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Increases in solar conversion efficiencies of the ZrO_2 nanofiber-doped TiO_2 photoelectrode for dye-sensitized solar cells

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Abstract

In this paper, in order to improve the efficiency of dye-sensitized solar cells, we introduced zirconia [ZrO_2] nanofibers into a mesoporous titania [TiO_2] photoelectrode. The photoelectrode consists of a few weight percent of ZrO_2 nanofibers and a mesoporous TiO_2 powder. The mixed ZrO_2 nanofibers and the mesoporous TiO_2 powder possessed a larger surface area than the corresponding mesoporous TiO_2 powder. The optimum ratio of the ZrO_2 nanofiber was 5 wt.%. The 5 wt.% ZrO_2-mixed device could get a short-circuit photocurrent density of 15.9 mA/cm^2, an open-circuit photovoltage of 0.69 V, a fill factor of 0.60, and a light-to-electricity conversion efficiency of 6.5% under irradiation of AM 1.5 (100 mW/cm^2).

Keywords: zirconia nanofiber, titania, DSSC

Introduction

Dye-sensitized solar cells [DSSCs] have generated a considerable research interest because of their high-energy conversion efficiency (approximately 11%) and low production costs [1-3]. A typical DSSC device contains a light-harvesting layer on a photoelectrode and a Pt-coated layer on a counter electrode; both electrodes are made of a transparent conducting oxide substrate; an iodine-based electrolyte fills the space between the photoelectrode and the counter electrode to serve as a redox mediator in a sandwich-type structure. Performance of the DSSC depends on many factors such as the TiO_2 surface morphology, particle size, thickness of the photoelectrode, nature of the dye, etc. [4-10].

A high light-to-electricity conversion efficiency results from a large surface area of the mesoporous TiO_2 photoelectrode, on which the dyes can be sufficiently adsorbed. In this study, we introduced zirconia [ZrO_2] nanofibers into the mesoporous titania [TiO_2] photoelectrode. The ZrO_2 nanofibers are prepared by electrospinning. The TiO_2 film composite with ZrO_2 nanofibers creates a larger surface area than the single TiO_2 film, in which case the amount of dye loading was increased and short-circuit photocurrent density and solar conversion efficiency are also increased.

Experimental details

The ZrO_2 nanofiber additives were prepared by electrospinning method. At first, mixed together, 6 ml zirconium acetate, 12 ml acetic acid, 12 ml ethanol, and 50 g poly(methyl methacrylate) were stirred for 24 h; then, the compounds were sintered at 700°C for 4 h. A detailed process is displayed in Figure 1.

The TiO_2 paste was prepared by mixing TiO_2 with Degussa P-25, polyethylene glycol, acetyl acetone, distilled water, triton X-100, HNO_3, and ZrO_2 nanofibers. The concentrations of ZrO_2 nanofibers were 0, 3, 5, and 7 wt.%. The mixed solutions were ball milled at 100 rpm for 10 h. The photoelectrode was fabricated using a clean fluorine-doped tin dioxide [FTO] (approximately 8 Ω/cm^2, Pilkington conductive glass, Seoul, South Korea) by squeeze printing. The coated photoelectrode was heat treated at 450°C for 30 min with a heating rate of 5°C/min. The obtained photoelectrode was immersed into the ethanol solution containing [*cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis(tetrabutylammonium)] (N719 dye, Solaronix, Aubonne, Switzerland) for 24 h. The active area of the

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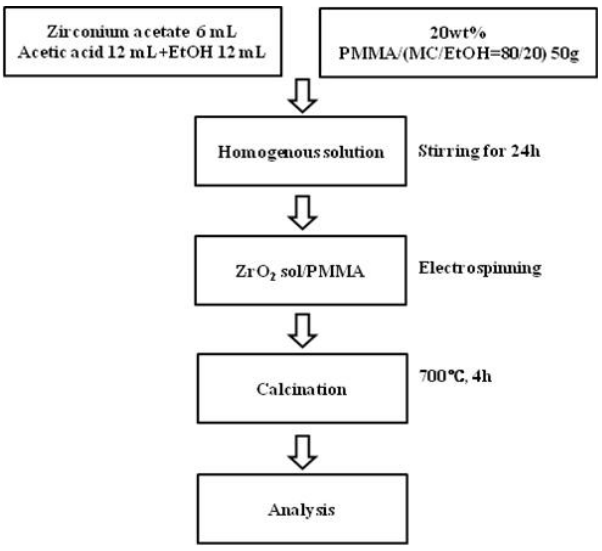

Figure 1 Preparation of the ZrO_2 nanofiber.

photoelectrode was 0.5 × 0.5 cm^2. On the other hand, the counter electrode was prepared similar to the photoelectrode preparation. Pt-Sol (Pt catalyst/SP, Solaronix) was coated onto the FTO glass by the squeeze printing method. The coated paste was heat treated at 450°C for 30 min with a heating rate of 5°C/min.

The electrolyte solution consisted of 0.3 M 1,2-dimethyl-3-propylimidazolium iodide, 0.5 M Li(I), 0.05 M I_2, and 0.5 M 4-t-butylpyridine in 3-methoxypropionitrile between the two electrodes. The dye-coated photoelectrode and the Pt-coated counter electrode were sandwiched using a 60-μm-thick hot-melt sealing foil (SX 1170-60, Solaronix).

The field-emission scanning electron microscope [FE-SEM] (S-4700, Hitachi, Seoul, South Korea) and BET were used to examine the morphology and the pore distribution volume of the TiO_2 film. In order to investigate the physical and optical characteristics of the dye-adsorbed TiO_2 films, the UV-visible [UV-Vis] spectrum measurement was performed. The photovoltaic properties were investigated by measuring the photocurrent-voltage characteristics under illumination with air mass [AM] 1.5 (100 mW/cm^2) simulated sunlight.

Results and discussion

Figure 2 shows the FE-SEM images of the TiO_2 film's surface and the 5 wt.% ZrO_2 nanofiber-added TiO_2 film's surface. In the ZrO_2 nanofiber-added TiO_2 film in Figure 2b, the ZrO_2 nanofiber was shown at the surface of the TiO_2 film, or the TiO_2 film was studded with the ZrO_2 nanofiber. The TiO_2 film's surface area was increased, and the dye adsorption contents became larger by the addition of the ZrO_2 nanofiber. So, we can

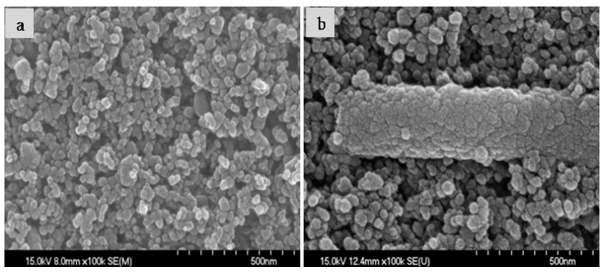

Figure 2 FE-SEM images of (a) TiO_2 film and (b) 5 wt.% ZrO_2 nanofiber-doped TiO_2 film.

forecast that the TiO_2 electrode is able to obtain high conversion efficiency.

Figure 3 shows the pore distributions calculated from adsorption data using the Barrett-Joyner-Halenda [BJH] method. As shown in Figure 3, a broad peak was found at around 25 nm, and an added 5 wt.% ZrO_2 nanofiber at around 30 nm was observed. Compared to the pure TiO_2 film, the 5 wt.% ZrO_2 nanofiber-added TiO_2 films show a significant change in the pore size distribution. A large pore volume in BJH was observed on the TiO_2 film with 5 wt.% ZrO_2 nanofibers, which is in agreement with the results of the FE-SEM image.

Figure 4 shows the UV-Vis absorption spectra of the dye-adsorbed TiO_2 film and the 3, 5, and 7 wt.% ZrO_2 nanofiber-doped TiO_2 films. From the results, the absorption spectra increased at around 538 nm with added ZrO_2 nanofibers doped in the TiO_2 film and also enhanced the amount of dye loading. So, the 5 wt.% ZrO_2 nanofiber-doped TiO_2 film had the best dye

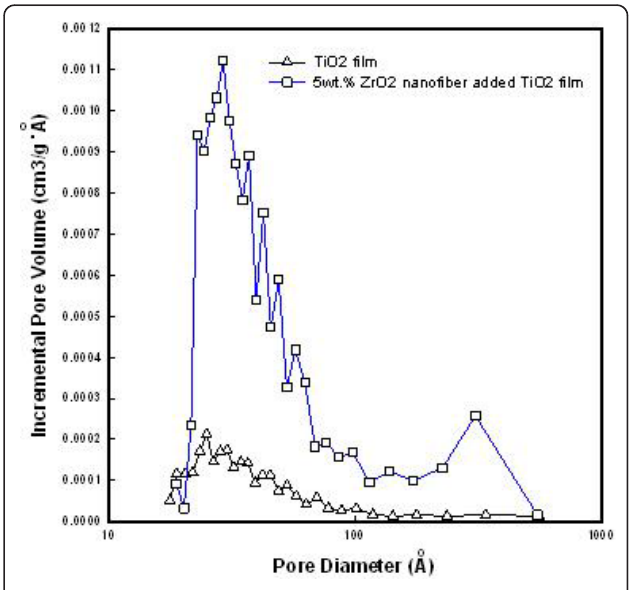

Figure 3 BJH curve of TiO_2 film (triangle) and 5 wt.% ZrO_2 nanofiber-doped TiO2 film (square).

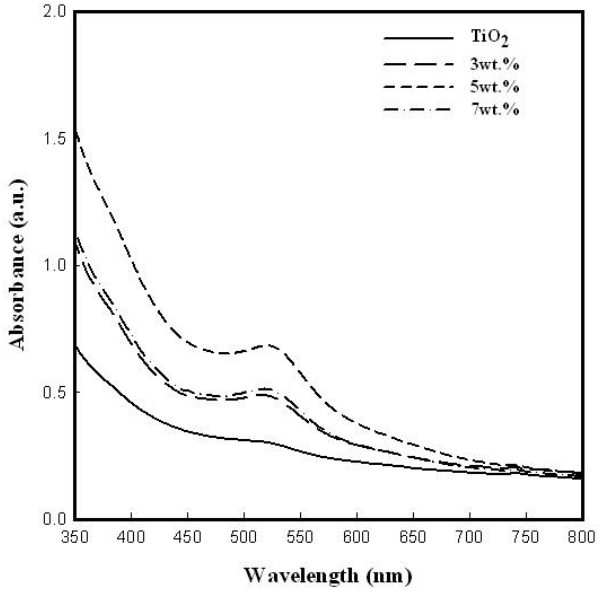

Figure 4 UV-Vis spectrum of TiO_2 film and ZrO_2 nanofiber-doped TiO_2 film after 24-h dye absorption.

loading, and also, its solar conversion efficiency was the best among the samples.

In order to determine the factors that influence the stability of the DSSCs, electrochemical impedance spectroscopy [EIS] was performed. Figure 5 shows that the Nyquist plot of EIS of the DSSCs exhibits semicircles, which are assigned to the electrochemical reaction at the Pt counter electrode, the charge transfer at the TiO_2/dye/electrolyte interface, and the Warburg diffusion process of I^-/I_3^- [9,10]. As shown in Figure 5, the second semicircle is the resistance (R_2) related to the electron transport in the TiO_2/dye/electrolyte interface which is reduced. It can be seen that the TiO_2 film and the 3, 5, and 7 wt.% ZrO_2 nanofiber-doped TiO_2 films are 13.2, 10.3, 9.6, and 11.9 Ω, respectively.

Figure 6 shows photocurrent-voltage characteristics of the DSSCs with the ZrO_2 nanofiber-doped TiO_2 film. The open-circuit photovoltage was almost the same, and the short-circuit photocurrent density increased with the added amount of ZrO_2 nanofibers and had reached the maximum at 5 wt.% of ZrO_2 nanofiber (15.9 mA/cm^2). The open-circuit photovoltage [V_{oc}], the short-circuit photocurrent density [J_{sc}], the fill factor [FF], and the light-to-electricity conversion efficiency [η] at 5 wt.% added ZrO_2 nanofiber were 0.69 V, 15.9 mA/cm^2, 0.60, and 6.5%, respectively, as shown in Table 1. From the results, we can realize that the insertion of ZrO_2 nanofibers creates a larger surface area and reduces the resistance of the photoelectrode, especially for the optimal amount of ZrO_2 contents (7 wt.%) of the photoelectrode in DSSCs.

Conclusions

In summary, a ZrO_2 nanofiber-doped TiO_2 film was used as a photoelectrode in DSSCs. The ZrO_2 nanofiber-doped TiO_2 films had a larger surface area than the pure TiO_2 film, in which case the amount of dye loading was increased, and J_{sc} and η were also increased. The

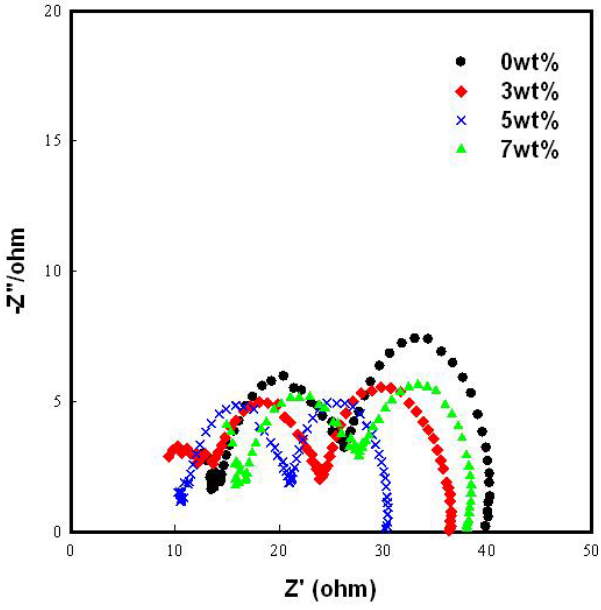

Figure 5 Nyquist plots of the DSSCs using TiO_2 film and ZrO_2 nanofiber-doped TiO_2 film. Black circle, 0 wt.%; red diamond, 3 wt.%; cross mark, 5 wt.%; green triangle, 7 wt.%.

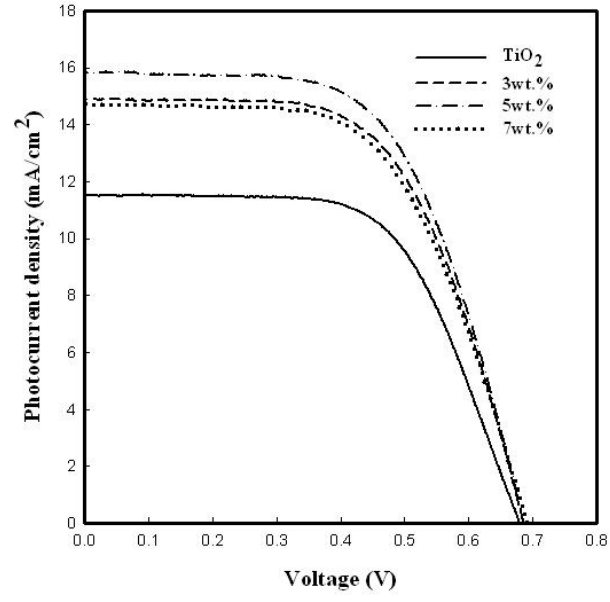

Figure 6 Photocurrent-voltage curve of the TiO_2 film and the TiO_2 films with ZrO_2 nanofibers.

Table 1 Photocurrent-voltage characteristics of DSSCs using TiO_2 with different amounts of ZrO_2 nanofibers

Sample	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
Pure TiO_2	0.68	11.5	0.62	4.9
3 wt.% ZrO_2 nanofiber-doped TiO_2	0.69	14.9	0.60	6.2
5 wt.% ZrO_2 nanofiber-doped TiO_2	0.69	15.9	0.60	6.5
7 wt.% ZrO_2 nanofiber-doped TiO_2	0.69	14.7	0.59	6.0

V_{oc}, open-circuit photovoltage; J_{sc}, short-circuit photocurrent density; FF, fill factor; η, light-to-electricity conversion efficiency; TiO_2, titania; ZrO_2, zirconia.

optimum ratio of the ZrO_2 nanofiber was 5 wt.%. The DSSC with the 5 wt.% ZrO_2 nanofiber photoelectrode provided the highest η of 6.5%, J_{sc} of 15.9 mA/cm^2, V_{oc} of 0.69 V, and FF of 0.60 under AM 1.5 (100 mW/cm^2) simulated sunlight illumination. Therefore, ZrO_2 fibers are a promising additive for the realization of high-efficiency DSSCs.

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Authors' contributions
JW fabricated the DSSCs and UV-Vis analysis. EMJ was the paper chaser and performed the analysis of photocurrent-voltage characteristics and impedance. WLW performed the BET analysis. J-YP prepared the ZrO_2 nanofibers. XGZ performed the FE-SEM analysis. H-BG was thesis director. All authors read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

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