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Research Article

Facile Synthesis of ZnO@TiO_2 Core-Shell Nanorod Thin Films for Dye-Sensitized Solar Cells

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ZnO nanorod thin films grown on fluorine-doped tin oxide (FTO) glasses have been synthesized via facile thermal evaporation. To optimize the performance of dye-sensitized solar cells (DSSCs), we fabricated ZnO@TiO_2 core-shell composite by a simple dip-coating method immersed in the mixed solution of $Ti(OC_4H_9)$ and ethanol. Results of solar cell testing showed that ZnO@TiO_2 core-shell nanorod thin films on FTO significantly increased open circuit voltage (from 0.47 V to 0.53 V), short circuit current (from 10.78 mA/cm^2 to 13.98 mA/cm^2), and fill factor (from 51% to 55%). The photoelectric conversion efficiency (PEC) increased from 3.3% for bare ZnO DSSCs to 4.85% for ZnO@TiO_2 core-shell structured DSSCs. This is mainly ascribed to the improvement in light harvesting efficiency, electron transfer, and the effective suppression of charge recombination.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted extensive attention during the past two decades due to their low cost, simple fabrication process, and relatively high energy conversion efficiency (PEC) [1–3]. The PEC of DSSCs is governed by the following three aspects: (i) light harvesting efficiency, (ii) electrons injection efficiency, and (iii) electrons collection efficiency [4–6]. To develop high-efficiency DSSCs, much effort was devoted to the optimization of performances. So far, the PEC up to ~12% has been obtained by using a photoanode of TiO_2 nanoparticles (NPs) film because of the large specific surface area that can enhance the dye adsorption [7]. However, the PEC of TiO_2 NPs-based DSSCs has reached the limitation due to the slow transportation of electrons through the randomly arranged NPs as well as the energy losses caused by the recombination [8]. Fabrication of film electrodes of one-dimensional (1D) nanostructures which are capable of providing a direct electron transport pathway has proven to be an effective way to facilitate electrons transfer [9, 10]. It is expected that 1D nanostructure as the photoanode electrodes could potentially facilitate electrons transport and effectively decrease the interfacial recombination, further improving the conversion efficiency.

As a versatile semiconductor (Eg = 3.37 eV), ZnO has been applied in many fields including gas sensors [11], field-effect transistors [12], lithium-ion battery [13], and photocatalysis [14]. Particularly, ZnO has attracted much attention as a fascinating alternative to TiO_2 photoanode in DSSCs because both ZnO and TiO_2 exhibit similar lowest conduction band edges and quickly electron injection process from the excited dyes [15]. More importantly, ZnO has higher electron mobility than TiO_2, which is favorable for electron transfer [16]. Therefore, it is expected that reduced recombination would be achieved when ZnO is used as photoanode in DSSC due to rapid electron transfer and collection. Recently, DSSCs based on 1D ZnO nanostructures, including nanowires [17], nanorods [18], and nanotubes [19], have attracted wide attention because of better electron mobility in 1D nanostructures, which is quite beneficial for DSSCs application. However, ZnO are not chemically stable and are prone to form insulating complexes (Zn^{2+}/dye agglomerates) when exposed to dye-loading solutions, which may hinder electron injection from the dye molecules to the

semiconductor [20]. The way to overcome this issue is to coat a chemically stable (e.g., Al_2O_3, SiO_2, or TiO_2) shell on 1D ZnO nanostructures. The role of the shell was always to suppress the formation of Zn^{2+}/dye complex and thereby to reduce the recombination between injected electrons and triiodide (I^{3-}) ions at ZnO surface. Among the numerous semiconductors oxides, TiO_2 is an excellent coating material to modify ZnO due to its higher overall conversion efficiency. Recently, the ZnO-TiO_2 core-shell nanostructures such as NRs [21], NFs [22], NWs [23], and NTs [24] for DSSCs have been reported, which can enhance the conversion efficiencies compared with the bare ZnO nanostructures.

In this work, a simple two-step process was used to synthesize ZnO@TiO_2 core-shell nanorod thin films. First, ZnO nanorod thin films are fabricated via facile thermal evaporation. In the following, the ZnO nanorod thin films were immersed into the TiO_2 growth solution to coat a thin layer of TiO_2 on the surface of individual ZnO nanorod uniformly. In order to demonstrate their energy conversion behavior, we have measured the ZnO@TiO_2 core-shell nanorod thin films as anode materials for DSSCs. An enhancement of performance was observed by the core-shell structured DSSCs (the PEC of 4.85%), compared to the bare ZnO nanorods DSSCs (3.3%).

2. Experiment

2.1. Synthesis. The thin films of ZnO nanorod on FTO substrate were prepared as illustrated in Scheme 1(a–d). First, a ZnO seed layer was coated on the FTO, as demonstrated by Feng et al. [25]. Briefly, zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and diethanolamine were added to ethanol according to the certain proportion at 60°C and stirred for 30 min to yield a clear and homogeneous solution. Then, a piece of FTO substrate which is washed by sonication was immersed in the abovementioned solution for 2 min and slowly lifted up and finally annealed at 400°C in air for 1 h. For the thermal evaporation growth nanorod thin films, the seeded substrate with conductive surface facing down was placed on an alumina boat including $Zn(CH_3COO)_2{\cdot}2H_2O$ powder and annealed at 350°C in air for 9 h. As a result, ZnO nanorod thin films could be obtained. For coating TiO_2, ZnO nanorod thin film grown on FTO was immersed into $C_{16}H_{36}O_4Ti$ ethanol solution for 30 min and slowly taken out. Then, the immersed product was annealed at 400°C for 2 h, resulting in the formation of ZnO@TiO_2 nanorod thin films.

2.2. Characterization and Cell Fabrication. The samples of ZnO and ZnO@TiO_2 nanorod thin films on FTO substrates were characterized by X-ray powder diffraction (XRD, Y-2000, λ = 1.5418 Å) and scanning electron microscopy (SEM, JSM-6700F, 10 kV).

ZnO and ZnO@TiO_2 nanorod thin films were immersed into N719 dye at 60°C for 2 h before assembling solar cells. The DSSCs are photoelectrochemical system; the schematic illustration is as illustrated in Scheme 2.

At the heart of the device is the ZnO@TiO_2 nanorod thin film with adsorbed dye molecules deposited on FTO, which act as dye-sensitized photoanode. Pt-coated FTO substrate was used as the counter electrode. The dye-sensitized electrode and counter electrode were assembled in a typical sandwich-type cell and the counter electrode was placed over the dye-sensitized electrode. The electrolyte (containing LiI, I_2, 4-*tert*-butylpyridine, and tetrabutylammonium iodide in acetonitrile) was injected into the dye-sensitized electrode and the counter electrode. During operation, photoexcitation of the dye molecules results in injection of an electron into the conduction of the oxide film and holes are released by the redox couples in the liquid electrolyte. The photocurrent-voltage characteristics of different assembled solar cells were evaluated in air under AM 1.5 filter 100 mW cm^{-2} illumination from a solar simulator (Oriel, 91192).

3. Results and Discussion

Figure 1 shows the XRD pattern of ZnO@TiO_2 nanorod thin film. As observed, the diffraction peaks marked by star match well with standard powder diffraction pattern of ZnO (JCPDS card number 36-1451). Other peaks marked by circles originate from the FTO substrate and the diffraction peaks marked with rhombus are all indexed to TiO_2. With respect to the formation of ZnO@TiO_2 structure, the overall chemical reactions can be expressed as follows:

$$\mathrm{Ti}\left(\mathrm{C_4H_9O}\right)_4 + 4\mathrm{H_2O} \longrightarrow \mathrm{Ti}\left(\mathrm{OH}\right)_4 + 4\mathrm{C_4H_9OH} \quad (1)$$

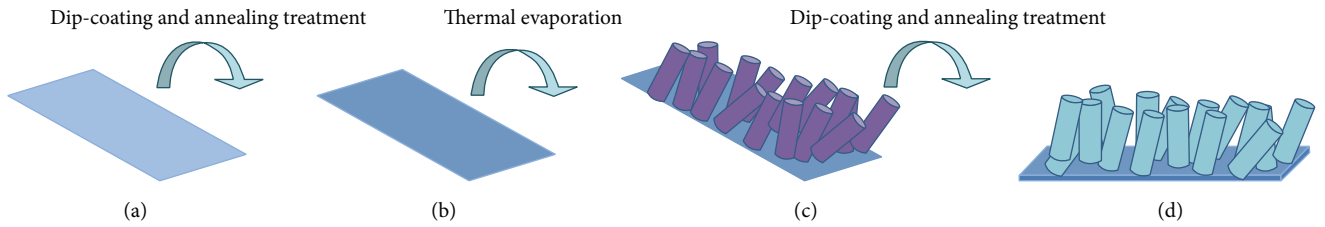
$$\mathrm{Ti}\left(\mathrm{OH}\right)_4 \longrightarrow \mathrm{TiO_2} + 2\mathrm{H_2O} \quad (2)$$

It is known that the hydrolysis of $C_{16}H_{36}O_4Ti$ (see (1)) readily takes place in a H_2O-containing atmosphere. To avoid or slow down its hydrolysis, $C_{16}H_{36}O_4Ti$ is usually dissolved or stored in organic solvents. In the following step, $Ti(OH)_4$ could be completely transformed into TiO_2 by annealing at 400°C, as described in (2).

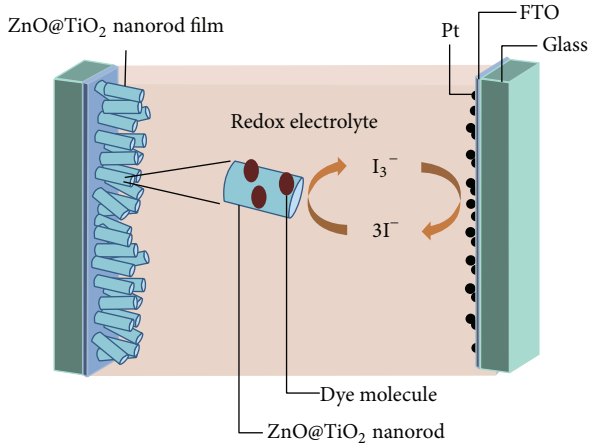
Figure 2(a) shows the SEM image of ZnO nanorod thin film on FTO substrate. As can be seen, the prepared ZnO nanorods have a diameter range of 30–40 nm and uniformly grown on the FTO substrate. More importantly, there is enough space between nanorods, which is crucial for the formation of TiO_2 shell but also helpful for the entrance of dye molecules. Figure 2(b) displays the SEM image of ZnO@TiO_2 nanorod thin film. It can be seen that ZnO@TiO_2 also exhibits the same morphology, but the diameter of nanorods has a change of 40–50 nm, revealing the formed TiO_2 shell.

Figure 3 shows the UV-vis absorption spectra of the ZnO and ZnO@TiO_2 nanorod thin films with sensitization by N719 dye. It may be clearly seen that the ZnO@TiO_2 nanorod thin film shows a higher absorption than that of the bare ZnO nanorod thin film for the same sensitization time in the range of 450–650 nm, indicating that the ZnO@TiO_2 core-shell structure enhances the light absorption largely, which may result from the higher light harvesting properties of TiO_2-decorated materials.

The photocurrent-voltage characteristic of ZnO and ZnO@TiO_2 nanorod thin films DSSC is shown in Figure 4. Generally, the fill factor (FF) and PEC can be calculated using the relations FF = $P_{max}/(V_{oc} \times J_{sc})$ and PEC = $[(\mathrm{FF} \times V_{oc} \times J_{sc})/P_{in}] \times 100$, respectively, where J_{sc} = short circuit current,



Scheme 1: Schematic illustration showing the evolution of the ZnO@TiO_2 thin film: (a) a clean FTO substrate, (b) ZnO seed layer coated substrate obtained from dip-coating and annealing treatment, (c) ZnO nanorod thin film obtained from thermal evaporation, and (d) ZnO@TiO_2 thin film obtained from dip-coating and annealing treatment.



Scheme 2: Schematic illustration of a dye-sensitized solar cell.

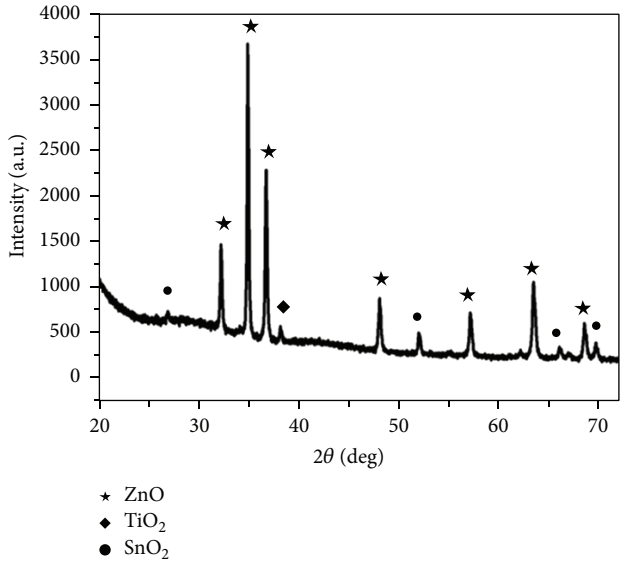


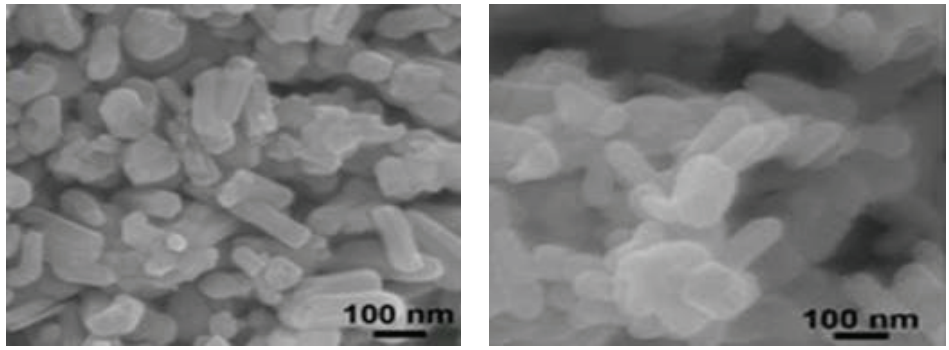
Figure 1: XRD pattern of ZnO@TiO_2 nanorod thin film.

V_{oc} = open circuit voltage, P_{max} = the maximum power, and P_{in} = input power, respectively. As observed, for the bare ZnO nanorod thin film electrode, the device exhibits J_{sc} of 10.78 mA/cm^2, V_{oc} of 0.47 V, and FF of 51%. An overall energy conversion efficiency of 3.3% is achieved. Meanwhile, it can be seen that the addition of TiO_2 shells to the ZnO nanorods resulted in considerable improvement of cell performances. For the ZnO@TiO_2 nanorod thin film electrode, J_{sc} increases to 13.98 mA/cm^2, V_{oc} increases to 0.53 V, and FF jumps to 55%. Overall, the cell conversion efficiency is 4.85%, which is increased by 47% in comparison with that of the DSSCs based on the bare ZnO.

There are several reasons resulting in the improvement of performances of ZnO@TiO_2 nanorod thin films DSSCs. First, TiO_2 is more chemically stable than ZnO in acidic dye solutions [26]. Thus, the presence of TiO_2 shell would prevent ZnO surface atoms from being dissolved and formation of Zn^{2+}/dye agglomerates. It is believed that the TiO_2 shell plays a role in increasing the injected electrons and more dye absorption, which lead to a higher light harvesting efficiency. Second, it is reported that the conformal shell will reduce recombination by forming an energy barrier between the photoinjected electrons and the oxidized species in the electrolyte, by forming a tunneling barrier to confine the photoinjected electrons within the core, and by passivating the recombination centres on the core surface [20]. Thus, the TiO_2 shell would effectively reduce recombination. Thirdly, the charge transfer would be significantly improved because ZnO has much higher electron mobility (~155 cm^2/Vs) than TiO_2 (~105 cm^2/Vs). Therefore, all of these advantages contribute to the improved cell performance for ZnO@TiO_2 nanorod thin films. Though 1D nanostructures as the photoanode are capable of providing a direct electron transport pathway which could potentially facilitate electrons transport, insufficient surface area for dye absorption limits the number of photoelectrons by photoexcitation of the dye molecules. As is now well known, mesoporous nanoparticles have large surface area and strong light scattering property. In the subsequent work, we would like to design hierarchical structures photoanode by combining the advantage of mesoporous nanoparticles for rich dye absorption and the merit of 1D nanostructure for rapid electron transfer. It is anticipated that hierarchical structures will help improve the efficiency of solar cells. More work needs to be done about this issue.

4. Conclusion

In summary, ZnO nanorod thin films have been grown on FTO substrates using facile thermal evaporation. TiO_2 thin shells were grown on the ZnO nanorods by dip-coating method. With the DSSC fabricated by ZnO@TiO_2, its overall



(a) (b)

Figure 2: SEM image of (a) bare ZnO and (b) ZnO@TiO_2 nanorod thin films.

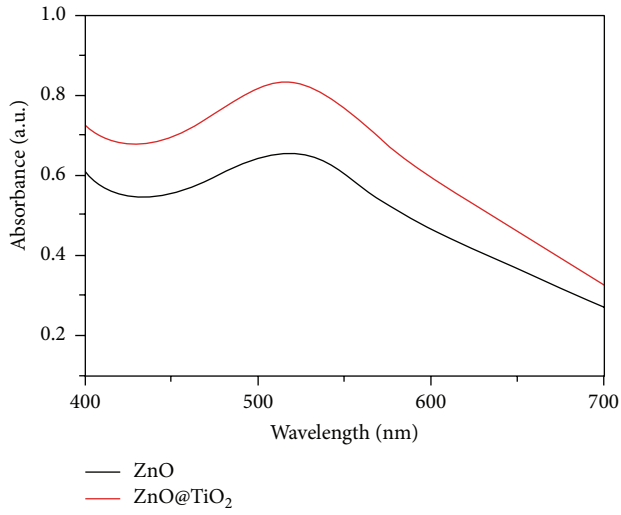


Figure 3: UV-vis absorption spectra of bare ZnO and ZnO@TiO_2 nanorod thin films.

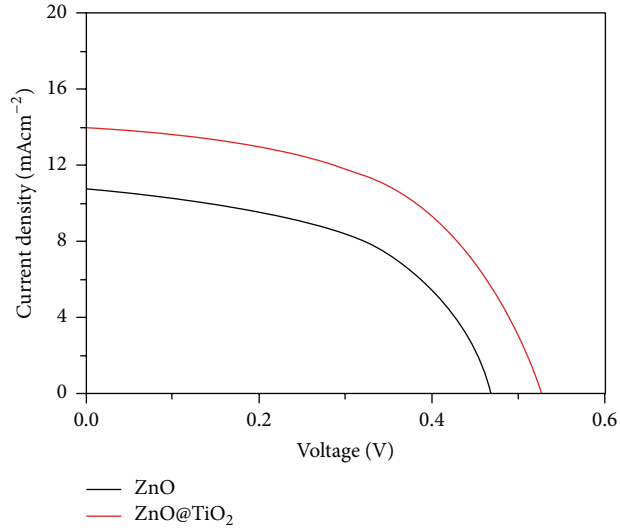


Figure 4: *I-V* curves of DSSCs under AM 1.5 simulated full sunlight (100 mW cm^{-2}) illumination based on bare ZnO and ZnO@TiO_2 nanorod thin films.

conversion efficiency is 4.85%, which exhibits improvements of 47% over the DSSC based on bare ZnO. This improvement of overall conversion efficiency is mainly due to the increase of the loading dye, the reduced recombination, and the high electron mobility.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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