Effect of TiO₂ shell layer prepared by wet-chemical method on the photovoltaic performance of ZnO nanowires arrays-based quantum dot sensitized solar cells

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TiO₂ shell layer on the surface of ZnO nanowires (NWs) was synthesized by a layer by layer adsorption and reaction (LBLAR) method. Scanning electron microscopy image shows that the prepared ZnO–TiO₂ core–shell NW arrays have a similar morphology with the well-aligned ZnO core NW arrays, providing the LBLAR cycles is controlled within a certain number. The prepared ZnO–TiO₂ core–shell NW arrays were sensitized with CdS quantum dots to assemble quantum dots sensitized solar cells. Results indicate that a dramatic increase in open-circuit voltage and fill factor is achieved with an introduction of the TiO₂ shell layer with a thickness of about 7 nm, resulting in a substantial improvement of the overall energy conversion efficiency. A rapid electron transfer from the CdS QDs to the ZnO NWs and a reduced electron recombination rate due to the energy barrier occurred at the interface between the ZnO core and the TiO₂ shell are believed to contribute to the improved performance of the solar cells based on the ZnO–TiO₂ core–shell NW arrays. In addition, effects of the TiO₂ shell thickness on the performance of the as-fabricated devices are also discussed in detail.

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1. Introduction

Quantum dots sensitized solar cells (QDSSCs) have attracted considerable attention over the past few years due to several significant factors, including the higher absorption coefficient than the dye molecules, the tailored absorption by controlling the size and shape of quantum dots (QDs), as well as the possibility of boosting the energy conversion efficiency beyond the traditional Shockley and Queisser limit of 32% for Si based solar cells [1,2]. Actually, the energy conversion efficiency of QDSSCs increased rapidly to near 5% in the past few years, but it is still very low compared to that of dye sensitized solar cells (DSSCs) [3,4].

To improve the performance of QDSSCs, various nanostructures have been employed to fabricate the photoanodes, such as mesoporous films [5–7], hierarchical sphere [3], nanowires (NWs), nanorods (NRs) and nanotubes (NTs) arrays [8–12]. Recently, many new strategies, especially the surface and interface treatment, were also employed to modify the nanostructures of the photoanodes, aiming to reduce the recombination and improve the transport of the photo-excited carriers at the interface [3]. For example, it has been demonstrated that a blocking layer pre-deposited on the fluorine-doped tin oxide (FTO) plays an important role in reducing the recombination of the photo-excited carriers at the FTO/electrolyte interface; thus, resulting in higher open-circuit voltage, short-circuit current, and consequently the overall energy conversion efficiency [13]. Better device performance can be obtained if the surface of QDs is covered with a thin layer of ZnS, which is believed to passivate the surface of QDs, reduce the recombination of electrons from TiO₂ with the electrolyte and increase the life time of electrons in the device [5,14,15]. An insulating SiO₂ layer was also demonstrated to be effective to reduce the recombination at the electrolyte/photoanode interface [16]. Besides, a thin TiO₂ coating layer on the surface of CdS QDs not only improved the stability of QDSSCs using I⁻/I₃⁻ electrolyte, but also decreased the recombination of electrons from the QDs and the mesoporous TiO₂ with the electrolyte [17]. Particularly, the solar cells based on ZnO–TiO₂ core–shell NW arrays have been reported and many methods have been explored to fabricate ZnO–TiO₂ core–shell NWs arrays, such as atomic layer deposition [18,19], radio frequency magnetron sputtering [20,21] and chemical vapor deposition [22]. However, to the best of our knowledge, there are few reports on the effect of TiO₂ coating layer on the performance of QDSSCs based on ZnO NW arrays.

Here, we report an all wet-chemical route to synthesize ZnO–TiO₂ core–shell NW arrays, which includes a liquid growth of ZnO NW arrays and a layer by layer adsorption and reaction...
2. Experimental

ZnO NW arrays were prepared by a liquid growth process. Before the growth of the ZnO NWs, a ZnO seed layer was deposited on the FTO substrate by a sol–gel method as reported in our previous works [23,24]. The seed-coated substrate was then immersed in a bottle filled with about 100 mL precursory growth solution, which contains 0.05 M Zn(NO₃)₂, 0.05 M hexamethylenetetramine and 0.005 M ethyleneimine polymer solution (M.W. = 1800, PEI, Aladdin Reagent Co. Ltd., China). Then the bottle was capped and kept in an oven at 95 °C for about 12 h. Finally, the ZnO NW arrays were rinsed with deionized water and dried with air.

A LBLAR method was employed to deposit TiO₂ coating layer on the surface of the ZnO NWs. The as-obtained ZnO NW array film was successively immersed into three different solutions for 45 s each, which were TiO₂ sol, pure ethanol and deionized water, respectively. Then the film was rinsed with pure ethanol to dissolve excess water and weakly bound TiO₂ before the next dipping. Above procedure illustrated in Fig. 1 was considered as one LBLAR cycle and denoted as 1TiO₂. Different cycles were repeated according to the requirement thickness of the TiO₂ coating layer. The TiO₂ sol was prepared by dissolving 0.05 M tetrabutylacetone (TBT) and 0.05 M acetylacetone in 100 mL ethanol. The prepared ZnO–TiO₂ core–shell NWs arrays were then calcined at 550 °C for 1 h.

The CdS layer was deposited onto the surface of the ZnO–TiO₂ core–shell NWs by a SILAR process [25]. In brief, the NWs arrays film was successively immersed into four different solutions for 30 s each, which were 0.05 M CdCl₂ in ethanol, pure ethanol, 0.05 M Na₂S in methanol and pure methanol, respectively. Then the film was rinsed with pure ethanol for 30 s or longer to remove excess precursors before the next dipping. The above procedures were considered as one SILAR cycle and 16 cycles were carried out to obtain the CdS sensitized photoanodes.

The as-prepared photoanode and an Au-sprayed FTO substrate were sealed with transparent hot-melt film by hot-pressing. Here, the Au electrode was reported to show higher activity than the Pt electrode in polysulfide electrolyte [26]. An active area of the device was limited to 0.25 cm². A solution containing 1 M Na₂S, 2.5 M S, and 0.2 M KCl in water/methanol (7:3, v:v) was used as the electrolyte. It should be mentioned that there would be a current

![Fig. 1. Schematic illustration of preparation of TiO₂ shells on the ZnO NWs arrays.](image-url)
doubling effect due to the nonregenerative methanol oxidation at the working electrode, resulting in erroneously high power conversion efficiencies [4]. However, the main aim of this article is to study the effect of TiO$_2$ shell on the performance of ZnO NW arrays-based QDSSC, therefore, the same electrolyte containing methanol was used in all the devices in this research.

A scanning electron microscopy (SEM, JSM-6390, JEOL Inc., Japan) was used to characterize the morphological properties of the samples. Microstructural properties of the photoanodes were observed by a transmission electron microscopy (TEM, JEM-2100F, JEOL Inc., Japan). X-ray photoelectron spectroscopy (XPS) was used to analyze elemental composition of the samples, using Al K$_\alpha$ radiation as the X-ray source (ESCALAB MK-II model), operated at 12.5 kV and 20 mA under a vacuum pressure of 10$^{-8}$ Pa. The photocurrent density–voltage (J–V) curves of the cells were measured by an electrochemistry workstation (CS 350, Wuhan Cortest Instrument Co. Ltd.) under an irradiation of simulated solar light (AM 1.5G, 100 mW cm$^{-2}$). The light intensity of the illumination source was calibrated by using standard silicon photodiode.

### 3. Results and discussion

Fig. 2a can be seen the cross-sectional SEM image of the ZnO NW arrays. It can be seen that well-aligned ZnO NW arrays with a length of about 3 µm can be obtained by the liquid growth process and most NWs have a diameter in the range from 100 nm to 180 nm. After depositing TiO$_2$ layer with 20 LBLAR cycles (ZnO–20TiO$_2$) as shown in Fig. 2b, perpendicular ZnO–TiO$_2$ core–shell NWs arrays can be obtained and the morphology of the ZnO–TiO$_2$ core–shell NWs arrays is very similar to that of the ZnO NWs arrays as shown in Fig. 2a. The ZnO–TiO$_2$ core–shell NWs arrays were further observed by TEM and Fig. 2c shows the TEM image of a single ZnO–TiO$_2$ core–shell NW, in which a 7 nm thick shell layer can be clearly observed, indicating the formation of the core–shell nanostructure. The inset of Fig. 2c is the corresponding electron diffraction pattern. Both the diffraction spots array of the ZnO NW core and the diffraction circles of the TiO$_2$ shell layer can be clearly observed in the electron diffraction pattern, indicating a single crystalline structure of the ZnO NW and a multicrystalline structure of the TiO$_2$ shell layer, respectively. A high-resolution transmission electron microscopy (HRTEM) image that shows the interface region between the ZnO NW core and the TiO$_2$ shell can be observed in Fig. 2d. A coherent interface between the ZnO NW core and the TiO$_2$ shell as seen in the image demonstrates a good attachment between the ZnO NW core and the TiO$_2$ shell. The spacing between two adjacent lattice fringes in the shell is 0.294 nm, which is close to the (001) plane of rutile TiO$_2$ (JCPDS card: 86-0147).

The element composition of surface structure of the ZnO–20TiO$_2$ core–shell NW arrays was characterized by XPS analysis and the results are shown in Fig. 3. The shift of binding energy due to relative surface charging has been corrected by using the C 1s level at 284.6 eV as an internal standard. Fig. 3a shows two adjacent peaks at 458.4 eV and 464.2 eV, which correspond to Ti2p$_{3/2}$ and Ti2p$_{1/2}$, respectively. These values are consistent with the location of standard Ti2p, but are different from the results as reported by Yan et al., for a notable shift to higher value of Ti2p peak for the ZnO/TiO$_2$ composite was found in their experiment [27]. We ascribe this difference to the different preparation method of the TiO$_2$ shell. As compared to the TiO$_2$ shell fabricated by LBLAR, the magnetron sputtered TiO$_2$ shells as reported in Ref. [27] provide a much more intense interaction between ZnO and TiO$_2$ at the interface due to the high energy of TiO$_2$, resulting in the shift of binding energy. Fig. 3b and c shows the XPS spectra of O1s and Zn2p$_{3/2}$. Unlike the results as shown in Ref. [27], which reported the shift and split of peaks for O1s and Zn2p$_{3/2}$, there is only a single peak at

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**Fig. 3.** XPS spectra of the ZnO–20TiO$_2$ core–shell NWs arrays: (a) Ti, (b) O and (c) Zn.
530.2 eV for O1s in Fig. 3b and a single peak at 1022.2 eV for Zn2p1/2 in Fig. 3d. Similar to the analysis for the spectrum of Ti2p, these differences should also be ascribed to the different preparation method.

The ZnO–TiO2 core–shell NWs arrays with different shell thickness were prepared by changing the LBLAR cycle number, and Fig. 4a and b shows the TEM images of the ZnO–TiO2 core–shell NW with different shell thickness and Fig. 4c is a plot of the TiO2 shell thickness versus the LBLAR cycle number. In order to obtain reliable data of the thickness, more than 6 samples per coating thickness were measured in our research. It is clearly observed that an ultra-thin TiO2 coating layer with a thickness of ∼2 nm can be deposited on the surface of the ZnO NWs when the LBLAR cycle number is 10. With increase the LBLAR cycle number up to 40, the thickness of the TiO2 shell increases to ∼16 nm. Interestingly, apart from the first several cycles, a linear relationship between the thickness of the TiO2 shell and the LBLAR cycles can be found. It should be mentioned that the deposition rate of the TiO2 shell is much slower than that of the TiO2 nanotubes walls which were prepared by a similar methods using ZnO NWs arrays as the template [28]. We believe the slow deposition rate should be related to a long time rinsing process which is carried out in each LBLAR cycle. Fig. 4d shows the cross-section SEM image of the ZnO–40TiO2 core–shell NWs arrays. Compared with the bare ZnO NW arrays, the diameter of the ZnO–40TiO2 core–shell NWs is much thicker due to the deposition of the TiO2 shell. In addition, it is noted that most NWs fuse at their roots, resulting in less space among NWs and fewer surface area of the core–shell NW arrays.

The as-prepared ZnO–TiO2 core–shell NW arrays were employed to load the CdS QDs and then assemble the QDSSCs. Fig. 5 shows the UV–vis absorption spectra of the samples with different TiO2 coating layers. After sensitized by the CdS QDs layer, the absorption ranges extend to the visible-light region. Interestingly, the absorption range for ZnO–40TiO2–16CdS NWs shift slightly to the blue side compared to those of other samples. This may result from that the evident fusion of the ZnO NWs as shown in Fig. 4d hinders the deposition of the CdS QDs, resulting in less loading of the QDs and consequently less absorption of light. Fig. 6a shows the J–V curves of the devices fabricated from the CdS sensitized NW arrays with different shell thickness. It can be seen that the thickness of the TiO2 coating layer has a dramatic effect on the performance of the devices. For example, the open circuit voltage ( Voc) and the fill factor (FF) of the device fabricated from the TiO2 shell layer with 20 LBLAR cycles are improved from 0.52 V and 0.294 to 0.61 V and 0.405, respectively. While the short circuit current density ( Jsc) varies little, resulting in an enhancement of the energy conversion efficiency from 0.479% to 0.748%. Therefore, the promotion of the device performance is mainly ascribed to the increase of Voc and FF. However, if the LBLAR cycle number is further increased, both the Voc and Jsc decrease seriously, leading to
a deterioration of the energy efficiency. The detailed photovoltaic parameters of the devices are presented in Table 1. The corresponding dark current experiments were also carried out. Although the dark current can not be directly related to the recombination due to the different electrolyte concentration and potential distribution in the nanowire films in dark as compared to that under illumination, the dark current measured at positive bias where electrons flow from the nanowires into the electrolyte still can provide useful information for the electron transfer process [29]. Therefore, it has been considered as a sign of the charge recombination between the nanostructures and the electrolyte in many works [18,30,31]. As shown in Fig. 6b, the dark-recombination current decreases a lot with depositing the TiO2 coating layer on the surface of the ZnO NWs, and particularly, the device fabricated with the ZnO–20TiO2 core–shell NWs array exhibits the lowest dark-recombination current, suggesting that the TiO2 shell layer is effective to attenuate the carrier recombination. 

\[ V_{OC} = \frac{E_{F, ZnO} - E_{F, redox}}{e} = \frac{K_0 T}{e} \ln \left( \frac{n_0}{n} \right) \]

where \( E_{F, ZnO} \) is the electron Quasi Fermi level under illumination, \( E_{F, redox} \) is the redox level of the electrolyte, \( K_0 T \) is the thermal energy, \( e \) is the positive elementary charge, \( n \) is the electron concentration under illumination and \( n_0 \) is the electron concentration in the dark. Clearly, lower recombination rate (dark-recombination current) will result in larger \( V_{OC} \) which is consistent with the \( J-V \) results. Although the ZnO–40TiO2 core–shell NW array has a lower dark current than the bare ZnO NWs array, it still shows the lowest \( V_{OC} \) because of the weakest photocurrent. The recombination rates of the QDSCs were further analyzed by the open-circuit voltage-decay (OCVD) technique. It should be mentioned that blocking the FTO substrate is essential for determination of the life time [33]. In our experiment, a dense ZnO seed layer was prepared for the nanowire growth which is believed to work as a blocking layer for the FTO substrate. As shown in Fig. 7a, all the cells fabricated with the ZnO–TiO2 core–shell NW arrays exhibit a slower photovoltaic-decay rate than that fabricated with the ZnO NWs arrays. A rapid electron transfer and a reduced recombination of the cell fabricated with the ZnO–20TiO2 core–shell NW arrays cause more electrons to accumulate in the ZnO core,

### Table 1

Photovoltaic parameters of the QDSSCs with different TiO2 shell thickness.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( J_{SC} ) (mA cm(^{-2} ))</th>
<th>( V_{OC} ) (V)</th>
<th>( FF )</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO NWs</td>
<td>3.13</td>
<td>0.52</td>
<td>0.294</td>
<td>0.479%</td>
</tr>
<tr>
<td>ZnO–10TiO2 NWs</td>
<td>3.22</td>
<td>0.52</td>
<td>0.328</td>
<td>0.549%</td>
</tr>
<tr>
<td>ZnO–20TiO2 NWs</td>
<td>3.03</td>
<td>0.61</td>
<td>0.405</td>
<td>0.748%</td>
</tr>
<tr>
<td>ZnO–40TiO2 NWs</td>
<td>2.51</td>
<td>0.49</td>
<td>0.314</td>
<td>0.387%</td>
</tr>
</tbody>
</table>

Fig. 6. (a) \( J-V \) curves of the CdS QDSSCs fabricated with the NWs arrays with different TiO2 shell thickness and (b) dark-recombination current of the CdS QDSSCs fabricated with the NWs arrays with different TiO2 shell thickness.

Fig. 7. (a) Experiment \( V_{OC} \) decays results of the CdS QDSSCs with different TiO2 shell thickness and (b) the calculated electron lifetime as a function of voltage.
concurrently, resulting in higher photovoltaic voltage. A decay-time constant can be calculated from the equation as introduced in Ref. [32]:

$$\tau = -\left(\frac{K_0 T}{e}\right) \left(\frac{dV_{OC}}{dt}\right)^{-1}$$

The calculated decay-time constants as a function of voltage are shown in Fig. 6b. It can be seen that as compared with the device fabricated with the ZnO NWs, the decay-time constant for the device fabricated with the ZnO–20TiO2 core–shell NW arrays increases more than one order of magnitude at almost all the voltages. The decay-time constants just show the opposite variation trend with the dark currents for these devices as shown in Fig. 6b, indicating a good consistence between these measurements because larger recombination results in smaller carrier life.

To analyze the electron transfer and recombination process in detail, the schematic band gap alignment of the CdS sensitized ZnO–TiO2 core–shell NWs is presented in Fig. 8a. Due to a Fermi level alignment, the energy band of the multilayered structure experiences a “band reconstruction” process and forms a stepwise band structure when they are immersed in electrolyte. As a result, the stepwise structure offers a large driving force for the electron transfer from the CdS QDs to the ZnO NWs, and thus the photoexcited carriers separate rapidly. While the electron transfer from the ZnO NWs to the electrolyte is blocked by the radial field at the interface between ZnO and TiO2, which also reduces the electron concentration at the surface of the ZnO NWs [18], resulting in less recombination from the ZnO NWs to the CdS QDs and the electrolyte. However, not all the ZnO–TiO2 core–shell NW arrays show a better device performance than the ZnO NW arrays in our experiment. Considering that QDSSC and DSSC have a similar work principle and the DSSCs based on ZnO–TiO2 core–shell NW arrays have been studied by many other groups [18,21,22], it is meaningful to compare our present results with these previous works. The performance of the DSSCs based on ZnO–TiO2 core–shell NW arrays depend on the thickness of TiO2 shell seriously. However, neither the serious decrease of JSC for the DSSC with an ultra thin TiO2 shell (less than 5 nm) nor the dramatic improve of device performance for the DSSC with thicker TiO2 shell (10–25 nm) [18] was observed in our QDSSC. Compared with the ultrathin amorphous TiO2 shell derived by ALD [18], the thin TiO2 (2–3 nm) shell derived by LBLAR in our experiment is weakly crystallized as shown in the inset of Fig. 4a, so it is only able to improve the electron transfer process to some extent, thus leading to a slight improvement of the device performance. For the thicker TiO2 shells (16 nm) with a dipping of 40 times LBLAR cycles, as shown in Fig. 5 and described previously, the light absorption is slightly weaker due to the less loading of QDs. What is more important, thick LBLAR-made TiO2 shells are composed of multilayer of small stacking nanoparticles [28], which are not propitious for the transport of the electrons from the CdS QDs to the ZnO core due to a plenty of the crystal boundaries as shown in the schematic picture in Fig. 8b. Because these crystal boundaries of the TiO2 nanoparticles may cause more electron trapping or recombination before the electrons injecting to the ZnO core. These results indicate that both of the above two factors contribute to the deterioration of the device performance for the cells based on the ZnO–40TiO2 core–shell NW arrays. Therefore, only the ZnO–20TiO2 core–shell NW arrays which has a single layer of the TiO2 nanoparticles film as shown in Fig. 2c and d are able to provide a rapid transfer path for the photoexcited electrons at the same time to maintain a low recombination at the interface between the photoanode and the electrolyte, and consequently results in a much better device performance. It should be mentioned here that another advantage of our TiO2 deposition process is that a dense TiO2 layer can be formed at the bottom of nanowires, which is believed to block the FTO surface and result in less recombination between FTO and the electrolyte [13,31,34]. Therefore, this phenomenon may also contribute to the better performance of the ZnO–TiO2 core–shell nanowire device.

4. Conclusions

The construction and performance of the QDSSCs based on the ZnO NW arrays coated with a thin TiO2 shell layer, which is
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