The building of ZnO double-shells hollow spheres for CdS quantum dots sensitized solar cell

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Abstract. Using carbonaceous spheres as templates, the ZnO single-shell and double-shells hollow spheres (HS) have been successfully constructed and employed as architectures in CdS quantum dots sensitized solar cells (QDSSCs). The scanning electron microscope (SEM), elemental mapping, and transmission electron microscope (TEM) are used to analyze and confirm the microstructure of ZnO HS. The photovoltaic performance of QDSSC based on ZnO double-shells HS shows a 160% increase in power conversion efficiency than ZnO single-shell HS. Further investigation reveal that the enlarged surface area and multiple reflection light pathway offered by double-shell ZnO HS are responsible for the enhancement of QDSSC’s photovoltaic performance.

1. Introduction
Nanostructured ZnO as supporting architectures in design of quantum dots sensitized solar cells (QDSSCs) have drawn considerable interest in the past years due to the similarity of the energy band gap and the electron-injection process to that of TiO₂ [1-3]. Moreover, ZnO can be easily fabricated into different structures such as solid particles (nanoparticles), hollow structures (nanotube or hollow spheres) [4-6]. For now, most research on QDSSCs based on ZnO mainly focuses on the ZnO nanowires, or nanotubes in view of the direct electron pathways [7-9]. However, the overall photovoltaic performance is somehow limited due to the insufficient surface area and weak light scattering of the ZnO nanowire or nanotube. According to Mie theory and Anderson localization of light [10, 11], resonant scattering of light is predicted to happen for spherical particles with size comparable to the wavelength of incident light. Therefore, the ZnO hollow spheres with more than one shell indicates potential application in QDSSCs. Because the hollow spheres with multiple shells may provide an enhanced surface area and generate multiple light reflection between shells of ZnO hollow spheres [12]. Although the ZnO hollow spheres have been reported previously in Li ion battery, their application in QDSSCs has not widely investigated to our best knowledge.

In view of these background, ZnO double-shells hollow spheres (HS) have been built by carbonaceous spheres template method, and were used as architectures in CdS quantum dots sensitized solar cells (QDSSCs). Based on ZnO double-shells HS, the power conversion efficiency of QDSSC can reach to 1.56%, which is great higher than that of QDSSC based on ZnO single-shell HS, indicating a potential strategy in design of high efficiency QDSSCs.
2. Experimental section

2.1. Chemicals
All reagents were analytical and purchased from Shanghai Aladdin Chemical Co. Ltd., and were used directly without further purification. Zinc nitrate were used as metal precursors for synthesis of ZnO HS. Cadmium nitrate and sodium sulfide were used as cation and anion precursors for sensitization of CdS QDs. Ethylcellulose, terpinol, and ethanol were used for preparation of adhesive paste.

2.2. Synthesis of double-shells ZnO HS
In a typical route [12-14], the carbonaceous microspheres obtained by hydrothermal process of 0.75 M sucrose aqueous solution at 180 °C for 8 h were employed as template for preparation of ZnO HS. 1.0 g carbonaceous spheres were dispersed in 20 mL 2 M of zinc nitrate aqueous solution, and the mixture was aged for 12 h at room temperature after 20 min of ultrasonic process. Then the suspension was filtered, washed, and dried to get black powders. The powders were further transferred to Muffle furnace and heated up to 500 °C, holding at this temperature for 4 h. After naturally cooling, the double-shells ZnO HS can be obtained. For the preparation of single-shell ZnO HS, the procedure is similar but the changing the metal precursor to 1 M of zinc nitrate.

2.3. Preparation of CdS@ZnO HS photoanode
The ZnO HS powders (3g), ethylcellulose (0.5g), terpinol (10 mL), and ethanol (3mL) were mixed together under magnetic stirring to form adhesive paste. The ZnO paste was doctor-bladed onto the FTO glass (2.0×1.5 cm). The ZnO film active area was controlled to be 0.25 cm^2 and the thickness of the film was tuned to be ~15 μm using the same thickness spacers. After drying in ambient, the products were annealed in muffle furnace at 500 °C for 1 h to eliminate the organic residuals.

The ZnO HS photoanode was sensitized by CdS quantum dots using classical successive ions layer adsorption and reaction (SILAR) method [15, 16]. Firstly, the ZnO HS photoanode was immersed in 0.05 M Cd^{2+} solution of methanol and deionized water (1:1, V/V) for 30 s, then followed by immersing in 0.05 M S^{2-} solution of methanol and deionized water (1:1, V/V) for another 30 s. After each immersing, the photoanode was thoroughly washed by methanol. These steps were defined as one SILAR cycle. In our experiment, we found that more or less than eight SILAR cycles would decrease I-V performance of the same type solar cells based on ZnO. Therefore, eight cycles were repeated to guarantee enough amount of CdS quantum dots loadings on ZnO HS. The photoanodes were designated as CdS@ZnO single-shell HS and CdS@ZnO double-shells HS.

2.4. Solar cell assembly
Cu_{2}S counter electrode which fabricated by immersing brass foil previously etched by HCl solution in polysulfide aqueous solution containing 1M Na_{2}S and S [16]. The photoanode and counter electrode were assembled together by filling one drop of polysulfide electrolyte for open QDSSC’s I-V test.

2.5. Characterization
Quanta 450 FEG scanning electron microscopy (SEM) which equipped with an energy dispersive X-ray spectrometer (EDS) was employed to record surface morphology and elemental mapping of the prepared samples. Tecnai G2 F20 transmission electron microscope (TEM) was used to reveal the fine structure of ZnO HS. Absorption spectra of the photoanodes were characterized by a U-3900H UV-vis spectrophotometer which is equipped with integrating sphere attachment for diffuse reflection measurement. Tristar II 3020 was used in BET surface area test of the ZnO single-shell HS and ZnO double-shells HS.

With the assistant of Oriel I-V test station, the I-V performance of the CdS QDSSCs based on ZnO single-shell and double-shells HS were investigated. A solar simulator was used to simulate sunlight illumination with intensity of 100 mW cm^{-2}. The incident photon to charge carrier generation
efficiency (IPCE) was measured as a function of wavelength by 150 W Xe lamp coupled with a computer controlled monochromator.

3. Results and discussion

![Images of SEM and elemental mapping](image)

**Figure 1.** (a) the SEM of carbonaceous spheres template obtained by hydrothermal reaction of sucrose; (b) the SEM of ZnO single-shell HS, the inset is broken part; (c) the SEM of ZnO double-shells HS, the inset is a broken double-shells HS; (d-f) elemental mapping of selected ZnO HS from SEM; (g) the formation diagram of ZnO single-shell and double-shells HS by carbonaceous spheres template method.
Figure 1(a) shows the SEM image of carbonaceous spheres acquired by hydrothermal process of 0.75 M sucrose aqueous solution, showing that the size of carbonaceous spheres is around 600 nm. Using these carbonaceous spheres as template, the ZnO HS were further obtained. Figure 1(b) displays the SEM image of ZnO HS in low magnification, showing that abundant ZnO microspheres can be obtained by carbonaceous spheres template method. The size of ZnO HS is around 500 nm, which is smaller than the carbonaceous template, indicating a shrinkage occurred during fabrication process. The single-shell structure can be evidenced from the inset of Figure 1(b), indicating that ZnO single-shell HS can be synthesized with 1M Zn\(^{2+}\) precursor solution. Increasing Zn\(^{2+}\) precursors to 2M, ZnO double-shells HS was also fabricated by this template method, as shown in Figure 1(c). Although this SEM image does not show much difference in morphology comparing with Figure 1(b), the broken part in the inset of Figure 1(c) presents a smaller sphere is encapsulated by a larger hollow sphere, indicating the formation of double-shells spherical structure. The reason responsible for the formation of double-shells HS is that the carbonaceous spheres absorbed with more Zn\(^{2+}\) experienced a gradual disappearing when heated, leading to a double times template effect and finally forming double-shells ZnO HS. The elemental mapping of the HS has also been analyzed from a selected zone of ZnO HS SEM, which is shown in Figure 1(d-f), two kinds of elements including Zn and O can be scanned, confirming the obtained hollow spherical structure consisted of ZnO. Figure 1(g) summarized the process of synthesizing ZnO HS. The carbonaceous spheres possess the affinity to Zn\(^{2+}\) that can adsorb much of Zn\(^{2+}\) on surface. When heated in air, the carbonaceous sphere template evaporated to CO\(_2\) and formation of ZnO shell [12]. The double-shells HS can be formed by providing enough precursor Zn\(^{2+}\) to the carbonaceous spheres.

Figure 2. (a) TEM of ZnO single-shell HS; (b) TEM of CdS@ZnO single-shell HS; (c) TEM of ZnO double-shells HS; (d) TEM of CdS@ZnO double-shells HS.
The structural variation of ZnO single-shell and double-shells HS before and after sensitized by CdS QDs were recorded by TEM, which is shown in Figure 2. From the TEM of bare ZnO single-shell HS in Figure 2(a), the shell structure and empty inside can be easily identified, further confirming the formation of ZnO HS. After sensitization by CdS QDs, the TEM of CdS@ZnO single-shell HS in Figure 2(b) shows the empty inside is filled with many small nanoparticles, implying that CdS QDs may be deposited into the hollow spherical structure. The ZnO double-shells HS structure can be further evidenced by TEM in Figure 2(c). Apparently, the inner and outer spheres are hollow spherical structure, and the size of inner hollow sphere is around 150 nm. After sensitization with CdS QDs, both the inner and outer ZnO HS are filled with small nanoparticles, indicating successful sensitization of QDs.

In order to prove that the CdS QDs deposition on ZnO HS, the CdS@ZnO double-shells HS was analyzed by elemental mapping. Figure 3(a) and (b-e) is the selected SEM zone of CdS@ZnO double-shells HS and its corresponding elemental mapping results. Apart from Zn and O element originated from ZnO, another two types elements including Cd and S can be tested on the surface of hollow sphere, evidencing the formation of CdS@ZnO double-shells HS.

Figure 3. (a) SEM of selected CdS@ZnO double-shells HS; (b-e) the elemental mapping of this selected CdS@ZnO double-shells HS.

Figure 4. (a) the I-V test results of CdS@ZnO single-shell and double-shells solar cells, respectively; (b) the principle of light to electric conversion of CdS@ZnO solar cell; (c-d) the CdS QDs adsorption model and light pathway for ZnO single-shell and double-shells.
Based on ZnO single-shell and double-shells, the CdS QDSSCs have been built and their corresponding I-V performance has been comparatively investigated in Figure 4(a). For CdS@ZnO single-shell solar cell, the power conversion efficiency ($\eta$) is about 0.60%, a remarkable increase of $\eta$ is found when ZnO double-shells HS is employed in QDSSC, reaching to 1.56%, with $J_{sc}$ of 9.41 mA cm$^{-2}$, $V_{oc}$ of 0.36 V, and FF of 0.46. We believe that the structural difference between ZnO single-shell and double-shells HS may be responsible for the variation of I-V performance. When illuminated, the CdS QDs absorb photons to generate electrons and inject electrons into the conduction band of ZnO, as shown in Figure 4(b). Figure 4(c-d) compares the model of CdS QDSSCs based on ZnO HS. The ZnO double-shells HS can provide two shells for adsorption of CdS QDs, which means a better BET surface area favourable to the more electrons generation. Moreover, ZnO double-shells HS may enable multiple light reflection and improve light scattering between spherical shells.

In order to testify our claims, the BET surface area of ZnO single-shell and double-shells HS has been analyzed by N$_2$ adsorption-desorption measurement, and the results are shown in Figure 5(a). Obviously, a larger surface area is possessed by ZnO double-shells HS, indicating that more CdS QDs can be loaded on the surface and more electrons generation for enhancement of I-V performance. The UV-vis spectrum of CdS@ZnO double-shells HS shown in Figure 5(b) presents a higher absorbance than CdS@ZnO single-shell HS, also proving more QDs are adsorbed by ZnO double-shells HS, which will facilitate photons absorption to yield more electrons, helping to improve the I-V performance.

Figure 5. (a) the BET surface area of ZnO single-shell HS and ZnO double-shells HS; (b) the UV-vis absorption spectra of ZnO double-shell HS, CdS@ZnO single-shell HS, and CdS@ZnO double-shells HS.

Figure 6. The IPCE spectra of CdS@ZnO single-shell and CdS@ZnO double-shells solar cells.
Figure 6 compares the incident photon to current conversion efficiencies (IPCE) of CdS@ZnO single-shell and double-shells QDSSCs, respectively. Apparently, the ZnO double-shells HS produces a higher IPCE value. The reason responsible for this phenomenon is that the double-shells can adsorb more CdS QDs and reflect the incident light multiple times, enhancing the light harvesting efficiency, and finally lead to the significant improvement of power conversion efficiency of CdS@ZnO double-shells solar cell.

4. Conclusions

ZnO double-shells HS was successfully synthesized by carbonaceous spheres template method, and was used as architectures in CdS QDSSCs. The I-V test results show that the power conversion efficiency of CdS@ZnO double-shells solar cell can reach to 1.56%, which is significantly higher than CdS@ZnO single-shell solar cell. The remarkable improvement of photovoltaic performance can be ascribed to the enhancement of light harvesting efficiency caused by the increased surface area and multiple light reflection pathway supplied by ZnO double-shells HS. This strategy of designing ZnO HS will deliver insights to fabricate QDSSCs for better photovoltaic performance.

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