Assembly of CdSe Quantum Dots onto TiO$_2$ Flower-rod Films for Quantum Dot-sensitized Solar Cell Applications

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Abstract. A hierarchical double-layered TiO$_2$ flower-rod structure composed of three-dimensional (3D) TiO$_2$ flowers and one-dimensional (1D) nanorods on transparent fluorine-doped tin oxide (FTO) conducting glass has been synthesized by a facile hydrothermal method and was applied as photoanode in CdSe quantum dots sensitized solar cells (QDSSCs). The 3D TiO$_2$ flowers with the increased surface areas can adsorb more QDs, which reinforce the absorption of light; meanwhile 1D TiO$_2$ nanorods beneath the flowers offer a direct electrical pathway for photogenerated electrons, accelerating the electron transfer rate. The effect of coating cycles of QDs on the photovoltaic performance was investigated by successive ionic layer adsorption reaction (SILAR) cycles. The best power conversion efficiency of solar cell based on flower-rod structure with 12 SILAR cycles of CdSe QDs can reached to 1.98% under one sun illumination (AM 1.5G, 100 mW/cm$^2$).

Introduction

As the increasing demand for energy and serious environmental pollution caused by extensive fossil fuels consumption, solar energy is becoming one of promising energy resources to take the place of the conventional ones. The photovoltaic cells are the most effective approach to realize the utilization of solar energy [1]. Among various solar cells, quantum dot sensitized solar cells (QDSSCs) have attracted much attention because of their low manufacturing costs and ease of fabrication [2]. Nanostructured TiO$_2$ was usually used as photoanode substrate for QDSSCs due to several advantages, including suitable conduction band position, stable chemical and physical properties, and inexpensive cost [3]. Up to now, nanostructured TiO$_2$ with various morphologies has been synthesized, such as nanoparticles, nanorods, nanotubes, and so on. But seldom researches have been reported on the formation of double-layered hierarchical TiO$_2$ nanostructures, which consisted of 1D rutile TiO$_2$ nanorods and 3D TiO$_2$ flowers. Fortunately, the hierarchical TiO$_2$ flower-rod structure prepared by one-step hydrothermal process was recently reported by our group, which shows an important effect on the improvement of solar cell performance as photoanode in Mn-doped CdS QDSSCs [4]. In QDSSCs, based on hierarchical TiO$_2$ flower-rod architecture, 1D nanorods can offer direct electronic pathway, accelerating the electrons transfer rate and reducing recombination of electrons and holes [5]; meanwhile, 3D TiO$_2$ flowers can provide the increased surface areas, leading to more adsorption of QDs and more light absorption. Furthermore, 3D TiO$_2$ flowers can also be used as a scattering layer to enhance the light harvesting and improve the performance of QDSSCs.

Narrow-band gap semiconductor quantum dots (QDs) are usually used as sensitizers in QDSSCs on account of their extraordinary optical and electrical properties, such as the tunable band gap of QDs, higher extinction coefficients, larger intrinsic dipole moments, multiple excitons generation (MEG) with a single photon by impact ionization, and hot electron injection [6]. Among these
semiconductor QDs, CdSe is a desirable candidate in photovoltaic application due to its narrow band gap of 1.70 eV and high absorption coefficient in the visible light region, which is in favor of the improvement of power conversion efficiency.

In this work, a hierarchical double-layered TiO$_2$ flower-rod film on FTO glass was successfully synthesized by a facile hydrothermal method and was decorated with CdSe QDs using the successive ionic layer adsorption and reaction (SILAR) to form photoanode in QDSSCs. By investigation the effect of SILAR cycles of CdSe QDs on the photovoltaic performance, we got a 1.98% power conversion efficiency with a short circuit current density of 11.81 mA/cm$^2$ and an open circuit voltage of 0.39 V correspondingly for the CdSe(12)/TiO$_2$ flower-rod solar cell.

**Experimental**

**Materials**

Titanium butoxide (Ti(OCH$_3$)$_4$), concentrated hydrochloric acid (HCl, 36.5–38 wt%), sodium chloride (NaCl), cadmium nitrate (Cd(NO$_3$)$_2$·4H$_2$O), sodium sulfide (Na$_2$S·9H$_2$O), selenium powder (Se), sodium sulfite (Na$_2$SO$_3$), sulfur powder (S), potassium chloride (KCl) and chloroplatinic acid (H$_2$PtCl$_6$·6H$_2$O) were purchased from Tianjin Chemical Reagents Co. Ltd. All the chemicals are of analytic grade and used directly in experiments without further purification. Deionized water (DI water, resistivity of 18.2 MΩ·cm) was obtained from MilliQ ultra-pure water system (Millipore, USA).

**Preparation of Hierarchical TiO$_2$ Flower-rod Substrates**

Hierarchical TiO$_2$ flower-rod film was prepared by a facile hydrothermal method and the details of the synthetic procedure were similar to that described by Liu and Aydil [7]. In brief, Fluorine-doped tin dioxide (FTO) conducting glasses were thoroughly cleaned by sonication in a mixed solution of DI water, acetone, and 2-propanol (volume ratios of 1:1:1) for 30 min, and finally dried in air. Then the FTO conducting glass was transferred to the Teflon-lined stainless steel autoclave at an angle against the wall of the Teflon-liner with the conductive side facing up. Subsequently, a transparent mixed solution consisted of 25 ml of DI water, 30 ml of concentrated hydrochloric acid, 5 ml of saturated NaCl aqueous solution and 1 ml of titanium butoxide was added into the Teflon-lined stainless steel autoclave, filling the 80% volume of the autoclave. Then the hydrothermal synthesis reaction was conducted at the temperature of 150 °C for 12 h in an electric oven. Afterwards, the autoclave was cooled to room temperature under flowing water and the product was taken out, rinsed thoroughly with DI water and ethanol respectively. Finally, the product was dried in ambient air.

**Sensitization of CdSe QDs on TiO$_2$ Flower-rod Electrodes by SILAR**

In situ growth of CdSe QDs on TiO$_2$ flower-rod electrode was carried out by the successive ionic layer adsorption and reaction (SILAR) method [8]. Sodium selenosulphate (Na$_2$SeSO$_3$) aqueous solution which was prepared by refluxing 0.3 M Se in 0.6 M Na$_2$SO$_3$ at 90 °C for about 6 h is used as the Se source for SILAR. Typically, a TiO$_2$ flower-rod film was dipped into a 0.1 M Cd(NO$_3$)$_2$ ethanol solution for 5 min, and rinsed with ethanol to remove the excess Cd$^{2+}$ ions, then dipped for another 5 min into Na$_2$SeSO$_3$ aqueous solution, leading to the formation of CdSe, and rinsed again with ethanol. The two-step dipping procedure is termed as one SILAR cycle; several times of the SILAR cycle were repeated to investigate the optimal cycles of CdSe QDs for the performance of QDSSCs.

**Solar Cell Fabrication and Photovoltaic Measurement**

The QDSSCs were assembled in a sandwich-type fashion with QD-sensitized TiO$_2$ flower-rod photoanodes and Pt coated FTO counter electrodes. Platinumized counter electrodes were prepared by thermal decomposition of H$_2$PtCl$_6$ solution (5 mM in isopropanol) dropped onto FTO glass at 400 °C for 15 min. The polysulfide redox electrolyte, containing 0.6 M Na$_2$S, 0.2 M S and 0.2 M KCl [9] in the co-solvent of water and methanol with volume ratio of 7:3, was used as electrolyte for QDSSCs.
The photocurrent density-voltage (J–V) properties of the QDSSCs were obtained under illumination with sunlight simulator at AM 1.5 G (100 mW cm\(^{-2}\)) condition. The illuminated area of all the QDSSCs was fixed to 0.16 cm\(^2\) by covering a mask.

**Characterization**

The crystal phases of the samples were characterized by X-ray diffraction (XRD), in a 2\(\theta\) range from 10° to 90°, using Cu K\(\alpha\) radiation (\(\lambda = 1.5416 \text{ Å}\)). The morphologies and lattice structures of the samples were examined with field-emission scanning electron microscope (FE-SEM), transmission electron microscopy (TEM), high-resolution TEM (HR-TEM). The elemental compositions of the samples were analyzed by energy dispersive spectroscopy (EDS). The optical absorption spectra of bare TiO\(_2\) flower-rod and QD-sensitized TiO\(_2\) flower-rod electrodes were recorded in the range from 250 to 800 nm by UV-Vis spectrometer.

**Results and discussion**

**Morphology and structure Characterization of TiO\(_2\) Flower-rod Structure**

A double-layered TiO\(_2\) flower-rod on FTO substrate was synthesized using a simple hydrothermal method with conducting surface of FTO glass facing up. Figure 1a is top view of the TiO\(_2\) flower-rod electrode. Two parts, 3D TiO\(_2\) flowers on the top and 1D TiO\(_2\) nanorod arrays at the bottom constitute the hierarchical TiO\(_2\) nanostructure, and it is observed that the flower is composed of nanorods. The flowers exhibit open structure with numerous nanorods extended outside, and become gradually compact inside. Obviously, this flower-rod structure enlarges the surface area of the TiO\(_2\) film, implying its potential application value in QDSSCs.

![Figure 1](image)

**Figure 1.** (a) Top view of TiO\(_2\) flower-rod; (b) cross-sectional view of TiO\(_2\) flower-rod; (c) digital photograph of TiO\(_2\) flower-rod film and (d) EDS spectra of TiO\(_2\) flower-rod.
The cross-sectional image of the TiO$_2$ flower-rod is shown in Fig. 1b, it can be seen more clearly that the TiO$_2$ flowers were grown on top of TiO$_2$ nanorods, which provide the evidence for the formation of the double-layered TiO$_2$ nanostructure. Figure 1c is the digital photograph of TiO$_2$ flower-rod film, showing the formation of TiO$_2$ on surface of FTO glass. Energy dispersive spectroscopy (EDS) was applied to indentify the elemental composition of the nanostructure, which is shown in Fig. 1d. It can be seen that Ti and O are dominant elements (atomic ratio of 1:2), which confirms that the nanostructure was mainly composed of TiO$_2$.

![Figure 2. XRD patterns of FTO and TiO$_2$ flower-rod electrodes.](image)

The crystal phases of the FTO glass and TiO$_2$ flower-rod electrodes have been characterized by X-ray diffraction (XRD), which is shown in Fig. 2. It is worth noting that all the characteristic peaks of TiO$_2$ flower-rod in the XRD patterns can be indexed to the tetragonal rutile phase of TiO$_2$ (JCPDS no. 21-1276), and the FTO glass also shows rutile structure (JCPDS no. 41-1445). The small lattice mismatch between FTO glass and rutile TiO$_2$ makes it possible to grow TiO$_2$ flower-rod on FTO glass. The sharpness of the diffraction peaks implies a high crystallinity of the TiO$_2$ flower-rod film. Compared to the other diffraction peaks in XRD patterns of the as-prepared TiO$_2$ flower-rod, the enhanced (002) peak indicates that the hierarchical TiO$_2$ architecture is highly oriented with respect to the substrate surface and grow along the [001] direction with the growth axis parallel to the substrate surface.

**Characterization of CdSe/TiO$_2$ Flower-rod Structure**

After sensitization with CdSe QDs, the surface of TiO$_2$ flower-rod became rougher than that of bare TiO$_2$ flower-rod (Fig. 1a) as shown in Fig. 3a, which means that the QDs have been successfully deposited on the surface of the TiO$_2$ flower-rod after SILAR. Figure 3b is the typical TEM image of the CdSe/TiO$_2$ flower-rod unit, it can be seen clearly that the surface of the flower-rod unit is covered by QDs, which could further confirm that QDs have been successfully deposited on TiO$_2$. Fig. 3c shows a HR-TEM image of the CdSe/TiO$_2$ flower-rod unit. The clear lattice fringes indicated high crystallinity of TiO$_2$ and CdSe. The lattice spacing measured for the crystalline plane is 0.322 nm, corresponding to the (110) plane of rutile TiO$_2$ (JCPDS no. 21-1276), and outer crystallites close to the TiO$_2$ layer with lattice spacing of 0.328 nm corresponds to the (101) plane of CdSe (JCPDS no. 08-0459). These results provide powerful evidence for successful coating of CdSe QDs on the surface of TiO$_2$ flower-rod. In Fig. 3d, the appearance of characteristic peaks of Se and Cd in the EDS of QD-sensitized TiO$_2$ flower-rod confirms that CdSe QDs are successfully assembled on the TiO$_2$ flower-rod.
Figure 3. (a) FE-SEM image of CdSe/TiO$_2$ flower-rod; (b) TEM image of CdSe/TiO$_2$ flower-rod unit; (c) HR-TEM image of CdSe/TiO$_2$ flower-rod unit and (d) EDS spectra of CdSe/TiO$_2$ flower-rod.

Optical Property of CdSe/TiO$_2$ Flower-rod Photoanode

The UV-Vis Diffuse reflectance absorption spectra were used to record the different light absorption properties of the bare TiO$_2$ flower-rod electrode and CdSe/TiO$_2$ flower-rod electrode. As shown in Fig. 4, the onset optical absorption of the bare TiO$_2$ flower-rod occurs at around 410 nm and the main light absorption centered on ultraviolet light region. This result was consistent with the band
gap of 3.0 eV for rutile TiO$_2$[10]. After the TiO$_2$ flower-rod was sensitized by CdSe QDs, the spectral response range was extended from ultraviolet region to visible region. The absorption edge of CdSe/TiO$_2$ flower-rod was approximately at 670 nm, and the corresponding band gap was calculated to be 1.85 eV, which was higher than the value of CdSe in bulk (1.70 eV), indicating that the size of CdSe particle deposited on the TiO$_2$ flower-rod electrode was within the scale of QD. According to the empirical equations given by Yu et al. [11], the size of CdSe particle was estimated to be 9.71 nm.

**Photoelectrochemical Characterization**

![Graph showing photocurrent density-voltage (J–V) characteristics](image)

Figure 5. Photocurrent density-voltage (J–V) characteristics of different SILAR cycles of CdSe QDs sensitized TiO$_2$ flower-rod solar cells.

Figure 5 displays the J–V characteristics of TiO$_2$ flower-rod solar cells sensitized by different SILAR cycles of CdSe QDs, and the corresponding J-V parameters of QDSSCs are presented in Table 1. It is found that the short circuit current density ($J_{sc}$) increased gradually with extending deposition cycles at initial stage (from 3 cycles to 12 cycles) and the open circuit voltage ($V_{oc}$) reduced first (from 3 cycles to 6 cycles) and then increased (from 6 cycles to 12 cycles). However, both the $J_{sc}$ and $V_{oc}$ declined as the further increase of the SILAR cycles from 12 cycles to 15 cycles. The photovoltaic parameters of these solar cells are summarized in Table 1. This variation trend can be interpreted as follows: first, with extending SILAR cycles of CdSe QDs from 3 to 12, more QDs were deposited on TiO$_2$ flower-rod, which can enhance the light harvesting, leading to the increase of $J_{sc}$. In addition, a slight enhancement of $V_{oc}$ also occurs with the increase of CdSe QDs cycles, which can be explained according to the Eq. 1 [12].

$$V_{oc} = \frac{E_{F_n} - E_{redox}}{e} = \frac{k_B T}{e} \ln(n/n_0)$$  \hspace{1cm} (1)

Where $E_{F_n}$ is the quasi-Fermi level of the electrons in semiconductor photoanode under illumination; $E_{redox}$ is the potential of redox electrolyte; $e$ is the positive elementary charge; $k_B T$ is the thermal energy; $n$ is the electron concentration in conduction band of the semiconductor photoanode under illumination; $n_0$ is the electron concentration in the dark condition. When the CdSe QDs cycles increase from 6 to 12 cycles, more electrons would be injected into the conduction band of TiO$_2$ under illumination and the value of $n$ is increased, leading to more negative shift of the $E_{F_n}$, while the $E_{redox}$ remains unchangeable, causing the improvement of $V_{oc}$. However, both $J_{sc}$ and $V_{oc}$ are found to decrease when the SILAR cycles of CdSe QDs are further increased. This phenomenon can be explained in three ways: Firstly, the excessive SILAR deposition cycles would cause the aggregation of CdSe QDs and form excessive grain boundaries between CdSe nanoparticles. These grain boundaries can act as potential barrier for charges transfer to enhance the possibilities of the
recombination between electrons and holes, leading to a decrease in the overall efficiency. Secondly, the excessive SILAR cycles can lead to the growth of CdSe QDs, resulting in the poor charge injection efficiency caused by the reduced size quantization of the large QDs [13]. Finally, the excessive SILAR cycles may hinder the diffusion of the electrolyte due to the local block caused by aggregation of CdSe QDs, which limit the efficiency of charge separation and charge extraction. According to the variation of the $J-V$ curves to SILAR cycles in Fig. 5, the best solar cell performance with the $J_{sc}$ of 11.81 mA/cm$^2$ and $V_{oc}$ of 0.39 V was obtained by 12 SILAR cycles of CdSe QDs.

Table 1. Photovoltaic parameters of QDSSCs based on TiO$_2$ flower-rod solar cells.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$J_{sc}$(mA/cm$^2$)</th>
<th>$V_{oc}$(V)</th>
<th>FF</th>
<th>$\eta$(%)</th>
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</thead>
<tbody>
<tr>
<td>CdSe(3)/TiO$_2$</td>
<td>4.78</td>
<td>0.34</td>
<td>0.36</td>
<td>0.59</td>
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<td>CdSe(6)/TiO$_2$</td>
<td>6.11</td>
<td>0.33</td>
<td>0.36</td>
<td>0.73</td>
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<tr>
<td>CdSe(9)/TiO$_2$</td>
<td>9.41</td>
<td>0.36</td>
<td>0.37</td>
<td>1.25</td>
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<tr>
<td>CdSe(12)/TiO$_2$</td>
<td>11.81</td>
<td>0.39</td>
<td>0.43</td>
<td>1.98</td>
</tr>
<tr>
<td>CdSe(15)/TiO$_2$</td>
<td>5.61</td>
<td>0.37</td>
<td>0.39</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Summary

In conclusion, the hierarchical TiO$_2$ flower-rod film was successfully prepared on FTO conducting glass by a facile hydrothermal method. The TiO$_2$ flower-rod film sensitized with CdSe QDs by SILAR was used as photoanode in solar cell. The effect of SILAR cycles on the performance of QDSSCs was investigated, and the optimal was 12 cycles of CdSe QDs. The short circuit current density of 11.81 mA/cm$^2$, the open circuit voltage of 0.39 V, and the power conversion efficiency of 1.98% were achieved with CdSe(12)/TiO$_2$ flower-rod solar cell under one sun illumination (AM 1.5G, 100 mW/cm$^2$). The acceptable efficiency reported here has shown a great potential value to design high efficiency QDSSCs.

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References


