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Preparation and Performance of Ordered Porous TiO_2 Film Doped with Gd^{3+}

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An organic template of polystyrene colloidal crystals was fabricated through dip-coating in a polystyrene emulsion. Based on the template, an ordered porous TiO_2 film doped with Gd^{3+} was deposited on a conductive glass. x-ray diffractometry (XRD), scanning electron microscopy (SEM), UV-vis spectroscopy were used to characterize the structures and properties of the film. The as-produced film was used as an electrode in dye-sensitized solar cells with a sandwich structure. XRD showed that anatase TiO_2 was obtained. SEM images clearly demonstrated that these films had an ordered porous structure, mainly in a hexagonal orientation. UV-vis spectroscopy revealed that the absorption was improved in both the ultraviolet and the visible areas. Under simulated solar illumination, a short circuit current of 0.618 mA and an open circuit voltage of 0.538 V were attained, which were better than the performances of only a TiO_2 film electrode and an ordered porous TiO_2 film electrode.

Keywords coatings, doping, dye-sensitized solar cell, energy, porosity, PS colloid crystal, thin films, titanium

1. Introduction

Nanocrystalline titanium dioxide (TiO_2) has recently attracted much attention for its highly stable and nontoxic properties as well as suitable redox potential (Ref 1-4) and versatile applications in photocatalysis, electrochemical sensors, and photovoltaic devices. TiO_2 has become the most widely used material for dye-sensitized nanocrystalline solar cells (DSSC) because of its simple preparation procedure, low cost, stable photo-to-electric performance, and environmentally friendly property (Ref 5, 6). Porous nanocrystalline TiO_2 films with high surface areas are able to accommodate more than sufficient dye absorption as well as facilitate the transport of electrons and electrolytes in DSSC, which would improve the photoelectric conversion efficiency of solar cells (Ref 7-9). The TiO_2 films with the disordered structures are unfavorable for the separation of electron-hole pairs and the transport of electrons. Thus, the photovoltaic conversion efficiency will be decreased (Ref 10). Fabricating ordered porous TiO_2 films with high performance is a key factor to increasing the efficiency of DSSCs. Colloidal crystal templates provide an effective way to prepare ordered porous TiO_2 films (Ref 11, 12). However, there are limitations, such as the wide band gap and charge recombination between the TiO_2 electrode and the electrolyte. Doping with the proper kind of metal ion could reduce the charge recombination and narrow the band gap of TiO_2, thus broadening the width of absorption under sunlight. Then, the additional absorbed solar energy could increase the efficiency of the solar cells. Recently, the study of modified porous TiO_2 films has been solely focused on the ordered structure or on ion doping. A combination of the two methods could be more favorable for increasing the efficiency of DSSCs.

In this article, polystyrene (PS) colloidal crystals are fabricated as templates using a dip-coating method. Then, based on the assembled PS templates, ordered porous TiO_2 films modified by Gd^{3+} are deposited on a conductive glass. Finally, using the TiO_2 film as electrode, a dye-sensitized solar cell with a sandwich structure is assembled, and its photovoltaic performance is investigated.

2. Experimental Details

Initially, monodispersed PS beads were prepared by surfactant-free emulsion polymerization of styrene, as reported elsewhere (Ref 13-15). Then, PS array templates were assembled by a dip-coating method on a conductive glass. First, conductive glass substrates were cleaned ultrasonically in acetone, isopropyl alcohol, ethanol, and deionized water. Then, the clean and dried glass substrate was settled vertically into the emulsion of PS for 3 min, and then slowly drawn out from the emulsion with a drawing rate of 4 cm/min followed by drying in oven at in oven at 40 °C for 1 h. Finally, the dip-coating method was also used to place the TiO_2 sol on the PS spherical templates. The as-prepared PS templates were kept in the TiO_2 sol for different time periods (3, 5, and 10 min), and then drawn out from the TiO_2 sol with a drawing rate of 4 cm/min and dried in oven at 60 °C for 1 h. At last, the poured templates were heated in air up to 500 °C for 2 h to remove the PS templates and obtain porous structure of TiO_2 thin films.

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Ordered porous TiO_2 film electrodes were immersed into an anhydrous ethanol solution of 0.5 mM N_3 dye (*cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II)) for 10 h. Upon illumination photons are absorbed by N_3 dye molecules, which inject electrons from their excited states into the conduction band of the TiO_2 nano-particles. After the dye adsorption, the electrodes were fabricated into sandwich-type solar cells. The counterelectrodes, thin platinum layers sputtered on FTO (Ref 16), were kept in contact with the dyed electrodes. Surlyn which could be used as heat-seal layer was inserted as a spacer between the working electrodes and the counterelectrodes to prevent a direct contact. The redox electrolyte composed of 0.3 M lithium iodide (LiI) solution and 0.03 M iodide (I_2) solution in acetonitrile was introduced to the gap between the counter and the working electrodes by a capillary force.

The crystalline structure and crystallographic orientation of the ordered porous TiO_2 films doped with Gd^{3+} were measured by an x-ray diffractometer (XRD, SEMENS D5000). The surface morphology of the as-produced film on glass substrates was observed by scanning electron microscopy (SEM, JEOL JSM-6700F). The absorbance of the samples was measured using a UV-vis spectrophotometer (UV-vis, PGENERAL UV-1901). The photovoltaic properties were measured with a computer-controlled digital source meter (Keithley, model 2400) under illumination with a Newport solar simulator (AM1.5, 100 mW/cm^2).

3. Results and Discussion

Figure 1(a) shows the SEM images of the PS colloidal crystal template prepared by the dip-coating method. It exhibited a close-packed, ordered arrangement. There were no structural defects, such as vacancies and dislocations, in most of the PS template. In addition, the hexagonal interspace formed by the PS cubic close packing structure was beneficial to the filling of TiO_2 sol.

Figure 1(b-d) shows the SEM images of TiO_2 thin films with different dipping times. As shown in Fig. 1(b), since there was not enough dipping time for TiO_2 sol to fill the interspaces, the inorganic wall was thin and even resulted in the collapse of the TiO_2 framework. In Fig. 1(d), excess TiO_2 sol was deposited on the surface of the PS microspheres when the interspace became full. This led to an increase in the TiO_2 wall thickness and even resulted in shrinkage of the porous structure. In conclusion, the dipping times played an important role in the formation of ordered TiO_2 porous films. In this experiment, the suitable dipping time was about 5 min. From the image in Fig. 1(c), well-ordered TiO_2 porous films were formed. It reproduced the pore size distribution of the PS templates. The average pore size was about 250 nm. Porous structures, as well as the ordered TiO_2 materials, were arrayed periodically and formed a three-dimensional ordered macroporous network structure, which was favorable for the separation

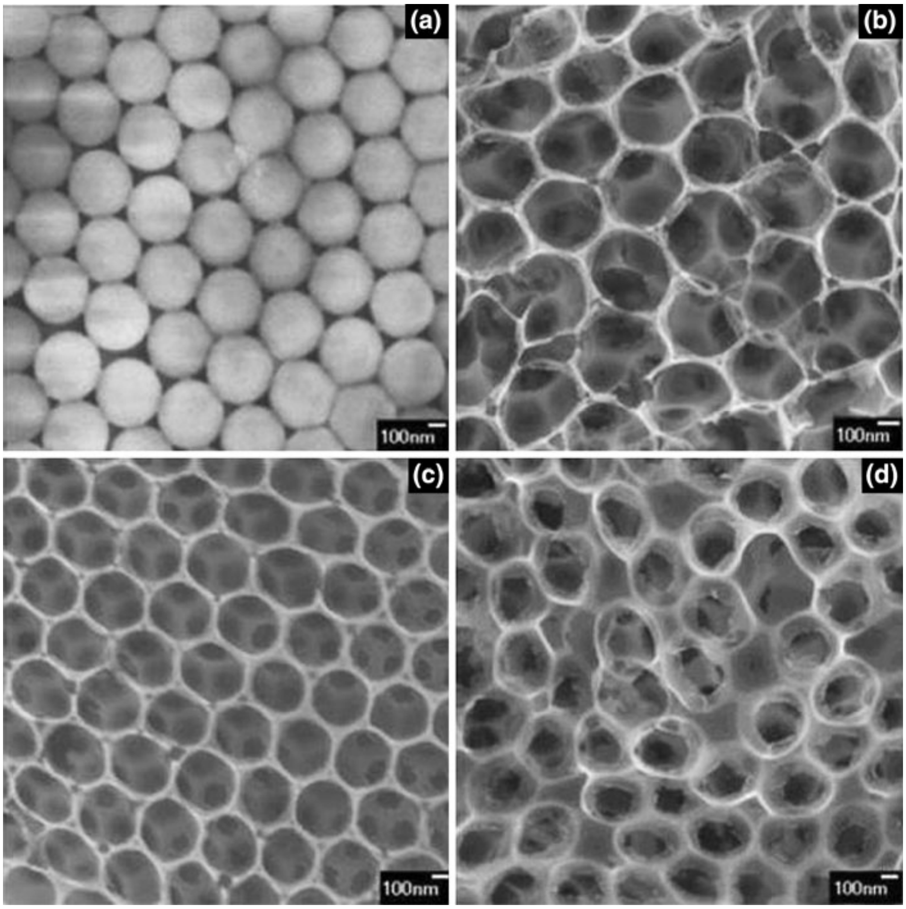

Fig. 1 SEM images of (a) PS colloidal crystal template; (b) TiO_2 thin films with dipping time of 3 min, (c) TiO_2 thin films with dipping time of 5 min, (d) TiO_2 thin films with dipping time of 10 min

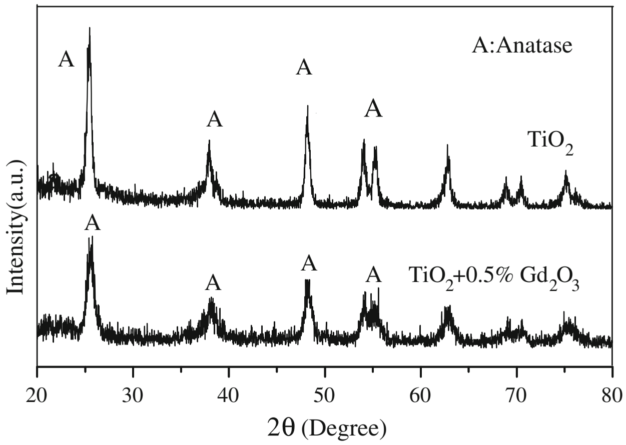

Fig. 2 XRD patterns of TiO_2 and TiO_2 doped with 0.5% Gd^{3+}

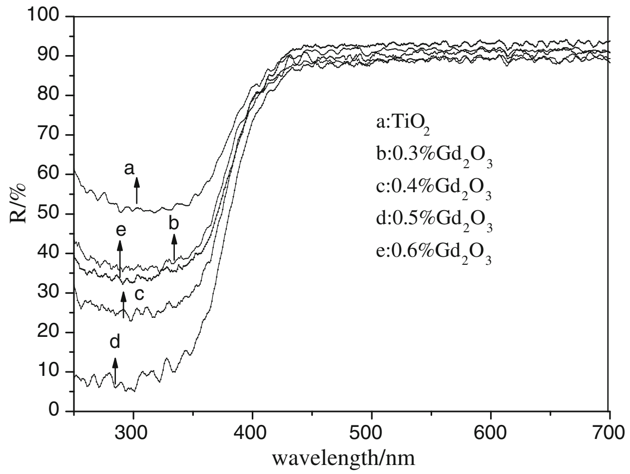

Fig. 3 Diffuse reflectance spectra of TiO_2 with different Gd-doping content

of electron/hole pairs and the transport of electrons. Thus, the photovoltaic conversion efficiency can be increased.

Figure 2 illustrates the XRD patterns of the TiO_2 and TiO_2 doped with 0.5% Gd^{3+}. The peaks centered at 25.60°, 38.10°, and 48.26° (2θ) were clearly observed and could be assigned as the (101), (004), and (200) orientations of the anatase phase, respectively. The result also indicated that no trace of diffraction peak for the Gd_2O_3 structure was detected in the case of TiO_2 doped with 0.5% Gd^{3+}. This means that the addition of a small amount of Gd_2O_3 did not change the structure of the anatase TiO_2. In addition, the average grain size of anatase TiO_2, calculated by the Scherrer equation from the XRD data, was found to be about 8.7 nm. This indicated that the TiO_2 nanoparticles were the main structural components in the ordered porous TiO_2 film.

Figure 3 gives the UV-vis spectra showing the diffused reflectance spectra of TiO_2 with different Gd-doping content. The modification of TiO_2 with Gd^{3+} significantly affected the light absorption property of TiO_2. We could see that the reflectance of TiO_2 doped with Gd^{3+} was lower than that of TiO_2 in the wavelength region from 250 to 700 nm. Within certain doping content range (0.1-0.5%), the absorption edge broadened and the light absorption increased with increasing the Gd^{3+} doping content, but the reflectance increased when the Gd^{3+} doping content increased from 0.5 to 0.6%. This is because the excess Gd^{3+} in TiO_2 could act as the recombination centers of photogenerated electrons and holes, resulting in decreasing of photoelectric properties (Ref 17).

Table 1 Photovoltaic properties of TiO_2 film electrodes

Sample	J_{sc}, mA	V_{oc}, V	ff
TiO_2 film electrode	0.559	0.490	0.486
Ordered porous TiO_2 film electrode	0.599	0.500	0.483
Ordered porous TiO_2 film electrode doping with Gd^{3+}	0.618	0.538	0.475

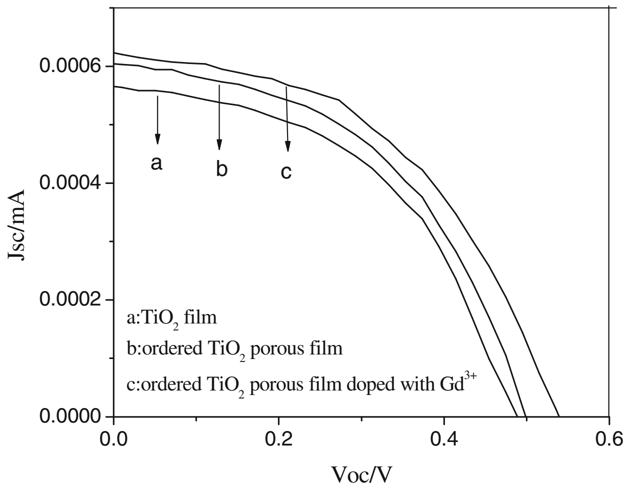

Fig. 4 Photocurrent-voltage characteristics of TiO_2 film electrodes

Table 1 shows the photovoltaic properties of the TiO_2 film electrode, ordered porous TiO_2 film electrode, and ordered porous TiO_2 film electrode doped with Gd^{3+}. The DSSC using ordered porous TiO_2 film doped with Gd^{3+} showed a short circuit current (J_{sc}) of 0.618 mA and an open circuit voltage (V_{oc}) of 0.538 V. These results were an improvement in comparison to the results from using pure TiO_2 electrode (V_{oc} = 0.490 V, J_{sc} = 0.559 mA) and ordered porous TiO_2 electrode (V_{oc} = 0.500 V, J_{sc} = 0.599 mA), but there was no change in the fill factor (ff) which is one of the most important properties of DSSC. The decline of ff could be attributed to the slight destruction of ordered porous TiO_2 film which is expected to reduce the recombination between the electrolyte and the FTO substrate and improve the ff of DSSCs (Ref 18).

Figure 4 compares the photocurrent-voltage (*I*-*V*) curve of the above three electrodes (i.e., TiO_2 film electrode, ordered porous TiO_2 film electrode, and ordered porous TiO_2 film electrode doped with Gd^{3+}). From Table 1 and Fig. 4, we can see that the photoelectric properties were improved using ordered porous TiO_2 films and Gd^{3+}-doped ordered porous TiO_2 films, which could increase the short circuit current and open circuit voltage. This is because the structure of the ordered porous TiO_2 films could increase both the amount of dye molecules and the diffusion rate of redox electrolyte (I_2/LiI). Furthermore, the structure is favorable for the separation of electron/hole pairs and the transport of electrons. In addition, doping with Gd^{3+} has a good influence on the energy band structure of nano-TiO_2. In particular, it is beneficial to the separation and transition of electrons and increases the photoelectrical conversion.

4. Conclusion

An organic template of PS colloid crystal was fabricated by a dip-coating method using a PS suspension. Based on the hexagonal orientated template, ordered porous TiO_2 films were deposited on conductive glass. Ordered porous TiO_2 films and Gd^{3+}-doped ordered porous TiO_2 films could increase the photoelectric conversion. Under a simulated sunlight illumination, a short circuit current of 0.618 mA and an open circuit voltage of 0.538 V were measured from the ordered porous TiO_2 film electrode doped with Gd^{3+}. These values were better than those measured from the TiO_2 film electrode and ordered porous TiO_2 film electrode.

Acknowledgments

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