Synthesis of Zn_{x}Cd_{1-x}Se@ZnO Hollow Spheres in Different Sizes for Quantum Dots Sensitized Solar Cells Application

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Abstract: Zn_{x}Cd_{1-x}Se@ZnO hollow spheres (HS) were successfully fabricated for applications in quantum dots sensitized solar cells (QDSSCs) based on ZnO HS by ion-exchange process. The sizes of Zn_{x}Cd_{1-x}Se@ZnO HS could be tuned from ~300 nm to ~800 nm using ZnO HS pre-synthesized by different sizes of carbonaceous spheres as templates. The photovoltaic performance of QDSSCs, especially the short-circuit current density (J_{sc}), experienced an obvious change when different size of Zn_{x}Cd_{1-x}Se@ZnO HS are employed. The Zn_{x}Cd_{1-x}Se@ZnO HS with average size distribution of ~500 nm presented better performance than QDSSCs based on other sizes of Zn_{x}Cd_{1-x}Se@ZnO HS. When using the mixture Zn_{x}Cd_{1-x}Se@ZnO HS in different sizes, the power conversion efficiency can be further improved. The size effect of hollow spheres, light scattering, and composition gradient structure Zn_{x}Cd_{1-x}Se@ZnO HS are responsible for the enhancement of photovoltaic performance.

Keywords: alloyed quantum dots; hollow spheres; sensitized solar cells; zinc oxide.

1. Introduction

The huge consumption of fossil fuels and global warming caused by worldwide industry have forced the exploration of clean, environmental friendly energy [1-3]. Solar energy is one of the best candidates for future energy source. The common use of solar energy is various of photovoltaic devices including silicon solar cells, thin film solar cells, dye-sensitized solar cells, quantum dots sensitized solar cells, and perovskite solar cells [4-6]. Among them, quantum dots sensitized solar cells (QDSSCs) have become a focus of investigation due to their intrinsic advantages including superior extinction coefficient, possibility of multiple excitons generation, and higher theoretical power conversion efficiency (44%) than semiconductor solar cells based on Schockley-Queisser limit (33%) [7-9].

The power conversion efficiency of QDSSCs have constantly improved in recent years as a result of research efforts. The most remarkable is that a power conversion efficiency over 10% using Zn-Cu-In-Se quantum dots based on TiO_{2} film [10,11]. However, there is still many challenges need to be overcome to reach the theoretical limit (44%), indicating that the design of QDSSCs still have not been well optimized. As key part of photoanode in QDSSCs, the metal oxide particles in ~25 nm are most commonly used due to a high specific surface area for QDs loading [12-14]. However, typical metal oxide particles ~25 nm in the photoanode are weak to generate light scattering due to the size of particles is far smaller than the wavelength of visible light, causing a less light harvesting efficiency. Based on Mie theory and Anderson localization of light [15], resonant scattering of light is predicted to occur for spherical particles only when the particle size is comparable to the wavelength of incident
light [16]. To tackle this issue, metal oxide hollow spheres seem to be an appropriated choice for application in QDSSCs. Among these hollow structures, ZnO hollow spheres (HS) are particularly attractive as photoanode for QDSSCs due to their high electron mobility and low production cost [17]. Moreover, the size of ZnO HS is easy to control during fabrication process by using carbonaceous spheres as templates to generate better light scattering among hollow spheres, improving light harvesting capability.

Using ZnO HS as photoanode, many types of QDs such as single CdS, CdSe, CdTe, PbS, PbSe, cosensitized CdS/CdSe QDs, CdS:Se-, and ZnCd:Se alloyed QDs can be loaded for solar cell application [18-23]. Ternary alloyed QDs have drawn much attention recently because gradation composition heterostructures can be formed to tailor the alignment of conduction band edges of QDs, which is helpful to improve the electron injection efficiency [24-26]. For example, ZnO-ZnCd:Se core/shell nanowire arrays QDSSCs form a stepwise energy alignment at the heterojunctions, where both the conduction and valence bands of the shell are either higher or lower in energy than that of core [19,27-29], leading to a preferable transfer of electrons across the interface from ZnCd:Se to ZnO.

In view of these backgrounds, we constructed QDSSCs based on ZnCd:Se@ZnO hollow spheres (HS) with different sizes by using a simple ion-exchange route. The strategy for fabrication of ZnCd:Se@ZnO HS is based on the difference of solubility product constant (Ksp) of ZnO (6.8 × 10-17), ZnSe (3.6 × 10-29), and CdSe (6.31 × 10-36) [29], implying that the pre-prepared ZnO HS can be employed as sacrificial templates to form ZnCd:Se@ZnO HS by Se2- ion exchange and Cd2+ cation exchange in sequence. Furthermore, the size ZnCd:Se@ZnO HS could be controlled in accord with visible light region by using carbonaceous spherical templates, contributing to a stronger light scattering ability. To our best knowledge, the investigation of size effect of ZnCd:Se@ZnO HS on photovoltaic performance of QDSSCs has seldom been reported. Based on experimental results, reasons for the enhancement of photovoltaic performance of ZnCd:Se@ZnO HS QDSSCs are discussed.

2. Materials and Methods

2.1 Materials

The commercial chemical reagent including sucrose, zinc nitrate, cadmium nitrate, selenium powder, sodium borohydride, ethylcellulose, terpinol, ethanol, sodium sulfide, and sulfur powder were obtained from Aladdin Co. Ltd. The fluorine-doped tin oxide (FTO) conductive glass was purchased from Opvtech Co. Ltd. All materials were used directly without further purification.

2.2 Preparation of ZnO hollow microspheres

The ZnO hollow spheres (HS) were synthesized by a carbonaceous microspheres template method [30]. 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 (the size of carbonaceous can be modulated with different concentration of sucrose solution) were dispersed in the 1M aqueous solution of zinc nitrate 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 2 °C min-1, with holding of the temperature at 500 °C for 1 h. Finally, the resultant ZnO HS powders in white were acquired. The size of ZnO HS can be controlled using carbonaceous microspheres in different sizes.

2.3 Construction of ZnCd:Se@ZnO HS photoanodes and QDSSCs

The ZnO HS powders (3 g), ethylcellulose (0.5 g), terpinol (10 mL), and ethanol (3 mL) were mixed together under magnetic stirring to form a viscous 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 cm2 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. Types of photoanodes constructed by different sizes of ZnO HS including 300 nm, 400 nm, 500 nm, 800 nm,
and mixture of ZnO HS in different sizes (25 wt% for each size ZnO HS) are prepared for comparative investigation.

ZnCdSe@ZnO were obtained by immersing ZnO HS photoanodes in Se\(^{2-}\) and Cd\(^{2+}\) aqueous solution, respectively. Firstly, the ZnO HS were immersed in 0.1 M Se\(^{2-}\) ion solution prepared by reacting Se powder with Na\(_2\)H\(_2\). The immersing process was kept at 80 °C for 12 h, and was repeated two times to get a desirable ZnSe thickness of ZnSe@ZnO HS. Then the ZnSe@ZnO HS were put into 0.1 M Cd\(^{2+}\) solution at 80 °C for 12 h, this process was also repeated two times to gain the final product of ZnCdSe@ZnO HS photoanodes.

For solar cells application, the ZnCdSe@ZnO HS photoanode and Cu:S counter electrode, prepared according to previous literature [31], were assembled together by filling one drop of electrolyte consisted of 1 M S and 1 M NaI:S in water/methanol (1:1 in volume ratio) solution. We prepared QDSSCs based on ZnCdSe@ZnO HS in different sizes for comparative investigation of size effect on the performance of QDSSCs.

2.4 Characterization

We employed Quanta 450 FEG scanning electron microscopy (SEM) and Tecnai G2 F20 transmission electron microscope (TEM) which equipped with an energy dispersive X-ray spectrometer (EDS) for elemental analysis to record morphology of the prepared products. The optical absorption properties of the photoanodes were recorded by a U-3900H UV-vis spectrophotometer which is equipped with integrating sphere attachment for diffuse reflection measurement.

With the assistant of Oriel I-V test station, we investigated the I-V performance of the QDSSCs. 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 discussions

![Figure 1. The SEM images of carbonaceous spheres in different size prepared by varying concentration of sucrose: (a) 0.5 M, (b) 0.75 M, (c) 1 M, (d) 2 M.](image)
The carbonaceous spheres are important for the synthesis of ZnO HS due to their role of template. The size controllable preparation of carbonaceous spheres can be completed by varying concentration of sucrose aqueous solution. Fig. 1 records the morphology changes of resultant carbonaceous spheres as the increase of sucrose concentration. The diameters of these carbonaceous spheres could be tuned from ~400 nm to ~2 µm by simply increasing sucrose concentration from 0.5 M to 2 M. Based on this experimental facts, we selected carbonaceous spheres in size of ~400 nm, ~600 nm, ~800 nm and 1 µm as template. Because the scattering of light by spherical particles may occur when the particle size is comparable to the wavelength of incident light according to the Mie theory, and these selected carbonaceous spheres are available for synthesis of ZnO HS in appropriate diameter to generate light scattering.

ZnO HS can be obtained using carbonaceous spheres as template. Fig. 2(a) shows the SEM image of carbonaceous sphere in size of ~600 nm, from one of the broken sphere it can be seen that they are solid spheres. After formation of ZnO HS, the surface morphology of spheres changed to rougher than original carbonaceous spheres. As shown in Fig. 2(b), it seems that the ZnO HS is aggregated by a large number of nanoparticles. The average diameter of ZnO HS is ~500 nm, which is smaller than that of carbonaceous sphere templates, demonstrating a shrinkage of ZnO HS occurred during the heating process. This phenomenon is in accordance with previous reports[32,33]. The inset of Fig. 2(b) provides SEM image of a broken ZnO HS, the empty inside can be easily discerned, proving the obtained spherical structure is hollow spheres.

![Figure 2](image)

**Figure 2.** (a) The SEM image of carbonaceous spheres template in size of ~600 nm; (b) ZnO HS obtained by soaking carbonaceous spheres in 1 M Zn(NO₃)₂ solution, the inset is the SEM of a broken ZnO HS.

The hollow structures of the ZnO HS were further confirmed by TEM analysis, which are presented in Fig. 3 (a-d). Generally, all the products show hollow spherical structure with an identifiable shell, indicating that ZnO HS can be successfully synthesized using carbonaceous spheres as templates. Moreover, the TEM result also indicate that the size of ZnO HS can be controlled using carbonaceous spheres in different sizes. As shown in Fig. 3 (a-d), the sizes of ZnO HS can be tuned from ~300 nm to ~800 nm by different sizes of carbonaceous template. Fig. 3(e) is a selective area electron diffraction (SAED) pattern of ZnO HS. The appearance of diffraction rings indicating that the ZnO HS is in polycrystalline structure. Lattice fringes of the ZnO HS are observed by HRTEM image in Fig. 3(f). By careful measurements, the lattice spacing is measured to 0.26 nm, which corresponds to the (002) plane of hexagonal ZnO (JCPDS # 36-1451).
Figure 3. (a-d) TEM images of ZnO HS in size of ~300 nm, ~400 nm, ~500 nm, and ~800 nm, respectively; (e) the SAED pattern of ZnO HS; (f) the HRTEM of ZnO HS.

Figure 4. (a) The SEM of ZnO HS, the inset is magnified image of selected zone; (b) the TEM of ZnO HS; (c) the EDS of ZnO HS; (d) the SEM of ZnCd1-xSe@ZnO HS, the inset is magnified image of selected zone; (e) the TEM of ZnCd1-xSe@ZnO HS; (f) the EDS of ZnCd1-xSe@ZnO HS.

Based on ZnO HS, the ZnCd1-xSe@ZnO HS were further fabricated through ion-exchange process by soaking ZnO HS in Se²⁻ and Cd²⁺ aqueous solution, respectively. The morphology variation has been recorded by SEM and TEM images. Fig. 4(a) and its inset show the surface morphology of ZnO HS, big particles structure can be observed. The fine structure is further revealed by TEM in Fig. 4(b), the obvious shell and empty inside confirm the hollow spherical structure of ZnO HS. After the ion-exchange process, a slight morphology variation on surface of sphere is shown in Fig. 4(d) and its inset. Smaller nanoparticles are formed on surface, indicating new substance formed on surface of ZnO HS. Moreover, the TEM image in Fig. 4(e) shows the inside of the hollow sphere are filled with small particles after the ion-exchange process, demonstrating that the ion-exchange process can
transform ZnO HS to Zn$_{x}$Cd$_{y}$Se@ZnO HS. The EDS analysis further testified the formation of Zn$_{x}$Cd$_{y}$Se@ZnO HS by elemental analysis.  

Based on experimental facts and TEM results, the formation mechanism of Zn$_{x}$Cd$_{y}$Se@ZnO HS is proposed in Fig. 5. The first important step is that the use of carboxylic and hydroxyl functional groups which are affinity to Zn$^{2+}$ ion for a large amount of ion adsorption [34]. The carboxylic spheres are immersed in 1 M Zn$^{2+}$ aqueous solution for 6 h, and then taken out to be heated in air. During sintering, the carbonaceous spheres turn to CO$_2$, leading to formation of ZnO hollow spheres. The size of ZnO hollow spheres are tuned by selecting different size of carboxylic spheres templates. The second key step is the ion-exchange process to formation of Zn$_{x}$Cd$_{y}$Se@ZnO HS. Sharp difference of solubility product constant (K$_{sp}$) among ZnO (6.8×10$^{-17}$), ZnSe (3.6×10$^{-20}$), and CdSe (6.1×10$^{-26}$) [24,29] make it possible that the ZnO HS can be used as sacrificial templates to get more stable ZnSe@ZnO HS and further convert into Zn$_{x}$Cd$_{y}$Se@ZnO HS. As illustrated in Fig. 5, the ZnO hollow spheres initially conducted anion exchange with Se$^{2-}$ ions to form ZnSe@ZnO hollow spheres, and followed with surface conversion of ZnSe to Zn$_{x}$Cd$_{y}$Se through cation replacement of Zn$^{2+}$ by Cd$^{2+}$, leading to the final Zn$_{x}$Cd$_{y}$Se@ZnO hollow spheres (HS).

Figure 5. Illustration of the template approach to fabrication of ZnO HS and the ion-exchange process to preparation of Zn$_{x}$Cd$_{y}$Se@ZnO HS.
Figure 6. The UV-visible absorption spectra of ZnO HS, ZnSe@ZnO HS, and Zn$_{0.5}$Cd$_{0.5}$Se@ZnO HS photoanodes, respectively.

The UV-vis absorption spectra of photoanodes are illustrated in Fig. 6. The absorption onset of ZnO HS centers at ~385 nm, corresponding to the band gap of 3.2 eV. After anion exchange process, the absorption onset exhibits an obvious redshift to ~460 nm, corresponding band gap of 2.60 eV. This redshift phenomenon indicates that the formation of ZnSe@ZnO HS enlarge the light absorption range to visible region. A further redshift of absorption onset to 690 nm, which corresponds to 1.79 eV, after the cation exchange process implies that the successful formation of Zn$_{0.5}$Cd$_{0.5}$Se@ZnO HS.

The significant enlargement of light absorption means that most of light in visible region can be involved to excite Zn$_{0.5}$Cd$_{0.5}$Se for generation of electrons, providing potential application in QDSSCs.

Figure 7. (a) Current density-voltage (J-V) curves of QDSSCs based on Zn$_{0.5}$Cd$_{0.5}$Se@ZnO HS in size of 300 nm, 400 nm, 500 nm, and 800 nm; (b-e) the corresponding TEM images of Zn$_{0.5}$Cd$_{0.5}$Se@ZnO HS in different sizes with their PCE.

Since the size of Zn$_{0.5}$Cd$_{0.5}$Se@ZnO HS can be controlled using carbonaceous spheres in different sizes, it is reasonable to believe that the Zn$_{0.5}$Cd$_{0.5}$Se@ZnO HS photoanodes will have effects on the photovoltaic performance in QDSSCs. Fig. 7(a) recorded the current-density-voltage (J-V) behavior of the QDSSCs assembled with Zn$_{0.5}$Cd$_{0.5}$Se@ZnO HS. The Zn$_{0.5}$Cd$_{0.5}$Se@ZnO hollow spheres in size of ~300 nm, ~400 nm, ~500 nm, and ~800 nm are revealed by TEM image as shown in Fig. 7(b-e). The corresponding photovoltaic parameters of these QDSSCs including short-circuit current density (J$_{sc}$), open-circuit voltage (V$_{oc}$), fill factor (FF), and power conversion efficiency (PCE) are also summarized in Table 1.
Table 1. ZnCd₃Se@ZnO HS size influence on photovoltaic performance.

<table>
<thead>
<tr>
<th>Size (nm)</th>
<th>Jₘ (mA cm⁻²)</th>
<th>Vₘ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>~300</td>
<td>11.30</td>
<td>0.42</td>
<td>0.44</td>
<td>2.07</td>
</tr>
<tr>
<td>~400</td>
<td>11.61</td>
<td>0.41</td>
<td>0.46</td>
<td>2.19</td>
</tr>
<tr>
<td>~500</td>
<td>13.46</td>
<td>0.42</td>
<td>0.46</td>
<td>2.60</td>
</tr>
<tr>
<td>~800</td>
<td>8.79</td>
<td>0.40</td>
<td>0.49</td>
<td>1.72</td>
</tr>
</tbody>
</table>

The QDSSC based on ~300 nm ZnCd₃Se@ZnO HS photoanode exhibits a Jₘ of 11.30 mA cm⁻², a Vₘ of 0.42 V, and a FF of 0.44, producing a PCE of 2.07%. As the size of ZnCd₃Se@ZnO HS increased to ~400 nm, the QDSSC shows a Jₘ of 11.61 mA cm⁻², a Vₘ of 0.41 V, and a FF of 0.46, leading to PCE increased to 2.19%. A higher PCE of QDSSC is acquired by ~500 nm ZnCd₃Se@ZnO HS, which presents a Jₘ of 13.46 mA cm⁻², a Vₘ of 0.42 V, a FF of 0.46, yielding the highest PCE of 2.60% among these sample QDSSCs. However, further increasing ZnCd₃Se@ZnO HS to ~800 nm leads to a decrease of PCE to 1.72% with Jₘ of 8.79 mA cm⁻², Vₘ of 0.40 V, and FF of 0.49. Apparently, the only different among these sample QDSSCs is the size of ZnCd₃Se@ZnO HS. Therefore, we believe that a size effect of ZnCd₃Se@ZnO hollow spheres would probably be responsible for the changes of photovoltaic performance.

Figure 8. (a) The model of QDSSC based on ZnCd₃Se@ZnO photoanode; (b) the light pathway inside the ZnCd₃Se@ZnO HS; (c) the composition gradient structural model of ZnCd₃Se@ZnO HS; (d) band edges realignment in ZnCd₃Se@ZnO HS.

The explanations for the photovoltaic performance variation related to the structure of ZnCd₃Se@ZnO HS can be illustrated in Fig. 8. According to J-V curves results (Fig. 7), it can be concluded that the change of Jₘ among these ZnCd₃Se@ZnO solar cells is the main reason in the difference of photovoltaic performance. We believe that three factors, including light scattering on surface of hollow spheres, light reflection in hollow spheres, and a band edges realignment caused by gradient ZnCd₃Se@ZnO structure, have influence on the variation of Jₘ. Fig. 8(a) gives the working principle of QDSSC based on ZnCd₃Se@ZnO photoanode. Under illumination, the ZnCd₃Se@ZnO will be excited to generate electrons. More light absorbed will produce more electrons favorable to the increase of Jₘ. However, a significant portion of light emitted on the photoanodes would transmit through the photoanode without interacting with the ZnCd₃Se@ZnO HS due to the smaller size hollow spheres. Resonant scattering of light is anticipated to occur for spherical particles in size comparable to the incident light according Mie theory and Anderson localization of light [35].
In our case, the photoanode is packed by Zn$_2$Cd$_{0.1}$Se@ZnO HS, by controlling the size of hollow spheres, ~500 nm Zn$_2$Cd$_{0.1}$Se@ZnO HS is in the range of visible light, which results in a stronger scattering effect among Zn$_2$Cd$_{0.1}$Se@ZnO hollow spheres than other sizes hollow spheres, providing the photons more chances to be absorbed, and eventually leading to an enhanced light harvesting efficiency. In addition, hollow sphere structure of Zn$_2$Cd$_{0.1}$Se@ZnO allows light to be reflected by many times when it encounter the shell of hollow sphere due to its curved surface, as shown in Fig 8 (b), also leading to enhancement of light harvesting efficiency.

A sandwich composition gradient structure of Zn$_2$Cd$_{0.1}$Se@ZnO would be formed on the shell hollow spheres due to the ion-exchange process, as illustrated in Fig. 8(c), the ZnSe layer firstly formed ZnO HS surface during Se$^2-$ ion-exchange process, then a Cd$^{2+}$ ion-exchange process would replace Zn$^{2+}$ from surface of ZnSe layer to deep, forming sandwich composition gradient structure of Zn$_2$Cd$_{0.1}$Se@ZnO HS with Cd$^{2+}$ rich in surface. This sandwich structure would cause a band realignment as shown in Fig. 8(d), when Zn$_2$Cd$_{0.1}$Se@ZnO formed, the ZnO, ZnSe and Zn$_2$Cd$_{0.1}$Se are brought contact closely, the energy levels difference between ZnSe and Zn$_2$Cd$_{0.1}$Se would cause electron flow from ZnSe to Zn$_2$Cd$_{0.1}$Se, which is known as Fermi level alignment, triggering a downward and upward shift of band edges of ZnSe and Zn$_2$Cd$_{0.1}$Se, respectively [28]. The formation of stepwise conduction band edge alignment in order of Zn$_2$Cd$_{0.1}$Se > ZnSe > ZnO for sandwich composition gradient Zn$_2$Cd$_{0.1}$Se@ZnO HS is beneficial to enhance the injection and collection of photoexcited electrons to the conduction band of ZnO layer.

![Figure 9. The incident photo-to-current conversion efficiency (IPCE) spectra of QDSSCs based on Zn$_2$Cd$_{0.1}$Se@ZnO HS in size of ~300 nm, ~400 nm, ~500 nm, and ~800 nm, respectively.](image)

The IPCE spectra of QDSSCs based on Zn$_2$Cd$_{0.1}$Se@ZnO HS in different sizes can provide more information on the enhancement of J$_{sc}$. As seen in Fig. 9, two interesting observations can be identified comparing these spectra. The first one is that the range of photoreponse centers in the visible light region for all sample solar cells, demonstrating the excitation of Zn$_2$Cd$_{0.1}$Se as the primary event responsible for photocurrent generation. A second one is that considerable increase of IPCE with the increasing size of Zn$_2$Cd$_{0.1}$Se@ZnO HS in visible light region, especially the highest IPCE value produced by ~500 nm Zn$_2$Cd$_{0.1}$Se@ZnO HS. Considering its size in range of visible light region, thus its IPCE enhancement is mainly attributed to the increased of light scattering, contributing to the improvement of J$_{sc}$ eventually.

According to the above discussion, ~500 nm Zn$_2$Cd$_{0.1}$Se@ZnO HS show better scattering of light in visible light region than other HS sizes. However, the single size distribution of hollow spheres seem cannot take full use of visible light region to generate light scattering. Therefore, photoanode constructed by mixture of ZnO HS in different sizes from 300 to 800 nm was fabricated, and its photovoltaic performance is shown in Fig. 10. As the I-V curves shows in Fig. 10(a), the mixture of hollow spheres in different sizes can further improve the J$_{sc}$ to 20.77 mA cm$^{-2}$, leading to the
enhancement of PCE to 2.95%. The IPCE in Fig. 10(b) shows that the maximum IPCE value can reach to 85%, indicating a better utilization of visible light region to enhance the light harvesting efficiency. This significant improvement of photovoltaic performance using mixture hollow spheres can be ascribed to the enhanced light scattering in different wavelength of light caused by wide sizes range from 300 nm to 800 nm as shown in Fig. 10(c) than single size of hollow spheres, indicating the potential application of this strategy to design of QDSSCs.

Figure 10. (a) The J-V curve of QDSSC based on mixture of ZnO HS in different sizes from 300 nm-800nm; (b) the corresponding IPCE spectrum; (c) the SEM image of the corresponding photoanode.

4. Conclusions

In summary, unique Zn,Cd,Mn,Se@ZnO hollow spheres (HS) with a gradient position are successfully fabricated by ion-exchange process with assistance of carbonaceous spheres as template. The size of Zn,Cd,Mn,Se@ZnO hollow spheres can be controlled by using carbonaceous spheres in different sizes. The influence on QDSSSs caused by sizes variation of Zn,Cd,Mn,Se@ZnO hollow spheres was investigated. Light scattering and composition gradient structure of Zn,Cd,Mn,Se@ZnO hollow spheres are responsible for the enhancement of photovoltaic performance. Size of Zn,Cd,Mn,Se@ZnO hollow spheres ~500 nm show better effect than other sizes of hollow spheres. By using mixture of hollow spheres in different sizes from 300 nm to 800 nm, the PCE of QDSSC can be improved to 2.95%, showing the feasibility of Zn,Cd,Mn,Se@ZnO hollow spheres in design of high efficient QDSSCs.

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