CdSe@TiO$_2$ Hollow Spheres Photoanode for Quantum Dots Sensitized Solar Cells

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Abstract. TiO$_2$ hollow spheres (HS) with size around 200-300 nm were synthesized using carbonaceous sphere as sacrificial template. CdSe quantum dots were deposited on to TiO$_2$ HS by hydrothermal process employing thioglycollic acid (TGA) as linker molecular to form CdSe@TiO$_2$ HS photoanode for solar cell application. Based on CdSe@TiO$_2$ HS photoanode, the photovoltaic performances of solar cells were tested and showed that a 24 h hydrothermal process make CdSe@TiO$_2$ HS solar cells exhibit a power conversion efficiency of 1.49%, which is the best among the sample solar cells. Possible reason for the working principle of CdSe@TiO$_2$ HS solar cell was proposed according to experimental facts. This work provides a novel insight to design structure of photoanode for quantum dots sensitized solar cells.

1. Introduction

Quantum dots sensitized solar cells (QDSSCs) have become a focus of investigation due to several advantages such as low fabrication cost, high theoretical power conversion efficiency, and multiple excitons phenomenon [1, 2]. A typical QDSSCs consisted of a photoanode, polysulfide electrolyte solution, and a counter electrode [3, 4]. The photoanode constructed based on QDs sensitized TiO$_2$ is the most important component of QDSSCs, playing a key role for the light harvesting, charge generation, and charge transport [5]. The TiO$_2$ nanoparticles with sized around 25 nm are most commonly used in QDSSCs due to a high specific surface area for QDs loading. However, weak light scattering ability make TiO$_2$ nanoparticles not a suitable candidate to enhance light harvesting efficiency in visible light region. Because resonant scattering of light is predicted to happen when particle size is comparable to the wavelength of incident light according to Mie theory [6]. In view of these issues, fabrication of TiO$_2$ hollow spheres as photoanode materials are particular attractive for QDSSCs due to its large interfacial surfaces and enhanced light harvesting efficiency caused by light scattering and multiple times light reflection inside of hollow spheres [7, 8].

In this work, we explore the synthetic approach of TiO$_2$ hollow spheres (HS) using carbonaceous spheres as template. Based on TiO$_2$ HS, CdSe quantum dots were sensitized onto TiO$_2$ to form CdSe@TiO$_2$ HS photoanode for QDSSCs application. An acceptable power conversion efficiency of 1.49% for CdSe@TiO$_2$ HS solar cells proved that the TiO$_2$ hollow spheres have potential application in design of QDSSCs.

2. Experimental

All reagents were purchased from Aladdin and were analytical reagent (AR) grade, which were used directly without any further purification.

2.1. Fabrication of TiO₂ hollow sphere (HS) photoanode

The TiO$_2$ HS were synthesized using carbonaceous microspheres as template [9-11]. In a typical synthesis route, the carbonaceous microspheres, which were obtained by hydrothermal process of sucrose aqueous solution in Teflon-stainless autoclave at 180 °C for 8 h, were dispersed in the 1 M of TiCl$_4$ aqueous solution under ultrasonic for 20 min. Then the suspension was aged for 6 h. After aging, the suspension was filtered, washed and dried to get black powders. Subsequently, the black powders were heated to 500 °C in a muffle furnace at the rate of 1 °C min^{-1}, with holding of the temperature at 500 °C for 3h. Finally, the resultant TiO$_2$ HS powders in white were acquired.

The TiO$_2$ HS powders, ethylcellulose, terpinol, and ethanol were mixed to form a viscous paste. Then the paste was doctor-bladed onto the FTO glass (2.0×1.5 cm), and the active area was controlled to be 0.25 cm^{-2}. After drying in ambient, the products were annealed in muffle furnace at 500 °C for 1 h to eliminate the organic residuals.

2.2. Synthesis of CdSe@TiO HS photoanode

The decoration of CdSe quantum dots (QDs) onto TiO$_2$ HS was achieved by hydrothermal process using TGA as linker molecular. Cd precursor solution was prepared by mixing 1.2 mmol of Cd(NO$_3$)$_2$ and 1.2 mmol of TGA in 25 mL deionized wate, and was tuned to transparent by addition of NaOH solution (5 M) into the Cd-TGA solution. The 0.1 M of Na$_2$SeSO$_3$ solution prepared by refluxing Se powder and Na$_2$SO$_3$ at 96 °C was used as Se precursors. 4.0 mL Se source was added to the Cd-TGA reaction medium. Then the resultant solution was transferred to Teflon-lined stainless autoclave in which the TiO$_2$ HS photoanode was previously placed. The sealed autoclave was placed in an electric oven and maintained at 150 °C to form CdSe@TiO$_2$ HS photoanode. The products obtained by hydrothermal time of 12 h, 24h, and 36 h were used to investigate the influence of hydrothermal time on photovoltaic performance.

2.3. Solar cell assembly

Cu$_2$S prepared by immersing in polysulfide solution containing 1 M sodium sulfide and 1M sulfur in deionized water was employed as counter electrode for CdSe@TiO$_2$ HS solar cells.

For the photovoltaic applications, the prepared CdSe@TiO$_2$ HS photoanode and Cu$_2$S counter electrode were assembled in a fashion similar to sandwich. The space between the two electrodes was filled with polysulfide consisted of 1M sodium sulfide and 1M sulfur aqueous solution.

2.4. Characterizations

We employed Quanta 450 FEG scanning electron microscopy (SEM) and Tecnai G2 F20 transmission electron microscope (TEM) to record morphology of the prepared products. For crystal phase characterization, we used D/MAX-2400 X-ray diffractometer to analyse the crystalline nature and structure of the samples.

With the assistant of Oriel I-V test station, we investigated the I-V performance of the solar cells. A solar simulator was used to simulate sunlight illumination with intensity of 100 mW cm^{-2}.

3. Results and discussion

The key to synthesize TiO$_2$ hollow spheres (HS) is how to get homogeneous size of carbonaceous spheres. Figure 1 (a) shows the SEM image of carbonaceous spheres obtained by the hydrothermal process of sucrose aqueous solution at 180 ℃ for 8 h. Apparently, the carbonaceous spheres with size around of 500 nm can be successfully acquired after hydrothermal reaction, and the size

distribution is uniform, providing potential application as templates for fabrication of hollow spheres structure.

Based on these carbonaceous spheres, the TiO_2 hollow spheres (HS) are prepared. Figure 1 (b) gives the SEM image of TiO_2 HS. The spherical structure could be identified, and the inset image shows the broken hollow spheres which shell and empty inside can be observe.

The TEM of TiO_2 HS in Figure 1 (c) further give the fine structure of HS, the shell and empty inside of the HS can be easily discerned in the TEM image, indicating the carbonaceous spheres template method is an effective approach to obtain TiO_2 HS. As shown in Figure 1 (b) and (c), the size distribution of TiO_2 HS is between 200 nm - 300 nm, which is smaller than that of original carbonaceous spheres, indicating a shrinkage phenomenon occurred during annealing process in muffle furnace. The surface area measurements show the BET of TiO_2 HS is around 21.6 m^2g^{-1}. Figure 1 (d) displays TEM image of the CdSe@TiO_2 HS prepared by hydrothermal process with TGA as linker molecular. Although the hollow sphere structure is still remaining, many small particles have covered on the surface of TiO_2 HS, indicating the formation of CdSe@TiO_2 HS and providing its potential application as photoanode in QDSSCs.
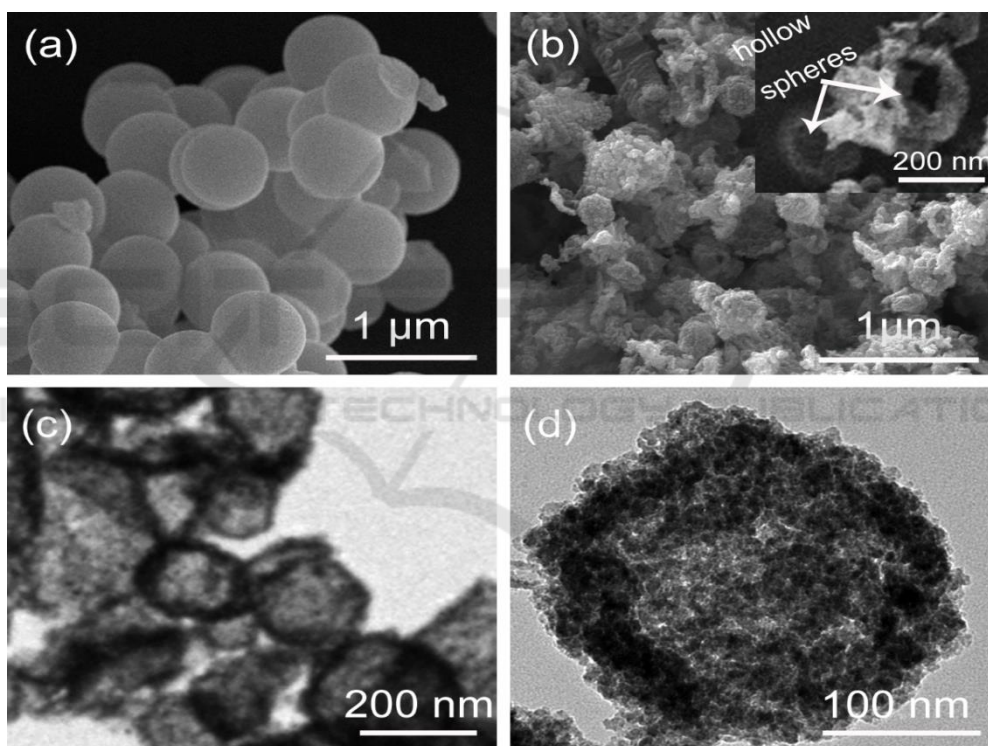

Figure 1. (a) the SEM of carbonaceous spheres; (b) the SEM of TiO_2 hollow spheres (HS), the inset is SEM of broken TiO_2 HS; (c) TEM of TiO_2 HS; (d) TEM of CdSe@TiO_2 HS.

The formation mechanism of CdSe@TiO_2 HS is illustrated in Figure 2 according to SEM and TEM analysis results. As templates, carbonaceous spheres obtain by hydrothermal reaction of sucrose play an important role in adsorption of Ti^{4+} due to rich carboxyl and hydroxyl function group on surface of carbonaceous spheres which are affinity to Ti^{4+}. After adsorption of Ti^{4+}, Ti^{4+}@carbon spheres are annealed in muffle furnace. The carbonaceous spheres are turned in CO_2, leading to the formation of TiO_2 HS. The disappearing of carbonaceous spheres is a gradually process due to the slow temperature increase rate. Hence, the final products of TiO_2 HS show a shrinkage in comparison with original carbonaceous spheres.

CdSe QDs can be anchored onto TiO_2 HS by hydrothermal process using TGA as linker molecular. The carboxylate group of TGA has a strong affinity to the TiO_2, while the thiol group of TGA can bind strongly to the CdSe QDs through the surface of Cd^{2+}. By dipping TiO_2 HS photoanode in precursor solution, the Cd^{2+} and Se^{2-} precursors can diffuse into the inside of the TiO_2 HS and bind chemically to the surface of hollow spheres, finally leading to the formation of CdSe@TiO_2 HS. The CdSe QDs can be decorated on the outer and inner surface of the TiO^2 HS shell because of the CdSe precursor solution is in ion scale which is beneficial to penetrate into hollow sphere from all directions.
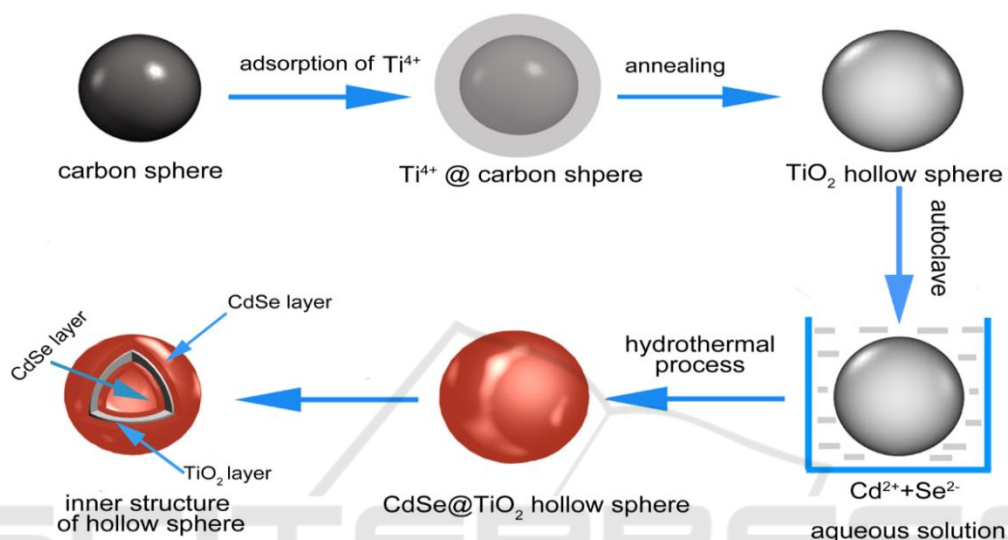

Figure 2. The illustration of carbonaceous spheres template method to construction of TiO_2 HS and hydrothermal process to preparation of CdSe@TiO_2 HS.
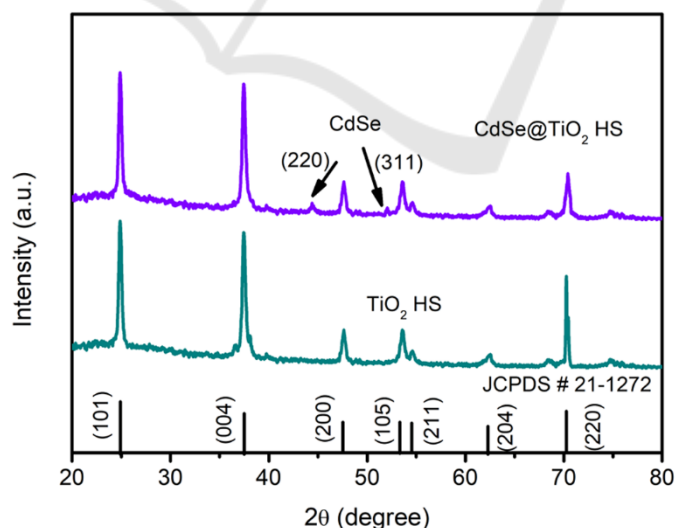

Figure 3. The XRD pattern of TiO_2 HS and CdSe@TiO_2 HS.

Figure 3 displays the XRD pattern of the TiO_2 HS and CdSe@TiO_2 HS. For the XRD patter of TiO_2 HS, several diffraction peaks can be discerned by careful comparison with standard diffraction pattern file of anatase TiO_2 (JCPDS # 21-1272), which can be respectively ascribed to the

corresponding planes of (101), (004), (200), (105), (211), (204), (220), indicating the crystal structure of TiO_2 HS belongs to anatase TiO_2. After the decoration of CdSe QDs on TiO_2 HS by hydrothermal process, two other diffraction peaks can be observed around 44.2° and 52.4° for XRD pattern CdSe@TiO_2 HS. These two diffraction peaks can be ascribed to the (220) and (311) planes of cubic CdSe (JCPDS #19-0191), demonstrating the successful decoration of CdSe QDs on TiO_2 hollow spheres.
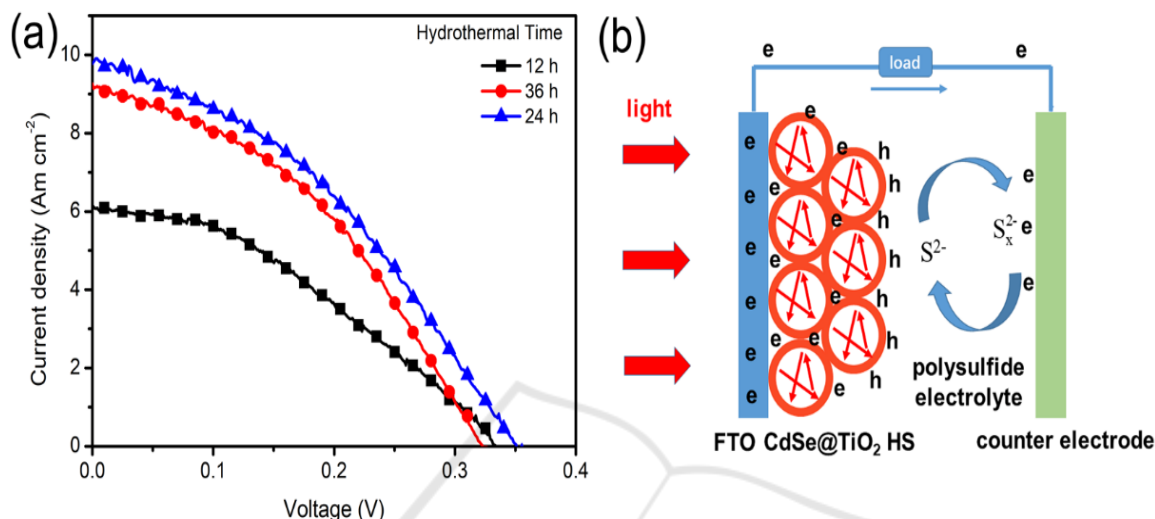

Figure 4. (a) I-V behaviours of CdSe@TiO_2 HS solar cells prepared by different hydrothermal reaction time; (b) working principle of the CdSe@TiO_2 HS solar cells.

Based on CdSe@TiO_2 HS photoanodes, solar cells are assembled, and the relationship between photovoltaic performance and hydrothermal reaction time of preparation CdSe@TiO_2 HS were investigated. Figure 4 (a) shows the I-V curves of solar cells assembled with CdSe@TiO_2 HS photoanode prepared by 12 h, 24 h, and 36 h of hydrothermal reaction time. Their photovoltaic parameters including open voltage (V_{oc}), short-circuit current density (Am cm^{-2}), fill factor (FF), and power conversion efficiency (PCE) are summarized in table 1.

Table 1. Parameters of CdSe@TiO_2 HS solar cells by different hydrothermal time

time	V_{oc} (V)	J_{sc} (Am cm^{-2})	FF	PCE (%)
12	0.33	6.11	0.36	0.74
24	0.35	9.78	0.43	1.49
36	0.32	9.26	0.45	1.36

As shown in Figure 4 (a), the best photovoltaic performance of CdSe@TiO_2 HS solar cells is achieved by 24 h of hydrothermal reaction, which shows a V_{oc} of 0.35 V, J_{sc} of 9.78 Am cm^{-2}, and FF of 0.43, yielding a PCE of 1.49%. Less or more hydrothermal reaction time (12 h or 36 h) for CdSe@TiO_2 HS photoanode produced a lower PCE than 24 h. Appropriate increase of hydrothermal reaction time for CdSe@TiO_2 HS may lead to more CdSe QDs deposition on TiO_2 hollow spheres, which can absorb more photons to generate excited electrons, resulting in the enhancement of PCE. However, overdose of CdSe QDs on TiO_2 HS may provide more recombination sites hindering the

efficient electrons transport, and leading to a decrease of PCE as indicated by CdSe@TiO$_2$ HS solar cells prepared by 36 h of hydrothermal process.

Figure 4(b) illustrated the working principle of CdSe@TiO$_2$ HS solar cells. The great potential to use TiO$_2$ HS as supporting architecture in QDSSCs is that the hollow sphere structure not only provides enough space for adsorption of QDs, but also generates an effect of full utilization of light caused by multiple times reflection of light inside of hollow spheres as shown Figure 4 (b), leading to the enhancement of light harvesting efficiency. When light is fully utilized to excite QDs generate more electrons, the photovoltaic performance of QDSSCs can be improved. Therefore, our CdSe@TiO$_2$ HS solar cell produced an acceptable PCE of 1.49%, showing great potential application of TiO$_2$ hollow spheres in design of QDSSCs.

4. Conclusions

The TiO$_2$ hollow spheres were synthesized using carbonaceous spheres template method. Furthermore, CdSe@TiO$_2$ hollow spheres photoanode were constructed by a simple hydrothermal process using TGA as linker molecular. The TEM, SEM, and XRD analysis results proved our strategy is feasible to obtain CdSe@TiO$_2$ hollow spheres photoanode for QDSSCs. The photovoltaic performance analysis results showed that the hydrothermal reaction time can influence the I-V behaviours of CdSe@TiO$_2$ hollow spheres solar cells. The QDSSCs with a better PCE of 1.49% can be obtained by 24 h of hydrothermal reaction time. The proposed working principle of the solar cell implies a potential application of TiO$_2$ hollow spheres for design of high power conversion efficiency QDSSCs.

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