Photodeposition of Ag$_2$S on TiO$_2$ nanorod arrays for quantum dot-sensitized solar cells

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Abstract

Ag$_2$S quantum dots were deposited on the surface of TiO$_2$ nanorod arrays by a two-step photodeposition. The prepared TiO$_2$ nanorod arrays as well as the Ag$_2$S deposited electrodes were characterized by X-ray diffraction, scanning electron microscope, and transmission electron microscope, suggesting a large coverage of Ag$_2$S quantum dots on the ordered TiO$_2$ nanorod arrays. UV–vis absorption spectra of Ag$_2$S deposited electrodes show a broad absorption range of the visible light. The quantum dot-sensitized solar cells (QDSSCs) based on these electrodes were fabricated, and the photoelectrochemical properties were examined. A high photocurrent density of 10.25 mA/cm$^2$ with a conversion efficiency of 0.98% at AM 1.5 solar light of 100 mW/cm$^2$ was obtained with an optimal photodeposition time. The performance of the QDSSC at different incident light intensities was also investigated. The results display a better performance at a lower incident light level with a conversion efficiency of 1.25% at 47 mW/cm$^2$.

Keywords: Ag$_2$S, Quantum dot-sensitized solar cell, Photodeposition, TiO$_2$ nanorod

Background

Quantum dot-sensitized solar cells (QDSSCs) have attracted increasing attention due to their relatively low cost and potentials to construct high-efficiency energy conversion systems [1]. Compared with organic dyes used in dye-sensitized solar cells (DSSCs), semiconductor sensitizers in the form of quantum dots (QDs) present higher extinction coefficients and adjustable absorption spectra by controlling their size [2,3]. However, the best efficiency (approximately 5%) reached by QDSSCs is much lower than that of conventional DSSCs [4,5]. The deposition of QD sensitizers on the electron acceptor (e.g., TiO$_2$) related to the loading amount and the connection between QDs and electron acceptor plays a key role in the QDSSC performance. QDs with various sizes should be deposited on the surface of mesoporous TiO$_2$ separately as a requirement for efficient charge separation [6]. Typically, the coverage of mesoporous TiO$_2$ by QDs is much less than a full monolayer [6,7], which leads to insufficient light harvesting and back electron transfer from exposed TiO$_2$ to electrolyte. Besides, deposition of typically 3 to 8 nm diameter QDs into mesoporous TiO$_2$ with relative narrow pores is rather difficult, and large QDs that inserted into mesoporous TiO$_2$ may also cause pore blocking and subsequently inhibit the penetration of electrolyte deep into the holes [8]. The efficiency enhancement of QDSSCs could be achieved by applying an advanced deposition method as well as suitable TiO$_2$ nanostructure. For the former, several deposition methods have been developed to anchor QDs on the surface of TiO$_2$ including ex-situ and in-situ methods [6], where photodeposition is a promising candidate by taking advantage of the photocatalytic properties of TiO$_2$ in the deposition process [9-11]. Photoreduction on the surface of TiO$_2$ leads to a large and uniform coverage of QDs and intimate contact between the QDs and TiO$_2$ for efficient interfacial charge transfer [11]. For the latter, one-dimensional oriented arrays (nanotube or nanorod arrays) possess large surface area and efficient electron transfer property that can be employed to improve the performance of QDSSCs [12,13]. Importantly, the high-oriented arrays provide uniform pore size that is favorable for QD anchoring with rare pore blocking.

Ag$_2$S is an important photoelectric material and has a broad application in terms of photocatalysis and electronic...
devices [14-17]. With bulk bandgap of 1.0 eV, close to the optimal bandgap of 1.1 to 1.4 eV for photovoltaic devices [18], Ag$_2$S is a potential sensitizer superior to others used in QDSSCs. Several researches that concentrated on the Ag$_2$S-QDSSCs have been reported since the first application of Ag$_2$S in QDSSCs [19-23]. However, the reported conversion efficiency ($\eta$) remains lower than that of QDSSCs based on other narrow bandgap semiconductor (e.g., CdS and CdSe) [24,25], which is partly attributed to the low coverage of Ag$_2$S on the surface of TiO$_2$.

To improve the efficiency of Ag$_2$S-QDSSCs, we apply a modified photodeposition as well as an oriented TiO$_2$ nanorod array (NRA) on the cell. Typically, the oriented TiO$_2$ NRA was prepared by a simple hydrothermal method. Photodeposition of Ag$_2$S was conducted by two steps: photoreduction of Ag$^+$ to Ag by TiO$_2$ NRA followed by the sulfurization of Ag to Ag$_2$S QDs. To our knowledge, this is the first report of Ag$_2$S QD-sensitized TiO$_2$ NRA solar cells. Results show that a large coverage of Ag$_2$S QDs on the TiO$_2$ NRs has been achieved by this modified photodeposition, and the photoelectrochemical properties of these electrodes suggest that Ag$_2$S has a great potential for the improvement of QDSSCs.

**Methods**

**Growth of TiO$_2$ NRA**

TiO$_2$ NRA was grown on the fluorine-doped SnO$_2$-coated conducting glass (FTO) substrate (resistance 25 $\Omega$/square, transmittance 85%) by a hydrothermal method as described in the literature [26]. Briefly, 30 mL deionized water was mixed with 30 mL concentrated hydrochloric acid (36.5% to 38.0% by weight). The mixture was stirred for 5 min followed by an addition of 1 mL titanium butoxide (98%, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China). After stirring for another 5 min, the mixture was transferred into a Teflon-lined stainless steel autoclave of 100-mL volume. The FTO substrate was placed at an angle against the wall of the Teflonliner with the conducting side facing down. After a hydrothermal treatment at 150°C for 20 h, the substrate was taken out, washed with ethanol, and transferred into methanol solution consisting 1 M Na$_2$S and 2 M S. The sulfurization reaction was conducted at 50°C for 8 h. Finally, the photoanodes were passivated with ZnS by dipping into 0.1 M Zn(CH$_3$COO)$_2$ and 0.1 M Na$_2$S aqueous solution for 1 min alternately.

**Solar cell assembly**

The counter electrode was prepared by dripping a drop of 10 mM H$_2$PtCl$_6$ (99.99%, Aldrich Company, Inc., Wyoming, USA) ethanol solution onto FTO substrate, followed by heating at 450°C for 15 min. Ag$_2$S-sensitized TiO$_2$ nanorod (NR) photoanode and Pt counter electrode were assembled into sandwich structure using a sheet of a thermoplastic frame (25-μm thick; Surlyn, DuPont, Wilmington, USA) as spacer between the two electrodes. The polysulfide electrolyte consisted of 0.5 M Na$_2$S, 2 M S, 0.2 M KCl, and 0.5 M NaOH in methanol/water (7:3 v/v). An opaque mask with an aperture was coated on the cell to ensure the illuminated area of 0.16 cm$^2$.

**Characterization**

X-ray diffraction (XRD) measurements were carried out using a RAD-3X (Rigaku Corporation, Tokyo, Japan) diffractometer with Cu-K$\alpha$ radiation. The morphology of the films was observed by field emission scanning electron microscopy (FESEM, S4800, Hitachi Ltd., Tokyo, Japan) and transmission electron microscope (TEM, JEM-2100, JEOL Ltd., Beijing, China). To prepare the TEM sample, TiO$_2$ NRs together with Ag$_2$S QDs were scratched from the FTO substrate and dispersed in ethanol by sonication. The UV–vis absorption spectra of TiO$_2$ NRA and Ag$_2$S-deposited TiO$_2$ NRA were
U-3010 spectroscopy. The photocurrent density-voltage \((J-V)\) characteristics of solar cells were examined by a Keithley 2400 sourcemeter (Keithley Instruments, Inc., Cleveland, USA) under illumination by a solar simulator (AM 1.5 G). Incident light intensity was calibrated by standard silicon solar cell and light intensity meter (FZ-Aradiometer) simultaneously. The stability of the solar cell was measured by electrochemical workstation (pp211; Zahner, Elektrik GmbH & Co.KG, Kronach, Germany) with continuous illumination on the solar cell.

Results and discussion

Morphology of the TiO2 NRA

Figure 2 shows the FESEM images of TiO2 NRA grown on the FTO substrate (FTO/TiO2) viewed from top (a) and cross-section (b). The TiO2 film is composed of separate NRs with consistent orientation, forming a uniform array that covered the entire surface of the substrate. The top view of FTO/TiO2 shows that the top surface of NRs contains many step edges facilitating further growth. The NRs are tetragonal in shape with square top facets, consistent with the growth habit of tetragonal crystal structure. The average side length of the top squares is 200 nm, and the space between them is about the same size. The cross-section view of FTO/TiO2 shows that the NRs are 2 to 3 \(\mu\)m in length with smooth sides. At the bottom of the TiO2 NRA, a thin layer composed of short disordered NRs adhering to the FTO substrate is found. The compact layer may reduce the recombination of electron from the FTO to the electrolyte in the working course of QDSSCs by segregating them.

Photodeposition of Ag2S QDs

The photodeposition of Ag2S QDs was conducted by two separate processes: photoreduction of Ag\(^+\) to Ag and sulfuration of Ag to Ag2S. Photocatalytic properties of TiO2 play an essential role in the reduction of Ag\(^+\). The mechanism of TiO2 photocatalytic-reduction metal ions was described in the literature [27]. The main reaction processes of photoreduction Ag\(^+\) are as follows (reactions 1 to 4): (1) Typically, TiO2 surface exhibits strong adsorptivity for Ag\(^+\), and the adsorption equilibrium is reached soon after immersing FTO/TiO2 in Ag\(^+\) ethanol solution in the dark. (2) UV irradiation \((\lambda < 400 \text{ nm})\) excites TiO2 to generate electron–hole pairs. (3) The electrons reduce the Ag\(^+\) adsorbed preferentially on the surface to Ag, (4) while the holes are irreversibly scavenged by ethanol. Continuous reduction of Ag\(^+\) can produce Ag nucleates on the surface of TiO2 forming a Schottky junction between them. The charge-separation generated electrons are partially transferred to the Ag clusters from TiO2 [28]. Oxidation and reduction processes are carried on at the surface of TiO2 and Ag, respectively, as illustrated in Figure 3. Consequently, the reduction on the surface of Ag enables the crystal nucleus to grow up. After the photoreduction, the sulfuration reaction of Ag clusters occurs spontaneously, owing to the low reaction Gibbs energy of \(-47.1 \text{ kJ/mol} [29].\)

\[
\text{TiO}_2 + \text{Ag}^+ \rightarrow \text{TiO}_2\text{Ag}^+ \quad (1)
\]

\[
\text{TiO}_2 + \text{hv} \rightarrow \text{TiO}_2(e^- + h^+ \quad (2)
\]

\[
e^- + \text{Ag}^+ \rightarrow \text{Ag} \quad (3)
\]

\[
h^+ + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4\text{OH} \quad (4)
\]

Figure 4 shows XRD patterns of FTO/TiO2 (a), FTO/TiO2/Ag (b), and FTO/TiO2/Ag2S (c) electrodes. XRD patterns of FTO/TiO2 electrode reveal that the synthesized TiO2 NRs are tetragonal rutile structure (JCPDS card no. 21–1276). The enhanced (101) peak indicates the NRs are well-crystallized and grow in consistent orientation. In the XRD pattern of FTO/TiO2/Ag
electrode (b), all peaks indexed as TiO2 crystal have been weakened while the outstanding diffraction peaks of silver (silver-3C, syn JCPDS card no. 04–0783) emerged. This proves the large coverage of crystallized Ag on the surface of TiO2 nanostructure as a result of the photoreduction process. As compared with curve b, the XRD pattern of FTO/TiO2/Ag2S electrode shows five diffraction peaks which agreed well with acanthite Ag2S (JCPDS card no. 14–0072), suggesting a conversion of Ag to Ag2S. Additionally, the outstanding peaks of Ag in curve b are not observed in curve c which indicates that the reaction between Ag and S has been completed thoroughly.

Figure 5 displays a SEM image of a top view of FTO/TiO2/Ag2S electrode with 10-min photoreduction (a) and a TEM image of single NR stripped from the FTO/TiO2/Ag2S electrode (b). The two images clearly show that TiO2 NRs are coated by a layer of Ag2S crystallites not only on the top surface but also on the four side faces. The top view of FTO/TiO2/Ag2S electrode shows that the small steps within the top face of TiO2 NR observed in SEM image of FTO/TiO2 electrode (Figure 2a) are invisible due to the coverage of Ag2S crystallites. The interval between NRs is reserved as well as the ordered TiO2 NRA structure. The TEM image (b) shows that the entire NR is coated with QDs from the bottom to the top. Most of the QDs that covered the surface of NR disperse well with an average diameter of 10 nm. A closer observation of the Ag2S QDs attached with TiO2 NR can be obtained by the high resolution transmission electron microscope (HRTEM) images (Figure 5c,d). The NR grows along the [001] direction, and lattice fringes with interplanar spacing d_{110} = 0.321 nm are clearly imaged. The Ag2S QDs anchoring on the side surface of TiO2 NR are composed of small crystallites as observed by the fringes which correspond to the (121) planes of Ag2S.

Optical and photoelectrochemical properties of Ag2S QDs-sensitized TiO2 NRA

Figure 6 shows the absorption spectra of FTO/TiO2 electrode and FTO/TiO2/Ag2S electrodes with different photoreduction times (t_p). The absorption edge around 400 nm is consistent with bandgap of rutile TiO2 (3.0 eV). While Ag2S QDs are deposited on TiO2 NRs, absorption spectra are successfully extended to visible wavelength. With t_p increasing from 3 to 15 min, the absorption range changes from 400 to 520 nm until covering the entire visible spectrum; moreover, the absorbance obviously increases. The bandgap of bulk Ag2S is 1.0 eV. The redshift of absorption edge for FTO/TiO2/Ag2S electrodes with prolonged t_p indicates the fact that the size of Ag2S QDs gradually increases, and the quantization effect of ultrasmall QDs gradually vanishes. The enhanced absorbance is due to the increased amount of deposited Ag2S QDs.

Figure 7 shows J-V characteristics of solar cells fabricated with different photoanodes under AM 1.5 illumination at 100 mW/cm². The photovoltaic properties of these cells are listed in Table 1. TiO2/Ag2S cell with t_p = 3 min possesses a much higher J_sc and a decreased V_oc compared with bare TiO2 solar cell. The increased J_sc value is attributed to the sensitization of TiO2 by Ag2S QDs, while the slightly decreased V_oc value is mainly due to the band bending between Ag2S QDs and TiO2. With t_p increasing from 3 to 10 min, the J_sc is promoted from 4.15 to 10.25 mA/cm². The improved J_sc value is caused by an increasing loading amount of Ag2S QDs and a broaden absorption spectrum (as shown in Figure 6). Meanwhile, the V_oc values are slightly improved, which is probably due to electron accumulation within TiO2 shifting the Fermi level to more negative potentials. The optimal solar cell performance is obtained with a η of 0.98% and a superior J_sc of 10.25 mA/cm² when t_p = 10 min. The J_sc value is much
higher than those of other reported Ag$_2$S QD sensitized solar cells even though they were prepared by a TiO$_2$ nanoparticle matrix with a larger surface area. The enhancement in $J_{sc}$ is a result of the synergy of larger QD loading amount and fine connection between QDs and TiO$_2$. Compared with typical QDSSCs based on other narrow bandgap semiconductors (e.g., CdS and CdSe), the $V_{oc}$ values of Ag$_2$S-QDSSCs are quite low which are almost equivalent to half of the others (CdS-QDSSCs, 0.6 to 0.7 V). Despite of the high $J_{sc}$ values owing to a broad absorption spectrum, $\eta$ is limited by the low $V_{oc}$ values. When $t_p$ was elongated to 15 min, $\eta$ decreases sharply with a halving $J_{sc}$ and a lower Fill factor (FF). This phenomenon is speculated to be caused by too long deposition time which results in excess Ag$_2$S nanoparticles generated on TiO$_2$ NRs, consequently decreases effective electron injection and increases recombination rate. The slightly reduced FF as $t_p$ increases also indicates that recombination rate rises with growing amount of loading Ag$_2$S nanoparticles.
The $J$-$V$ curves of a Ag$_2$S QD-sensitized solar cell measured at three different light intensities are shown in Figure 8. The photovoltaic performance parameters are listed in Table 2. The $\eta$ reaches a value of 1.25% at 47 mW/cm$^2$ solar intensity. The $J_{sc}$ value accumulates to 11.7 mA/cm$^2$ as incident light intensity increases to 150 mW/cm$^2$ (150% sun). However, $J_{sc}$ produced by per unit light power is decreased by a factor of 40.9 compared with lower light level condition of 47% sun. This suggests that the incident light is not effectively converted into electricity at a higher photon density, which may be attributed to a lower rate of photon capture due to the insufficient QDs loading on TiO$_2$ nanorods. By employing longer TiO$_2$ NRs, the response of the photocurrent should be promoted to be linear with the incident light intensity, and a higher conversion efficiency should be reached at full sunlight.

The photostability of Ag$_2$S QDSSC was measured by illuminating it at 100 mW/cm$^2$ sunlight for 2 h and characterized by recording the $J_{sc}$ and $V_{oc}$ of the device (Figure 9). During illumination, the $J_{sc}$ remained relatively steady with a drop less than 5%, and the $V_{oc}$ fluctuated within 2%. This shows that the Ag$_2$S QDs are robust in resisting photo corrosion in the presence of polysulfide electrolyte, and the small decline is probably caused by the loss of the solvent.

**Conclusions**

We have deposited Ag$_2$S QDs on TiO$_2$ NRA by a two-step photodeposition. The deposition process was conducted by photoreduction of Ag$^+$ to Ag on the surface of TiO$_2$ NRs followed by chemical reaction with sulfur. By controlling the photoreduction period, we have obtained Ag$_2$S-sensitized TiO$_2$ NRs with a large coverage and superior photoelectrochemical properties. QDSSCs based on the Ag$_2$S-sensitized TiO$_2$ NRAs were fabricated. Under optimal condition, the Ag$_2$S-QDSSC yields a $J_{sc}$ of 10.25 mA/cm$^2$ with a conversion efficiency of 0.98% at AM 1.5 solar light of 100 mW/cm$^2$. We also investigated the solar cell performance under varied incident light intensities. Results show that a drawback of these cells in full sun condition compared with the maximum efficiency achieved at lower light level. The key factor that limits the solar cell performance is the low $V_{oc}$ values we obtained. By employing suitable redox electrolyte, we believe the Ag$_2$S-QDSSCs will have a great promotion with increased $V_{oc}$ values.

**Table 1 Photovoltaic parameters of solar cells fabricated with different photoanodes under AM 1.5 illumination at 100 mW/cm$^2$**

| Solar cell | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF | $\eta$ (%) |
|------------|----------------------|--------------|----|------------|
| Bare TiO$_2$ | 1.34 | 0.32 | 0.30 | 0.13 |
| 3 min | 4.15 | 0.24 | 0.42 | 0.41 |
| 5 min | 9.00 | 0.27 | 0.38 | 0.83 |
| 10 min | 10.25 | 0.29 | 0.32 | 0.98 |
| 15 min | 4.71 | 0.28 | 0.29 | 0.38 |

**Table 2 Photovoltaic parameters of Ag$_2$S QD-sensitized solar cell measured at different light intensities**

| $P_{in}$ (mW/cm$^2$) | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF | $\eta$ (%) |
|----------------------|----------------------|--------------|----|------------|
| 150 | 11.7 | 0.3 | 0.37 | 0.87 |
| 100 | 10.3 | 0.29 | 0.33 | 0.98 |
| 47 | 6.2 | 0.26 | 0.36 | 1.23 |
| 38 | 4.6 | 0.25 | 0.32 | 0.97 |

![Figure 8: J-V curves of Ag$_2$S QD-sensitized solar cell measured at different light intensities.](image)

![Figure 9: Photostability of Ag$_2$S QD-sensitized solar cell under AM 1.5 illumination at 100 mW/cm$^2$.](image)
Abbreviations

\( \eta \): conversion efficiency; DSSCs: dye-sensitized solar cells; FESEM: field emission scanning electron microscopy; FF: fill factor; FTO: fluorine-doped SnO\(_2\)-coated glass conducting layer; HRTEM: high resolution transmission electron microscope; J\(_p\): short circuit current density; NR: nanorod; NRA: nanorod array; QDs: quantum dots; QDSSCs: quantum dot-sensitized solar cells; SEM: scanning electron microscope; TEM: transmission electron microscope; \( t_p \): photoreduction time; \( V_{oc} \): open voltage; XRD: X-ray diffraction.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

HWH carried out the experiments and wrote the manuscript. JND and NYY conceived the study, participated in its design, and amended the paper. SZ participated in the discussion and interpretation of the data. YL and LB participated in the experiments. All authors read and approved the final manuscript.

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