CuInS\textsubscript{2} quantum dot-sensitized TiO\textsubscript{2} nanorod array photoelectrodes: synthesis and performance optimization

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Abstract

CuInS\textsubscript{2} quantum dots (QDs) were deposited onto TiO\textsubscript{2} nanorod arrays for different cycles by using successive ionic layer adsorption and reaction (SILAR) method. The effect of SILAR cycles on the light absorption and photoelectrochemical properties of the sensitized photoelectrodes was studied. With optimization of CuInS\textsubscript{2} SILAR cycles and introduction of In\textsubscript{2}S\textsubscript{3} buffer layer, quantum dot-sensitized solar cells assembled with 3-\mu m thick TiO\textsubscript{2} nanorod film exhibited a short-circuit current density (I\textsubscript{sc}) of 4.51 mA cm\textsuperscript{-2}, an open-circuit voltage (V\textsubscript{oc}) of 0.56 V, a fill factor (FF) of 0.41, and a power conversion efficiency (\eta) of 1.06%, respectively. This study indicates that SILAR process is a very promising strategy for preparing directly anchored semiconductor QDs on TiO\textsubscript{2} nanorod surface in a straightforward but controllable way without any complicated fabrication procedures and introduction of a linker molecule.

Keywords: CuInS\textsubscript{2}, Quantum dots, TiO\textsubscript{2}, Nanorod arrays, Photoelectrochemical properties

Background

Since the introduction of an important advancement of using a nanostructured dye-sensitized photo-active electrode in a solar cell by O’Regan and Grätzel in 1991 [1], the dye-sensitized solar cells (DSSCs) have attracted a lot of attention in the past two decades and been considered as a potential low-cost alternative to conventional silica-based solar cells [2-5]. The latest energy conversion efficiency of DSSCs was reported to exceed 12% [6]. Further improvement of the efficiency of DSSCs is impeded by the design of new dyes which could absorb all photons above a threshold energy of 1.3 to 1.4 eV (roughly 940 to 890 nm) without affecting the injection efficiency and regeneration rate [7,8]. Another attractive strategy is to use semiconductor quantum dot (QD) as a substitute for organic dye [9-12]. For enhancement of the conversion efficiency, it is still necessary to select a semiconducting material with the proper band gap that absorbs strongly for photon energies above 1.3 eV. Ternary chalcopyrite CuInS\textsubscript{2}, which is a direct band gap semiconductor with Eg = 1.55 eV (bulk) has many favorable features including high absorption coefficient (10\textsuperscript{5} cm\textsuperscript{-1}) and proper band gap well matched to the solar spectrum [13,14], as well as non-toxicity and good stability. It has been demonstrated as a promising photosensitizer successfully used in quantum dot-sensitized solar cells (QDSSCs) [15,16].

Up to now, the reports on CuInS\textsubscript{2}-based QDSSCs are almost exploited a presynthesis method, in which the CuInS\textsubscript{2} colloidal QDs are presynthesized and anchored to the electrodes by means of bifunctional linker molecules or direct adsorption [16,17]. This process suffers from rather low QD loading and relatively weaker electronic coupling between QDs and TiO\textsubscript{2} [18]. Another approach for QD sensitization is direct growth of QDs on TiO\textsubscript{2} by successive ionic layer adsorption and reaction (SILAR), in which the ions in the precursor solution are adsorbed directly onto the bare surface of TiO\textsubscript{2} to form a very thin conformal covering film [19,20]. The SILAR process has recently emerged as the best method for adsorbing QDs onto TiO\textsubscript{2} electrodes, owing to its facile and reproducible preparation, high QD loading together with well controllable in size and density of the target semiconductor QDs, and efficient electron transfer to TiO\textsubscript{2}.
[18,20]. Very recently, Chang et al. have reported CuInS2 QD-sensitized TiO2 nanoparticle film by SILAR process [21]. For assembly of QDSSCs, one dimensional (1D) TiO2 nanostructure arrays possess the superiority over other nanomaterials due to its more open structure which was preferable for both sensitizer and electrolyte filling [22]. Moreover, 1D nanostructure can provide a direct and efficient pathway for electrons from sensitizer to conductive substrate compared to the disordered electron pathway in nanoparticles [23-26]. Therefore, TiO2 has been fabricated into various 1D nanostructure arrays such as nanowires (NWs), nanorods (NRs), and nanotubes for photovoltaic devices. Single-crystalline TiO2 NW or NR array is preferable over polycrystalline one in electron transfer because of electron scattering or trapping at grain boundaries of polycrystal [22]. However, the exploitation of CuInS2 QD-sensitized single-crystalline TiO2 NRs for QDSSCs has not been systematically investigated.

In this study, using the SILAR procedures, CuInS2 QDs were successfully assembled onto vertically oriented single-crystalline TiO2 nanorod array (NRA), which was grown directly onto transparent conductive fluorine-doped tin oxide (FTO) substrates. A detailed structural characterization and photoelectrochemical investigation of the CuInS2-sensitized TiO2 nanorod array photoelectrodes were discussed in this article. Furthermore, by introduction of a cadmium-free In2S3 buffer layer to adjust the interfacial properties of CuInS2 and TiO2, the photoelectrical properties of QDSSCs were remarkably improved.

**Methods**

**Materials**

Copper (II) sulfate (CuSO4, 99%), indium (III) sulfate (In2(SO4)3, 98.0%), sodium sulfide (Na2S, 98%), and titanium butoxide (97%) were purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. Potassium phosphate monobasic (KH2PO4, 99.99%), sodium hydroxide (NaOH, 98%), sodium sulfite (Na2SO3, 97%), and concentrated hydrochloric acid (HCl, 37% by weight) were obtained from Tianjin Chemical Reagents Company (Tianjin, China). All the materials were used directly without further purification. Triply deionized water (resistivity of 18.2 MΩ cm−1) was obtained from a Milli-Q ultrapure water system (EMD Millipore Corporation, MA, USA). FTO-coated glass slides (F: SnO2, 14 Ω/square, Nippon Sheet Glass Group, Tokyo, Japan) were thoroughly washed with a mixed solution of deionized water, acetone, and 2-propanol (volume ratios of 1:1:1) under sonication for 60 min.

**Synthesis of TiO2 NRAs**

The TiO2 NRAs were grown directly on transparent FTO substrates by a hydrothermal method; details of the synthesis procedure can be found in Liu and Aydil [27]. In a typical synthesis, 30 mL of concentrated HCl was added to 30 mL of deionized water with stirring. After 5 min of stirring, 1 mL of titanium butoxide was added dropwise to the solution and stirred continuously for another 5 min to obtain a clear transparent solution. The resulting solution was then transferred into a 120-mL Teflon-lined stainless-steel autoclave. Then, one piece of cleaned FTO glass was placed into the autoclave at an angle of about 45° against the wall of the Teflon lining with the conducting side facing down. Subsequently, the autoclave was sealed and placed inside an electronic oven. The hydrothermal synthesis was conducted at 150°C for 20 h, and the obtained TiO2 NRAs on FTO glass substrates were taken out of the cooled autoclave, rinsed extensively with distilled water, and finally dried in air.

**Fabrication of CuInS2 QD-sensitized TiO2 NRA electrodes**

CuInS2 QDs were attached to TiO2 NRAs by the SILAR process, which was similar to that described by Wu et al. [28]. Briefly, the TiO2 nanorod array substrate was dipped sequentially in aqueous solutions of 0.1 M In2(SO4)3 for 60 s, and S ion precursor solution (0.075 M Na2S, with pH equal to 11.3 adjusted by a buffer composed of 0.1 M KH2PO4 and 0.1 M NaOH) for 240 s, following in 0.01 M CuSO4 aqueous solutions for 20 s, and S ion precursor solution for 240 s. Between each dip, the films were rinsed with deionized water for 30 s to remove excess precursors and dried in air before the next dipping. Such an immersion procedure is termed as one cycle for copper indium sulfide deposition, and this immersion cycle was repeated several times until the desired amount of CuInS2 QDs was incorporated. To increase the crystallinity and the concentration of sulfur in the SILAR-deposited CuInS2, the samples were annealed in furnace under sulfur ambiance (using S powder as the S source) at 500°C for 30 min after SILAR deposition.

An In2S3 buffer layer was introduced between TiO2 and CuInS2 layer also by SILAR. For In2S3 deposition from their precursor solutions, 0.1 M indium nitrate in ethanol was used as cation source, and 0.1 M sodium sulfide in 1:1 methanol and water as anion source.

**Characterization**

The as-prepared CuInS2 QD-sensitized TiO2 NRA electrodes were characterized by various analytical and spectroscopic techniques. The morphology of the sample was studied by a field-emission scanning electron microscopy (FESEM, JSM-7001 F, JEOL Co., Ltd., Beijing, China). Transmission electron microscopy (TEM), and
high-resolution TEM (HRTEM) investigations were carried out by a JEOL JEM-2100(UHR) microscope operating at 200 kV. The samples were detached from the FTO substrate, then dispersed in ethanol by sonication, and dropped onto a carbon film supported on a copper grid. Structure characterizations of the CuInS2-sensitized TiO2 NRA films were conducted using X-ray diffraction (XRD). The XRD patterns were recorded using a Philips X’Pert PRO X-ray diffractometer (Royal Philips Electronics, Amsterdam, The Netherlands) with Cu Kα1 radiation (λ = 1.5406 Å) from 20 to 70° at a scan rate of 2.4° min⁻¹. X-ray tube voltage and current were set at 40 kV and 40 mA, respectively. The absorption spectra for CuInS2 QD-sensitized TiO2 NRA electrodes were recorded on a CARY5000 UV-visible NIR spectrometer (Agilent Technologies Inc., CA, USA).

Photoelectrochemical measurements

To examine the photovoltaic properties of CuInS2 QD-sensitized TiO2 NRA electrodes, the electrodes were assembled into cells using a Pt-coated counter-electrode facing it, which had been prepared by sputtering with 100 nm of Pt on cleaned FTO glass using radio frequency sputtering at a power of 150 W and a working pressure of 3 × 10⁻³ Torr with argon gas for 60 s. The sandwich-type solar cells were then seeded with 60-μm thick hot-melt film (Sullyn 1702, Dupont, DE, USA) by hot pressing. Polysulfide electrolyte consisting of 0.24 M Na₂S and 0.35 M Na₂SO₃ in aqueous solution was injected into the interelectrode space by capillary force. A mask with an aperture of 0.16 cm² (0.4 cm × 0.4 cm) was used to define the active area of the cell and prevent stray light from producing photocurrents. The photocurrent-voltage (I-V) curves were measured under an illumination of a solar simulator (Oriel class A, SP91160A, Newport Corporation, CA, USA) at one sun (AM1.5, 100 mW cm⁻²) irradiation calibrated with a Si-based reference. A Keithley model 2400 digital source meter (Keithley Instruments, Inc., OH, USA) was used to record the I-V characteristics by applying an external bias potential to the cell and measuring the photocurrent.

Results and discussion

Characterization of CuInS2 QD-sensitized TiO2 nanorod array

Figure 1a,b shows the typical FESEM images of the bare TiO2 NRA films and CuInS2 QD-sensitized TiO2 NRA films. It is clear that the entire surface of the FTO substrate is covered uniformly and densely with vertical alignment of TiO2 nanorods. From the higher magnification (Figure 1c) and cross-sectional view (Figure 1e) of such array, the average diameter and length of nanorods are 90 nm and 3.0 μm, respectively, and the sides of the TiO2 nanorods are relatively smooth. The nanorods are tetragonal in shape, which is the expected growth habit for the tetragonal crystal. After assembled with CuInS2 QDs for 7 cycles, the vertically aligned TiO2 nanorod array structure is retained, as shown in Figure 1b. However, it is revealed that the average diameter of the nanorods increases, and the surface becomes rather rougher and possesses uniform particles in the enlarged FESEM image (Figure 1d). Figure 1f is a cross-sectional view of the CuInS2 QD-sensitized TiO2 NRAs, showing that the CuInS2 QDs have been uniformly deposited onto the surfaces of TiO2 nanorods along their major length.

It is important to directly observe the QD sensitizers on TiO2 surface. The TEM and HRTEM can provide detailed microscopic information on the size of QDs and their distribution over the TiO2 nanorods, which is crucial in understanding how they are deposited and how they would affect the photoelectrochemical properties of electrodes. Figure 2a shows the TEM image of a TiO2 nanorod deposited with CuInS2 for 7 SILAR cycles, displaying that the bare surface of TiO2 nanorod appears to be covered by a thin shell consisting of a large amount of smaller dots. Figure 2b shows the HRTEM image at the edge side of TiO2 nanorod, indicating the high crystallinity of TiO2 and CuInS2. The larger crystallite appearing in the left region of the image is identified to be TiO2, and the observed lattice spacing of 0.322 nm corresponds to the (110) plane of tetragonal rutile TiO2. The randomly oriented crossed fringe patterns with d = 0.320 nm on the edge of the nanorod can be assigned to the (112) planes of the tetragonal CuInS2; they did not have preferential alignment along the rod axis, and the diameter of the single-crystalline QDs was about 5 to 10 nm.

In addition, EDS analysis shows that the ratio of Cu/In/S is 1.02:1.00:1.91 (Additional file 1: Figure S1).

To further investigate the phase composition and phase structure of CuInS2 QD-modified TiO2 NRA films, XRD measurements were carried out. Figure 3 displays the X-ray diffraction patterns of the TiO2 NRA before and after modification with CuInS2. XRD shows that the TiO2 NRAs deposited on FTO substrate can be classified as tetragonal rutile. Eliminating the peaks originating from the FTO conductive glass (Figure 3a), all the diffraction peaks that appear upon nanorod growth films agree well with the tetragonal rutile phase (JCPDS file no.88-1175), which is in agreement with the HRTEM measurement. The significantly enhanced (002) peak in 2-theta of 63.20° indicates that the nanorods are well crystallized and grow perpendicular to the FTO substrate. As compared with curve (b), three additional peaks were observed after deposition with CuInS2 at 2θ = 27.9°, 46.5°, and 55.1° which can be indexed to the (112),
(204)/(220), and (116)/(312) planes of tetragonal CuInS$_2$, respectively (JCPDS No.85-1575). The mean diameter of CuInS$_2$ particles was calculated to be approximately 8.27 nm by Scherrer equation, which is consistent with that observed in TEM image.

**Photoelectric properties of CuInS$_2$ QD-sensitized TiO$_2$ nanorod arrays**

The absorption spectra of bare TiO$_2$ NRAs and CuInS$_2$-sensitized TiO$_2$ NRA electrodes fabricated with different SILAR cycles are compared in Figure 4. The TiO$_2$
nanorod film exhibits an absorption edge in the ultraviolet region and has no significant absorbance for visible light because of its large energy gap (3.2 eV) [29]. For the TiO\textsubscript{2} nanorod film sensitized with CuInS\textsubscript{2}, the light absorbance extends to the visible-light region, and the absorbance increases with increasing coating cycles, suggesting that the amount of CuInS\textsubscript{2} deposited on TiO\textsubscript{2} NRAs increased with the coating cycles. In addition to the increase of absorbance in the UV–vis spectra, the absorption edge undergoes a continual redshift with increasing coating cycles, indicating the growth of the CuInS\textsubscript{2} QDs.

The CuInS\textsubscript{2} QD-sensitized TiO\textsubscript{2} NRA electrodes with different SILAR cycles of deposition were used as photoanodes in the sandwiched QDSSCs. The $I$–$V$ curves measured under simulated AM 1.5 G sunlight illumination are shown in Figure 5. It is obvious from Figure 5 that the photovoltaic performance of the solar cells firstly increased in the initial 7 cycles, the optimum energy conversion efficiency was obtained after 7 cycles, with a short-circuit photocurrent of 4.22 mA cm$^{-2}$, an open-circuit photovoltage of 0.36 V, a fill factor of 0.31, and an overall power conversion efficiency ($\eta$) of 0.46%, respectively. The enhancement of the photoelectrochemical properties can be illuminated as the result of increased light absorption in the visible light range, which has been indicated in Figure 4. With increasing SILAR cycles, the incorporated amount of CuInS\textsubscript{2} on TiO\textsubscript{2} NRAs gradually increased, which could not only contribute to absorb more photons to generate more photoexcited electrons, but

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**Figure 2 TEM (a) and HRTEM (b) images of CuInS\textsubscript{2} quantum dots.** The CuInS\textsubscript{2} quantum dots are deposited onto a TiO\textsubscript{2} nanorod; the SILAR cycle number for CuInS\textsubscript{2} deposition was 7.

**Figure 3 XRD patterns.** (a) FTO substrate, (b) TiO\textsubscript{2} NRA film grown on FTO substrate, and (c) CuInS\textsubscript{2} absorbed TiO\textsubscript{2} NRA film.

**Figure 4 Diffuse reflectance absorption spectra.** Bare TiO\textsubscript{2} NRAs (curve a) and CuInS\textsubscript{2} QD-coated TiO\textsubscript{2} NRAs fabricated by the SILAR technique for 3 cycles (curve b), 5 cycles (curve c), 7 cycles (curve d), and 9 cycles (curve e), respectively.

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also form a uniform and dense shell to reduce direct contact areas between the bare TiO₂ surface and polysulfide electrolyte, consequently decreasing the probability of recombination from separated electrons in the TiO₂ to the hole-transport material of electrolyte [30-32].

However, the $I_{sc}$ and $\eta$ were found to somewhat decrease when the coating cycles increased to 9 cycles. The possible reason for the reduced cell performance may be attributed to the aggregations and growth of the CuInS₂ crystal nucleus, which will result in the presence of CuInS₂ crystals with no direct contact with the TiO₂, leading to higher recombination and thick sensitized layers blocking the infiltration of the electrolyte into the photoelectrode, thereby decreasing the regeneration efficiency of the photoelectrochemical cell [33,34]. Effects of SILAR cycles of CuInS₂ on the photovoltaic performance of the QDSSCs are listed in Table 1. It is noteworthy that the best conversion efficiency of our cell is higher than the value of 0.38% obtained from presynthesized CuInS₂ QDs directly attached to the TiO₂ nanocrystalline films as the photoanode [17]. These results manifest the superiority of single-crystalline TiO₂ NRAs to disordered TiO₂ nanoparticle films when used as the host material in QDSSCs; also, it demonstrates that the SILAR process is a more preferable way for depositing semiconductor nanocrystalline sensitizers over TiO₂ films.

In CuInS₂-based thin-film solar cells, it has been revealed that there are unmatched band alignments and high surface state density existed in the heterostructure between TiO₂ and CuInS₂ [17,35], which resulted in a high rate of recombination at the interface. Fortunately, this can be overcome by applying a buffer layer between TiO₂ and CuInS₂. Therefore, in order to modify the interfacial properties and to further improve the performance of CuInS₂ QD-sensitized QDSSCs, a non-toxic In₂S₃ buffer layer also by SILAR was deposited on the TiO₂ NRs before the deposition of CuInS₂ (Additional file 2: Figure S3). The comparison of the photovoltaic performance and parameters of photoelectrodes with and without In₂S₃ buffer layer was shown in Figure 6 and Table 2, respectively. In the control experiment, $V_{oc}$, FF, and then the efficiency increased dramatically in the presence of the In₂S₃ buffer layer, implying that the In₂S₃ buffer layer plays an important role in improving photovoltaic performance. Additional file 3: Figure S4 demonstrates the dark current–voltage characteristic curves of CuInS₂-based QDSSC with and without In₂S₃ buffer layer. The dark current results from the reduction of electrolyte by the conduction band electrons of TiO₂. The onset of the dark current of QDSSC with In₂S₃ buffer layer occurs at the higher forward bias, which indicates that the dark reaction was efficiently suppressed by applying a buffer layer of In₂S₃. This can be explained by the formation of cascade band structures at the TiO₂/In₂S₃/CuInS₂ interface (Additional file 4: Figure S6).

| Photoelectrodes | $I_{sc}$ (mA/cm²) | $V_{oc}$ (V) | Fill factor (%) | Efficiency (η%) |
|----------------|------------------|-------------|----------------|----------------|
| 3 cycles       | 2.04             | 0.302       | 27             | 0.17           |
| 5 cycles       | 3.02             | 0.351       | 31             | 0.42           |
| 7 cycles       | 4.22             | 0.355       | 31             | 0.46           |
| 9 cycles       | 3.59             | 0.371       | 32             | 0.43           |

Table 1 Photovoltaic performance of the CuInS₂-based QDSSC devices with different SILAR cycles

Figure 5 Solar cell characterization of the devices with different CuInS₂ coating cycles. The curves were measured under AM 1.5 illumination with an active area of 0.16 cm².

Figure 6 J-V characteristics of different working electrodes measured under AM 1.5 global filter of 100 mW/cm² sunlight. Curve (a) TiO₂/CuInS₂(7) and curve (b) TiO₂/In₂S₃(4)/CuInS₂(7). The active surface area was 0.16 cm².
which suppresses the back flow of electrons and restrains the electron–hole recombination [35–37]. It should be mentioned that the efficiency of the CuInS$_2$-based QDSSCs present in our study is still limited, which may be attributed to the limitation of TiO$_2$ NR length. The typical thickness of TiO$_2$ nanoparticle films is about 13 μm, but for TiO$_2$ NR array films used in our experiment, the length was just about 3 μm. As a result, although there are many advantages of 1D TiO$_2$ NRs, the insufficient length resulted in poor QD loadings and light harvesting, which constrained the efficiency of TiO$_2$ NR cells to relatively lower levels than that of nanoparticle-based ones. To further improve photovoltaic performances of 1D nanostructure-based QDSSCs, it is necessary to pay more attention to the internal surface area of TiO$_2$ NRAs and interfacial properties that are very critical to determine the fate of excitons generated inside the semiconductor QDs.

Conclusions
In this study, for the first time, we have employed a facile SILAR process to deposit CuInS$_2$ QD onto TiO$_2$ NRAs, which was prepared by a simple hydrothermal method. The CuInS$_2$ QD-sensitized TiO$_2$ NRAs were used as photoanodes to assemble sandwiched QDSSCs. The effect of SILAR cycles on the photoelectrochemical performance of the CuInS$_2$-sensitized solar cells was investigated. With optimal CuInS$_2$ SILAR cycles and introduction of In$_2$S$_3$ buffer layer to modify the interface, the best photovoltaic performance with an energy conversion efficiency of 1.06% under AM 1.5 G illumination, an open-circuit photovoltage of 0.56 V, a short circuit current density of 4.51 mA cm$^{-2}$, and a FF of 0.41 were achieved. The present CuInS$_2$-based QDSSC fabrication approach combined the advantages of 1D TiO$_2$ NRAs and in situ growing of the target semiconductor sensitized layers and buffer layer by SILAR, which can be used for construction of other useful optoelectronic devices and composite catalysts.

Additional files

Table 2 Photovoltaic performance for CuInS$_2$-sensitized TiO$_2$ NRA photoelectrodes with and without In$_2$S$_3$ buffer layer

| Photoelectrodes | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | Fill factor (%) | Efficiency (η) |
|-----------------|----------------------|--------------|----------------|----------------|
| TiO$_2$/CuInS$_2$(7) | 4.22 | 0.355 | 31 | 0.46 |
| TiO$_2$/In$_2$S$_3$(4)/CuInS$_2$(7) | 4.51 | 0.559 | 41 | 1.06 |

Additional file 2: Figure S5. SAED patterns of TiO$_2$ NR (a) and CuInS$_2$ QDs (b) Figure S3. EDS spectra of TiO$_2$ NRA photoelectrode after In$_2$S$_3$ deposition.

Additional file 3: Figure S4. Dark current–voltage characteristic curves of CuInS$_2$-based QDSSC with (red dots) and without (black squares) In$_2$S$_3$ buffer. Figure S5. IPCE spectra of CuInS$_2$ QD-sensitized solar cell with different SILAR cycles.

Additional file 4: Figure S6. Band diagram of CuInS$_2$. QD-sensitized solar cell. Buffer layers of In$_2$S$_3$ are applied to suppress electron–hole recombination at the interface.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
ZZ is the primary author and participated in the experiment design, experiment analysis, interpretation of data, and language modification. SY and JF carried out the experiments, characterization, and acquisition of data. ZH and WZ participated in the discussion. ZD and SW are the investigators who helped in the analysis and interpretation of data, drafting of the manuscript, and making revisions. All authors read and approved the final manuscript.

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References
1. O’Regan B, Grätzel M: A low-cost, high-efficiency solar-cell based on dye-sensitized colloidal TiO$_2$ films. Nature 1991, 353:737–740.
2. Grätzel M: Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells. J Photochem Photobiol A Chem 2004, 164:3–14.
3. Hagberg DP, Yum JH, Lee H, De Angelis F, Marinado T, Karlsson KM, Humphry-Baker R, Sun L, Hagfeldt Å, Grätzel M, Nazeeruddin MK: Molecular engineering of organic sensitizers for dye-sensitized solar cell applications. J Am Chem Soc 2008, 130:6259–6266.
4. Meyer GB: The 2010 millennium technology grand prize: dye-sensitized solar cells. ACS Nano 2010, 4:4337–4343.
5. Xu F, Sun L: Solution-derived ZnO nanostructures for photoanodes of dye-sensitized solar cells. Energy Environ Sci 2011, 4:818–841.
6. Yella A, Lee HW, Tsao HN, Yi C, Chandiran AK, Nazeeruddin MK, Diao EW, Yeh CY, Zakeeruddin SM, Grätzel M: Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency. Science 2011, 334:607–608.
7. Liang Y, Cheng F, Liang J, Chen J: Triphenylamine-based ionic dyes with simple structures: broad photoresponse and limitations on open-circuit voltage in dye-sensitized solar cells. J Phys Chem C 2010, 114:15842–15848.
8. Peter LM: The Grätzel cell: where next? J Phys Chem Lett 2011, 2:1861–1867.
9. Kamar PV: Quantum dot solar cells semiconductor nanocrystals as light harvesters. J Phys Chem C 2008, 112:18737–18753.
10. Sun WT, Yu Y, Pan HY, Gao XF, Chen Q: Peng LM: Cd$_5$S$_{29}$ quantum dots sensitized TiO$_2$ nanotube-array photoelectrodes. J Am Chem Soc 2008, 130:1124–1125.
11. Lee H, Leventis HC, Moon SJ, Chen P, Ito S, Haque SA, Torres T, Nuesch F, Geiger T, Zakeeruddin SM, Grätzel M, Nazeeruddin MK: PbS and CdS
quantum dot-sensitized solid-state solar cells: “old concepts, new results”, Adv Funct Mater 2009, 19(24):2375–2742.
12. Chen C, Xie Y, Ali G, Yoo SH, Cho SO: Improved conversion efficiency of AqS quantum dot-sensitized solar cells based on TiO2 nanotubes with a ZnO recombination barrier layer. Nanoscale Res Lett 2011, 6:462–470.
13. Tell B, Shay JL, Kasner HM: Electrical properties, optical properties, and band structure of CuGaS2 and CuInS2. Phys Rev B 1971, 4:2463–2471.
14. Nanu M, Schoonman J, Goossens A: Solar-energy conversion in TiO2/CuInS2 nanocomposites. Adv Funct Mater 2005, 15:95–100.
15. Kuo KT, Liu DM, Chen SY, Lin CC: Core-shell CuInS2/ZnS quantum dots assembled on short ZnO nanowires with enhanced photo-conversion efficiency. J Mater Chem 2009, 19:6780–6788.
16. Li TL, Lee YL, Teng H: CuInS2 quantum dots coated with Cds as high-performance sensitizers for TiO2 electrodes in photoelectrochemical cells. J Mater Chem 2011, 21:5089–5098.
17. Hu X, Zhang QX, Huang XM, Li DM, Luo YH, Meng QB: Aqueous colloidal CuInS2 for quantum dot sensitized solar cells. J Mater Chem 2011, 21:1905–1908.
18. Kontos AG, Likodimos V, Vassalou E, Kapogianni I, Raptis YS, Raptis C, Falaras P: Functionalized with In2S3 shell layer by a low-cost route for solar energy conversion. Chem Commun 2011, 48:4848–4850.
19. Lee JL, Lo YS: Highly efficient quantum-dot-sensitized solar cell based on co-sensitization of Cds/CdSe. Adv Funct Mater 2009, 19:604–609.
20. Li M, Liu Y, Wang J, Kim S, Park SM: Multilayered semiconductor (Cds/CdSe/ZnS)-sensitized TiO2 mesoporous solar cells: all prepared by previous ionic layer adsorption and reaction processes. Chem Mater 2010, 22:5636–5643.
21. Chang JY, Su LF, Li CH, Chang CC, Lin JM: Efficient “green” quantum dot-sensitized solar cells based on CuS–CuInS2–ZnSe structure. Chem Commun 2012, 48:4848–4850.
22. Li M, Liu Y, Wang H, Shen H, Zhao WX, Huang H, Liang CL, Cds/CdSe co-sensitized oriented single-crystalline TiO2 nanowire array for solar cell application. J Appl Phys 2010, 108:094304–094307.
23. Gao XF, Li HB, Sun WT, Chen Q, Tang FQ, Peng LM: CdTe quantum dots-sensitized TiO2 nanotube array photoelectrodes. J Phys Chem C 2009, 113:7531–7535.
24. Liu YB, Zhou HB, Li JH, Chen HC, Li D, Zhou BX, Cai WM: Enhanced photoelectrochemical properties of CuO-loaded short TiO2 nanotube array electrode prepared by sonochemical deposition. Nano-Micro Lett 2010, 2:277–294.
25. Gan XY, Li XM, Gao XD, Qiu JL, Zhuge FW: TiO2 nanorod arrays functionalized with In2S3 shell layer by a low-cost route for solar energy conversion. Nanotechnology 2011, 22:305601–305607.
26. Luan C, Vanek A, Susha AS, Xu X, Wang HE, Chen X, Xu J, Zhang W, Lee CS, Rogach AL, Zapen JA: Facile solution growth of vertically aligned ZnO nanorods sensitized with aqueous Cds and CdSe quantum dots for photocatalytic applications. Nanoscale Res Lett 2011, 6:340–347.
27. Liu B, Aydel ES: Growth of oriented single-crystalline rutile TiO2 nanorods on transparent conducting substrates for dye-sensitized solar cells. J Am Chem Soc 2009, 131:3985–3990.
28. Wu J, Jiang WT, Liao WP: CuInS2 nanotube array on indium tin oxide: synthesis and photoelectrochemical properties. Chem Commun 2010, 46:5895–5897.
29. Zhao WY, Fu WY, Yang HB, Tian CJ, Li MH, Ding J, Zhang W, Zhou XM, Zhao H, Li YX: Synthesis and photocatalytic activity of Fe-doped TiO2 supported on hollow glass microbeads. Nano-Micro Lett 2011, 3:20–24.
30. Robel I, Subramaniam V, Kuno M, Karnat PV: Quantum dot solar cells. harvesting light energy with CdSe nanocrystals molecularly linked to mesoscopic TiO2 films. J Am Chem Soc 2006, 128:2385–2393.
31. Tang YW, Hu XY, Chen MJ, Luo LJ, Li BH, Zhang LZ: CdSe nanocrystal sensitized ZnO core-shell nanorod array films: preparation and photocatalytic properties. Electrochim Acta 2009, 54:2742–2747.
32. Wei HW, Wang L, Li ZP, Ni SQ, Zhao QL: Synthesis and photocatalytic activity of one-dimensional Cds@TiO2 core-shell heterostructures. Nano-Micro Lett 2011, 3:6–11.
33. Wang H, Bai YS, Zhang H, Zhang ZH, Li JH, Guo L: Cds quantum dots-sensitized TiO2 nanorod array on transparent conductive glass photoelectrodes. J Phys Chem C 2010, 114:16451–16455.
34. Chen H, Fu WY, Yang HB, Sun P, Zhang YY, Wang LR, Zhao WY, Zhou XM, Zhao H, Jing Q, Qi XF, Li YX: Photosensitization of TiO2 nanorods with Cds quantum dots for photovoltaic devices. Electrochim Acta 2010, 56:919–924.
35. Nanu M, Schoonman J, Goossens A: Inorganic nanocomposites of n- and p-type semiconductors: a new type of three-dimensional solar cell. Adv Mater 2004, 16:453–456.
36. Zhang QX, Guo XZ, Huang XM, Huang SQ, Li DM, Luo YH, Shen Q, Toyoda T, Meng QB: Highly efficient Cds/CdSe-sensitized solar cells controlled by the structural properties of compact porous TiO2 photoelectrodes. Phys Chem Chem Phys 2011, 13:4659–4667.
37. Zhou N, Chen GP, Zhang XL, Cheng LY, Luo YH, Li DM, Meng QB: Highly efficient PbS/CdS co-sensitized solar cells based on photoanodes with hierarchical pore distribution. Electrochim Acta 2012, 2097–2100.