fig. 3a. Subsequently, we fabricated and characterized the photovoltaic devices with TiO$_2$/CIS photoelectrodes.

Figure 3b shows the J-V curves of CIS QDSSCs. With increasing the number of spin coating-assisted SILAR cycles, both $J_{SC}$ and PCE gradually increase from 2.49 mA cm$^{-2}$ and 0.14% for 4 cycles to 4.21 mA cm$^{-2}$ and 0.75% for 20 cycles, and then decrease to 4.05 mA cm$^{-2}$ and 0.72% for 24 cycles, respectively, as clearly revealed in Table 1. This result demonstrates that the cycle process in the initial stage aims to increase the coverage of CIS QDs through refilling the uncovered areas in TiO$_2$ mesoporous layer. It is no doubt that an enhancement of QD loading amount and a formation of QDs monolayer on the surface of TiO$_2$ photoanode are advantageous to generate much more excited electrons under light illumination, which would increase the photocurrent of solar cells [30]. Moreover, a higher surface coverage for TiO$_2$ is achieved with the increase of CIS QDs loading amount. The decrease of surface areas exposed directly to the HTM is favorable for the suppression of charge recombination process occurring at TiO$_2$/HTM interface, thus leading to a dramatic increase of $V_{OC}$ and an improvement of FF, especially in the early cycles. However, the thickness of the CIS layer could continuously increase after each spin coating-assisted SILAR cycle owing to the additional QD loadings. Because of the increased generation probability of charge recombination in CIS layer, the process of transporting photogenerated electrons from the QD layers to the TiO$_2$ matrix will become more difficult, as shown in the schematic drawing of Fig. 4. The electrons in the QD conduction band (CB) can be trapped by the surface defect states [31, 32], which serve as the recombination
centers, eventually giving a deterioration of the device. Meanwhile, the undesirable recombination path of the electrons in QD CB and the holes in QD VB could hinder the electron injection from CIS into TiO$_2$ as well. Therefore, after the evaluation and verification of these effects, it clearly indicates that the ideal number of cycles (20) should be performed for the deposition CIS QDs in this work.

Afterward, the influence of annealing treatment on the performance of photovoltaic devices is evaluated. Figure 5 presents the evolution of the absorption of CIS QD-sensitized TiO$_2$ films with different annealing temperatures. It is found that the absorption is improved gradually with increasing the annealing temperature. The absorbance gets to a saturation value at the temperature of 400 °C. Simultaneously, excessive annealing treatment would deteriorate CIS QD sensitizer due to the occurrence of aggregation and oxidation [33]. It results in a decrease in absorbance when the annealing temperature is further elevated to 500 °C. Therefore, it is inferred that an excessive increase of annealing temperature (> 400 °C) is disadvantageous to the performance of solar cells, unfortunately causing a significant decline in $J_{SC}$ and PCE. So the film annealed at 400 °C exhibits the best photovoltaic performance as compared with the other three samples. To assess the light absorption and the electron generation characteristics, IPCE spectra are shown in Fig. 6b. It exhibits a strong photoresponse with a value of 66% in the visible wavelength range between 400 and 550 nm for QDSSCs with the annealing temperature of 400 °C, with nearly 20% enhancement compared to that of 200 °C. The higher IPCE response generally ascribed the outstanding absorptivity of QDs in the spectral region. According to the spectral, it can be found that a wider response wavelength range and a higher IPCE value appeared, which is in accordance with the variation tendency of $J_{SC}$ as observed in J-V measurement. The result could be supported by the interpretation that the proper annealing treatment is potentially more favorable for the formation of an enforced interface connection between CIS and TiO$_2$, thus leading to the effective electron transfer in QDSSCs [34].

To analyze the transfer and recombination process of charge carrier, the devices are further investigated by EIS. Figure 7a displays the Nyquist plot of the obtained EIS results at $-0.4$ V bias, and the fitted values evaluated from the equivalent circuit are listed in Table 3, where the electron lifetime can be estimated by $\tau_n = R_r \times C_{\mu}$ [35–37]. At the HTM/counter electrode interface, the charge transfer resistance $R_{ct}$ which is related to the

| Temperatures | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | FF | PCE (%) |
|--------------|-------------|-----------------|-----|--------|
| 200 °C       | 0.50        | 5.63            | 0.37| 1.04   |
| 300 °C       | 0.53        | 7.76            | 0.41| 1.68   |
| 400 °C       | 0.68        | 11.33           | 0.41| 3.13   |
| 500 °C       | 0.68        | 8.58            | 0.42| 2.44   |
high-frequency semicircles presents no obvious differences, while the same HTM and counter electrode were employed in the present QDSSCs. The simulated datum of recombination resistance $R_r$ which is related to the low-frequency semicircles represents the electron transfer process at photoelectrode/HTM interface. This datum for QDSSCs with TiO$_2$/CIS photoelectrode annealed at 400 °C is larger as compared with the others, which is attributed to the suppressed interfacial recombination, resulting in an enhanced $V_{OC}$. Furthermore, the long-lived charge carriers could favor the improvement of charge collection efficiency, thereby contributing to the significant progress in IPCE and $J_{SC}$ [6]. According to Table 3, in the present case, the TiO$_2$/CIS photoelectrode annealed at 400 °C is indicated to remain the highest value of $\tau_n \sim 117$ ms, thus yielding the highest value of $J_{SC}$ as observed in the J-V measurement. Nevertheless, $\tau_n$ falls to $\sim 78$ ms when the higher temperature of 500 °C was applied. The $V_{app}$-dependent $C_\mu$ and $R_r$ extracted from EIS measurements are illustrated in Fig. 7b and c, respectively. $C_\mu$ increases exponentially with the $V_{app}$, as expected from the theoretical basis. The similar $C_\mu$ values of all the cells illustrate that different annealing temperatures do not produce a shift on the position of TiO$_2$ CB [38, 39]. In addition, with increasing the temperature from 200 to 400 °C, the $R_r$ value is improved gradually. Since the recombination rate occurring at photoelectrode/HTM interface is inversely proportional to $R_r$ [39], the greater value of $R_r$ means the reduced recombination rate occurring in the solar cell based on TiO$_2$/CIS photoelectrode annealed at 400 °C. Overall, from these EIS results, it can be concluded that the cell devices show a large recombination rate rather than a shift of TiO$_2$ CB. It also supports the lower recombination rate and longer electron lifetime for the solar cell based on TiO$_2$/CIS photoelectrode annealed at 400 °C, which is conducive to the enhanced $V_{OC}$, $J_{SC}$, and FF values for cells undergoing annealing treatment on photoelectrodes as observed in the J-V curves.

In order to further clarify the effect of annealing temperature on charge transfer, the time-resolved transient photoluminescence (TRPL) spectra of the samples are displayed in Fig. 8. It can be seen that the PL lifetime of the photoanode significantly decreases with the increase of the annealing temperature, which indicates that more electrons could transfer from CIS to TiO$_2$ efficiently, reducing the probability of internal photogenerated carrier recombination inside QDs to some extent. According to the calculation of the rate of electron transfer ($k_{et}$) [40, 41], it can be observed that the solar cell based on TiO$_2$/CIS photoelectrode annealed at 400 °C has the higher $k_{et}$ value of $1.17 \times 10^7$ s$^{-1}$, thus providing excellent charge transfer performance of QDSSCs. Consequently, it provides further evidence to support that the proper annealing treatment is potentially more favorable for obtaining an effective connection at TiO$_2$/QDs interfaces [33], which is extremely beneficial for the transport of charge carrier in QDSSCs, thereby leading to a higher efficiency.

### Table 3

| Temperatures | $R_s$ (Ω) | $R_{ct}$ (Ω cm$^2$) | CPE (mF/cm$^2$) | $R_r$ (Ω cm$^2$) | $C_\mu$ (mF/cm$^2$) | $\tau_n$ (ms) |
|--------------|-----------|-------------------|----------------|----------------|-------------------|----------------|
| 200 °C       | 67.87     | 11.88             | 0.40           | 153            | 0.12              | 18             |
| 300 °C       | 65.58     | 17.17             | 0.50           | 329            | 0.14              | 46             |
| 400 °C       | 60.68     | 16.66             | 0.40           | 618            | 0.19              | 117            |
| 500 °C       | 64.36     | 15.68             | 0.44           | 495            | 0.16              | 79             |

Fig. 7 a EIS spectra of the cell devices measured in the dark at $-0.4$ V bias. The inset in a illustrates the equivalent circuit simulated to fit the impedance spectra. $R_s$ represents the substrate resistance. $R_{ct}$ and CPE represent the charge transfer resistance and capacitance at the HTM/counter electrode interface, respectively. $R_r$ and $C_\mu$ represent the recombination resistance and chemical capacitance at the photoelectrode/HTM interface, respectively. b $C_\mu$ and c $R_r$ at different applied voltages ($V_{app}$), calculated from the fitting of the impedance spectra.
Conclusions

In summary, CIS QD-sensitized TiO$_2$ films were obtained by the spin coating-assisted SILAR method and further used as the promising photoelectrodes for solid-state QDSSCs. The spin coating-assisted SILAR method can control the amount of QD deposition accurately. Increasing the number of cycles could enhance the absorption ability, leading to more electrons generated under light illumination. The charge recombination process occurring at TiO$_2$/HTM interface would be suppressed with the increase in the QD loading amount as well. However, there would appear the undesirable recombination pathways in the thicker CIS layer due to the excessive increase in the number of cycles, which is extremely detrimental to the device performance. The following high-temperature annealing treatment plays a critical role in enhancing the contact between CIS QDs and TiO$_2$ photoanode and reducing the probability of internal photogenerated carrier recombination. According to J-V characteristics and EIS results, the most suitable annealing temperature for TiO$_2$/CIS photoelectrode film should be 400 °C, which shows the highest efficiency of 3.13% and the longest electron lifetime of 117 ms. IPCE of 66% between 400 and 550 nm and $k_{et}$ of $1.17 \times 10^7 \text{s}^{-1}$ are also achieved with the solid-state QDSSCs. This work may enlighten the way to fabricate the other kinds of sensitized photoelectrodes with high photovoltaic performance, and the next work will focus on improving the stability of cell devices.

Abbreviations

CB: Conduction band; CIS QDs: Copper indium sulfide quantum dots; EDS: Energy dispersive spectroscopy; EIS: Electrochemical impedance spectroscopy; FF: Fill factor; IPCE: Incident photon-to-current conversion efficiency; $J_{SC}$: Short-circuit photocurrent density; PCE: Power conversion efficiency; QDSSCs: Quantum dot-sensitized solar cells; SEM: Scanning electron microscopy; SILAR: Successive ionic layer adsorption and reaction; TRPL: Time-resolved photoluminescence; VB: Valence band; $V_{OC}$: Open-circuit voltage.

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Availability of Data and Materials

All the data are fully available without restrictions.

Authors’ Contributions

YL supervised the whole project and interpreted the results. FB performed the experiments and data analysis. DC classified and analyzed the reference papers. All authors contributed to the general discussion. All authors read and approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

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References

1. Kamat PV, Trvdy K, Baker DR, Radich IG (2010) Beyond photovoltaics: semiconductor nanoarchitectures for liquid-junction solar cells. Chem Rev 110:6664–6688
2. Green MA, Bremner SP (2017) Energy conversion approaches and materials for high-efficiency photovoltaics. Nat Mater 16:23–34
3. Nozik AJ, Beard MC, Luther JM, Law M, Ellingson RJ, Johnson JC (2018) Semiconductor quantum dots and quantum dot arrays and applications of multiple exciton generation to third-generation photovoltaic solar cells. Chem Rev 110:6873–6890
4. Zhou R, Yang Z, Xu J, Cao G (2018) Synergistic combination of semiconductor quantum dots and organic-inorganic halide perovskites for hybrid solar cells. Coord Chem Rev 374:279–313
5. Peng Z, Liu Y, Zhao Y, Chen K, Cheng Y, Kovalen VL, Chen W (2014) ZnSe passivation layer for the efficiency enhancement of CuInS$_2$ quantum dot sensitized solar cells. J Alloys Compd 587:613–617
6. Pan Z, Morasero I, Shen Q, Zhang H, Li Y, Zhao K, Wang J, Zhong X (2014) Bisquert J. High-efficiency “Green” quantum dot solar cells. J Am Chem Soc 136:9203–9210
7. Arici E, Sariciftci NS, Meissner D (2003) Hybrid solar cells based on nanoparticles of CuInS$_2$ in organic matrices. Adv Funct Mater 13:165–171
8. Ilayaraja P, Rakesh B, Das TK, Moehrer PSV, Sudakar C (2018) CuInS$_2$ quantum dot sensitized solar cells with high $V_{OC} \approx 0.9 \text{V}$ achieved using microsphere-nanoparticulate TiO$_2$ composite photoanode. Sol Energy Mater Sol Cells 178:208–222
9. Meng W, Zhou X, Qiu Z, Liu C, Chen JI, Yue W, Wang M, Bi H (2016) Reduced graphene oxide-supported aggregates of CuInS₂ quantum dots as an effective hybrid electron acceptor for polymer-based solar cells. Carbon 96:532–540
10. Deng C, Fu B, Wang Y, Yang L (2018) Fabrication of water-soluble CuInS₂ quantum dots by hot-injection method and phase transfer strategy. Nano Energy 13:8150114
11. Higashimoto S, Murano M, Arase T, Mukai S, Azuma M (2017) Takahashi M. Highly qualified copper-indium sulfide colloids prepared in water under microwave irradiation and their applications to the TiO₂-based quantum dot-sensitized solar cells. Sol Energy Mater Sol Cells 169:203–209
12. Xing H, Zhang Q, Huang X, Li D, Luo Y, Meng Q (2011) Aqueous colloidal CuInS₂ for quantum dot sensitized solar cells. J Mater Chem 21:15903–15905
13. Sixto G, Ván M, Lorena M, Nestor G, Teresa LV, Roberto G, Diguna LJ, Qing S, Taro T, Juan B (2009) Improving the performance of colloidal quantum-dot-sensitized solar cells. Nanotechnology 20:295204
14. Malak ST, Lafalce E, Jung J, Lin CH, Smith MJ, Yoon YJ, Smith MJ, Vardeny ZV, Malak ST, Lafalce E, Jung J, Lin CH, Smith MJ, Yoon YJ, Smith MJ, Vardeny ZV (2016) Significantly enhanced energy conversion efficiency of CuInS₂ quantum dot sensitized solar cells based on multiple exciton generation. Nano Energy 7:15–25
15. Wang W, Feng W, Du J, Xue W, Wang W, Feng W, Du J, Xue W, Zhong X (2018) Cosensitized quantum dot solar cells with conversion efficiency over 12%. Adv Mater 30:705746
16. Li TL, Lee Y, Teng H (2012) High-performance quantum dot-sensitized solar cells based on sensitization with CuInS₂ quantum dots/CdS heterostructure. Energy Environ Sci 5:5315–5324
17. Zhang X, Liu J, Johansson EMJ (2015) Efficient charge-carrier extraction from Ag₂S quantum dots prepared by the SILAR method for utilization of multiple exciton generation. Nanoscale 7:1454–1462
18. Sun L (2016) Employing ZnS as a capping material for PbS quantum dots and bulk heterojunction solar cells. Sci China Mater 59:817–824
19. Deng C, Fu B, Wang Y, Yang L (2018) Fabrication of water-soluble CuInS₂ quantum dots by hot-injection method and phase transfer strategy. Nano Energy 13:8150114
20. Xing H, Zhang Q, Huang X, Li D, Luo Y, Meng Q (2011) Aqueous colloidal CuInS₂ for quantum dot sensitized solar cells. J Mater Chem 21:15903–15905
21. Sixto G, Ván M, Lorena M, Nestor G, Teresa LV, Roberto G, Diguna LJ, Qing S, Taro T, Juan B (2009) Improving the performance of colloidal quantum-dot-sensitized solar cells. Nanotechnology 20:295204
22. Park JP, Heo HJ, Im SH, Kim S-W (2016) Highly efficient solid-state mesoscopic PbS with embedded CuS quantum dot-sensitized solar cells. J Mater Chem A 4:1461–1468
23. So D, Pradhan S, Konstantatos G (2016) Solid-state colloidal CuInS₂ quantum dot solar cells enabled by bulk heterojunctions. Nanoscale 8:16776–16785
24. Zhou Z, Yuan S, Fan J, Hou Z, Zhou W, Du Z, Wu S (2012) CuInS₂ quantum dot-sensitized TiO₂ nanorod array photoelectrodes: synthesis and performance optimization. Nanoscale Res Lett 7:652–653
25. Chang JY, Su LF, Li CH, Chang CC, Lin JM (2012) Efficient “green” quantum dot-sensitized solar cells based on CuS:CuInS₂:ZnSErSe architecture. Chem Commun (Camb) 48:4848–4850
26. Yang L, Ma Y, Liu J, Mai Y (2016) Improving the performance of solid-state quantum dot-sensitized solar cells based on TiO₂/CuInS₂ photoelectrodes with annealing treatment. RSC Adv 6:92869–92873
27. Gratzel M (2005) Solar energy conversion by dye-sensitized photovoltaic cells. Inorg Chem 44:6891–6891
28. Zhao H, Huang F, Hou J, Liu Z, Wu Q, Cao H, Jing Q, Peng S, Cao G (2016) Efficiency enhancement of quantum dot sensitized TiO₂/ZnO nanorod arrays solar cells by plasmonic Ag nanoparticles. ACS Appl Mater Inter B 26675–26682
29. Evangelista RM, Makuta S, Yonezu S, Andrews J, Tachibana Y (2016) Semiconductor quantum dot sensitized solar cells based on ferricyanide/ferrocyanide redox electrolyte reaching an open circuit photovoltage of 0.8 V. ACS Appl Mater Inter B 8:13957–13965
30. Li W, Zhong X (2015) Capping ligand-induced self-assembly for quantum dot sensitized solar cells. J Phys Chem Lett 6:796–806
31. Li L, Pandey A, Werder DJ, Khanal BP, Petyeja GM, Klimov VI (2011) Efficient synthesis of highly luminescent copper indium sulfide-based core/shell nanocrystals with surprisingly long-lived emission. J Am Chem Soc 133:1176–1176
32. Zhao K, Pan Z, Zhong X (2016) Charge recombination control for high efficiency quantum dot sensitized solar cells. J Phys Chem Lett 7:406–417
33. Pan Z, Zhang H, Cheng K, Hou Y, Hua J, Zhong X (2012) Highly efficient inverted type-I CdS/CdS e core/shell structure QD-sensitized solar cells. ACS Nano 6:3982–3991
34. Fan S, Kim D, Kim J, Jung D, Kang S, Ko J (2009) Highly efficient CdSe quantum dot-sensitized TiO₂ photoelectrodes for solar cell applications. Electrochim Commun 11:1337–1339
35. Yu X, Liao J, Qiu K, Kuang D, Su C (2011) Dynamic study of highly efficient CdS/CdSe quantum dot-sensitized solar cells fabricated by electrodeposition. ACS Nano 5:9494–9500
36. Yang L, Zhou R, Lan J, Zhang Q, Cao G, Zhu J (2014) Efficient band alignment for ZnₓCd₁–ₓSe QD-sensitized TiO₂ solar cells. J Mater Chem A 2:3669
37. Yang L, Mccue C, Zhang Q, Uchaker E, Mai Y, Cao G (2015) Highly efficient quantum dot-sensitized TiO₂ solar cells based on multilayered semiconductors (ZnSe/CdS/CdSe). Nanoscale 7:3173–3180
38. Boix PP, Larramona G, Jacob A, Delatouche B, Mora-Seró I, Bisquert J (2012) Hole transport and recombination in all-solid Sb₂S₃-sensitized TiO₂ solar cells using CuSCN as hole transporter. J Phys Chem C 116:1579–1587
39. Zarazúa I, Espada P, López-Luke T, Ceja-Fdez A, Reyes-Gomez J, Mora-Seró I, de la Rosa E (2016) Effect of the electrophoretic deposition of Au NPs in the performance CdSe QDs sensitized solar cells. Electrochim Acta 188:710–717
40. Kongkanand A, Tvrde K, Takechi K, Kuno M, Kamat PP (2008) Quantum dot solar cells. Tuning photoresponse through size and shape control of CdSe-TiO₂ architecture. J Am Chem Soc 130:4007–4015
41. Rebeld J, Kuno M, Kamat PP (2007) Size-dependent electron injection from excited CdSe quantum dots into TiO₂ nanoparticles. J Am Chem Soc 129:4136–4137