

**NANO REVIEW**

**Open Access**

# Increases in solar conversion efficiencies of the ZrO<sub>2</sub> nanofiber-doped TiO<sub>2</sub> photoelectrode for dye-sensitized solar cells

Jiao Wang<sup>1</sup>, En Mei Jin<sup>1</sup>, Ju-Young Park<sup>2</sup>, Wan Lin Wang<sup>1</sup>, Xing Guan Zhao<sup>1</sup> and Hal-Bon Gu<sup>1\*</sup>

## Abstract

In this paper, in order to improve the efficiency of dye-sensitized solar cells, we introduced zirconia [ZrO<sub>2</sub>] nanofibers into a mesoporous titania [TiO<sub>2</sub>] photoelectrode. The photoelectrode consists of a few weight percent of ZrO<sub>2</sub> nanofibers and a mesoporous TiO<sub>2</sub> powder. The mixed ZrO<sub>2</sub> nanofibers and the mesoporous TiO<sub>2</sub> powder possessed a larger surface area than the corresponding mesoporous TiO<sub>2</sub> powder. The optimum ratio of the ZrO<sub>2</sub> nanofiber was 5 wt.%. The 5 wt.% ZrO<sub>2</sub>-mixed device could get a short-circuit photocurrent density of 15.9 mA/cm<sup>2</sup>, 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<sup>2</sup>).

**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<sub>2</sub> 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<sub>2</sub> photoelectrode, on which the dyes can be sufficiently adsorbed. In this study, we introduced zirconia [ZrO<sub>2</sub>] nanofibers into the mesoporous titania [TiO<sub>2</sub>] photoelectrode. The ZrO<sub>2</sub> nanofibers are prepared by electrospinning. The TiO<sub>2</sub> film composite with ZrO<sub>2</sub> nanofibers creates a larger surface area than the single

TiO<sub>2</sub> 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

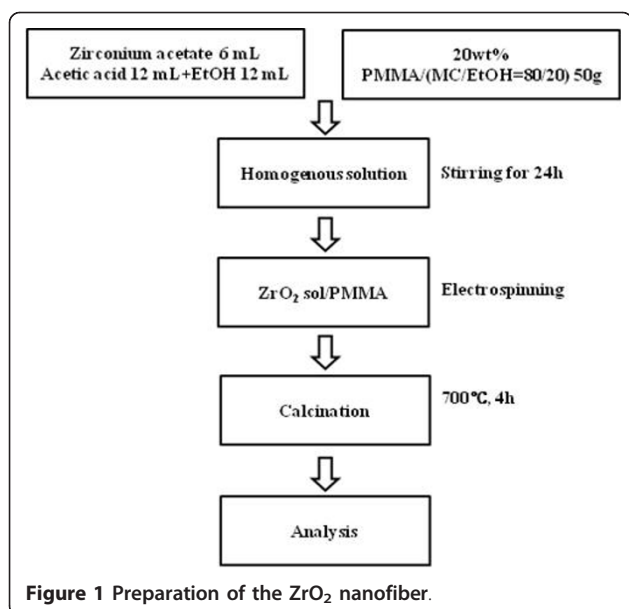
The ZrO<sub>2</sub> nanofiber additives were prepared by electrospinning method. At first, mixed together, 6 ml zirconium acetate, 12 ml acetic acid, 12 ml ethanol, and 50 g poly(methyl methacrylate) were stirred for 24 h; then, the compounds were sintered at 700°C for 4 h. A detailed process is displayed in Figure 1.

The TiO<sub>2</sub> paste was prepared by mixing TiO<sub>2</sub> with Degussa P-25, polyethylene glycol, acetyl acetone, distilled water, triton X-100, HNO<sub>3</sub>, and ZrO<sub>2</sub> nanofibers. The concentrations of ZrO<sub>2</sub> 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<sup>2</sup>, 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

\* Correspondence: hbg@chonnam.ac.kr

<sup>1</sup>Department of Electrical Engineering, Chonnam National University, Gwangju, 500-757, South Korea

Full list of author information is available at the end of the article



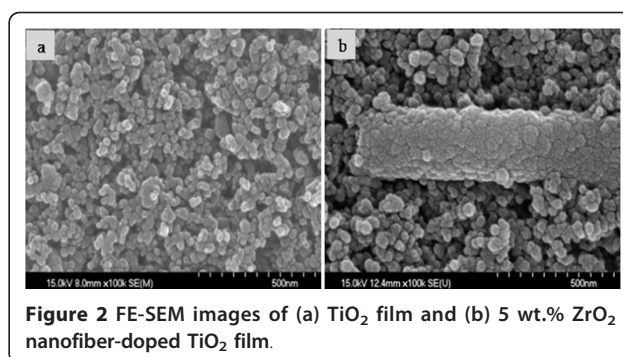
photoelectrode was  $0.5 \times 0.5 \text{ cm}^2$ . On the other hand, the counter electrode was prepared similar to the photoelectrode preparation. Pt-Sol (Pt catalyst/SP, Solaronix) was coated onto the FTO glass by the squeeze printing method. The coated paste was heat treated at  $450^\circ\text{C}$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

The electrolyte solution consisted of 0.3 M 1,2-dimethyl-3-propylimidazolium iodide, 0.5 M Li(I), 0.05 M I<sub>2</sub>, 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- $\mu\text{m}$ -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<sub>2</sub> film. In order to investigate the physical and optical characteristics of the dye-adsorbed TiO<sub>2</sub> 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 ( $100 \text{ mW}/\text{cm}^2$ ) simulated sunlight.

### Results and discussion

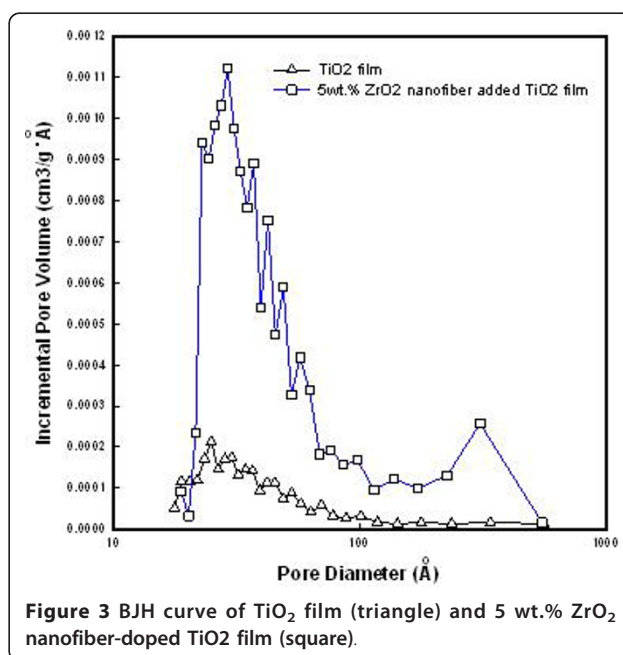
Figure 2 shows the FE-SEM images of the TiO<sub>2</sub> film's surface and the 5 wt.% ZrO<sub>2</sub> nanofiber-added TiO<sub>2</sub> film's surface. In the ZrO<sub>2</sub> nanofiber-added TiO<sub>2</sub> film in Figure 2b, the ZrO<sub>2</sub> nanofiber was shown at the surface of the TiO<sub>2</sub>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

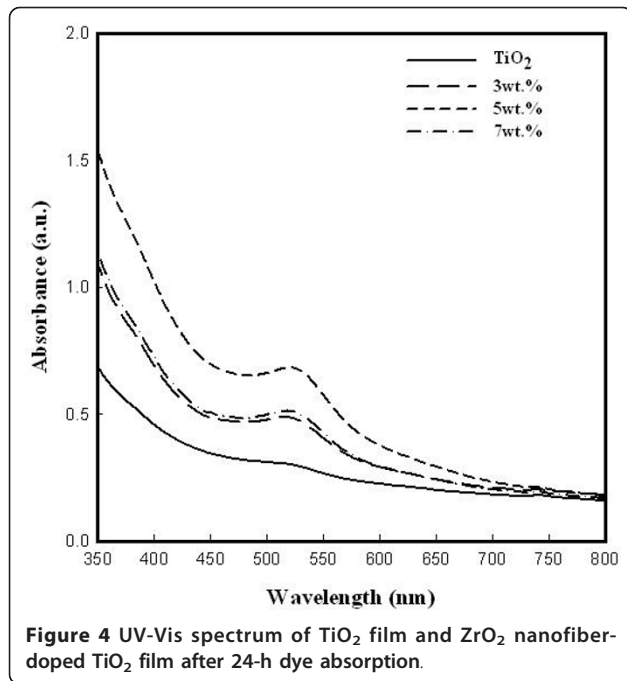


forecast that the TiO<sub>2</sub> electrode is able to obtain high conversion efficiency.

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<sub>2</sub> nanofiber at around 30 nm was observed. Compared to the pure TiO<sub>2</sub> film, the 5 wt.% ZrO<sub>2</sub> nanofiber-added TiO<sub>2</sub> films show a significant change in the pore size distribution. A large pore volume in BJH was observed on the TiO<sub>2</sub> film with 5 wt.% ZrO<sub>2</sub> nanofibers, which is in agreement with the results of the FE-SEM image.

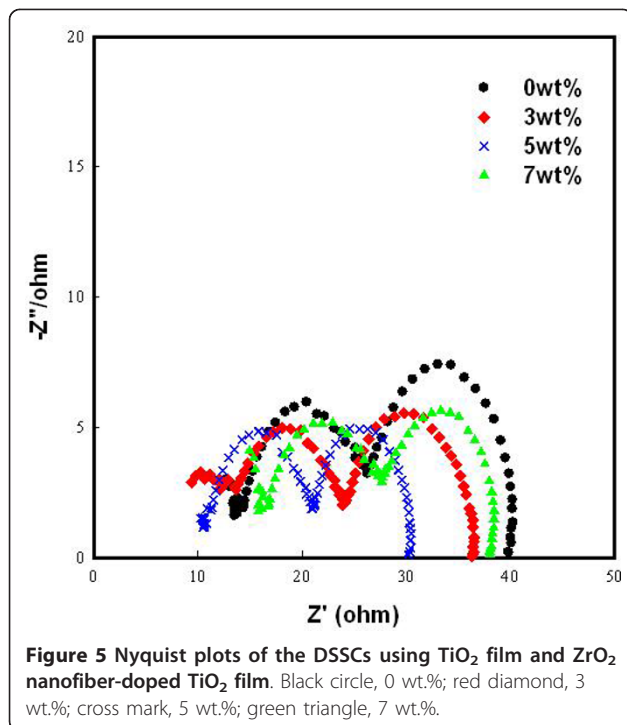
Figure 4 shows the UV-Vis absorption spectra of the dye-adsorbed TiO<sub>2</sub> film and the 3, 5, and 7 wt.% ZrO<sub>2</sub> nanofiber-doped TiO<sub>2</sub> films. From the results, the absorption spectra increased at around 538 nm with added ZrO<sub>2</sub> nanofibers doped in the TiO<sub>2</sub> film and also enhanced the amount of dye loading. So, the 5 wt.% ZrO<sub>2</sub> nanofiber-doped TiO<sub>2</sub> film had the best dye





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

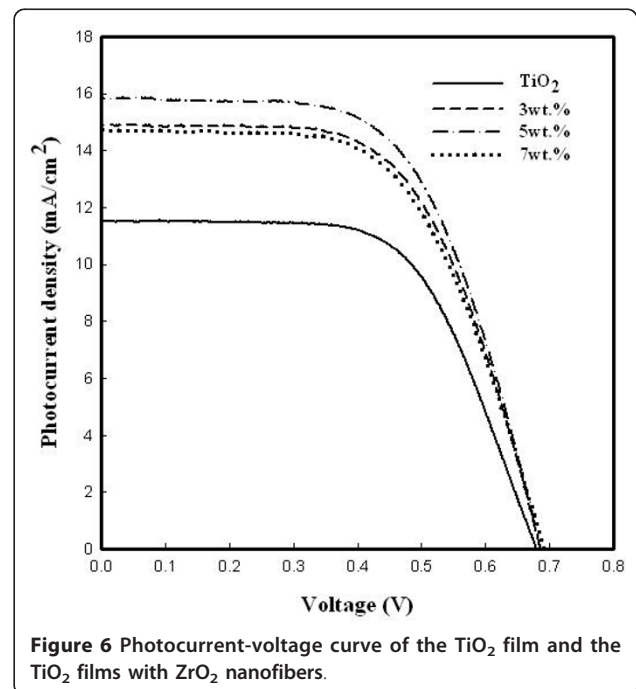


the Pt counter electrode, the charge transfer at the  $\text{TiO}_2$ /dye/electrolyte interface, and the Warburg diffusion process of  $\text{I}^-/\text{I}_3^-$  [9,10]. As shown in Figure 5, the second semicircle is the resistance ( $R_2$ ) related to the electron transport in the  $\text{TiO}_2$ /dye/electrolyte interface which is reduced. It can be seen that the  $\text{TiO}_2$  film and the 3, 5, and 7 wt.%  $\text{ZrO}_2$  nanofiber-doped  $\text{TiO}_2$  films are 13.2, 10.3, 9.6, and 11.9  $\Omega$ , respectively.

Figure 6 shows photocurrent-voltage characteristics of the DSSCs with the  $\text{ZrO}_2$  nanofiber-doped  $\text{TiO}_2$  film. The open-circuit photovoltage was almost the same, and the short-circuit photocurrent density increased with the added amount of  $\text{ZrO}_2$  nanofibers and had reached the maximum at 5 wt.% of  $\text{ZrO}_2$  nanofiber (15.9  $\text{mA}/\text{cm}^2$ ). The open-circuit photovoltage [ $V_{oc}$ ], the short-circuit photocurrent density [ $J_{sc}$ ], the fill factor [FF], and the light-to-electricity conversion efficiency [ $\eta$ ] at 5 wt.% added  $\text{ZrO}_2$  nanofiber were 0.69 V, 15.9  $\text{mA}/\text{cm}^2$ , 0.60, and 6.5%, respectively, as shown in Table 1. From the results, we can realize that the insertion of  $\text{ZrO}_2$  nanofibers creates a larger surface area and reduces the resistance of the photoelectrode, especially for the optimal amount of  $\text{ZrO}_2$  contents (7 wt.%) of the photoelectrode in DSSCs.

## Conclusions

In summary, a  $\text{ZrO}_2$  nanofiber-doped  $\text{TiO}_2$  film was used as a photoelectrode in DSSCs. The  $\text{ZrO}_2$  nanofiber-doped  $\text{TiO}_2$  films had a larger surface area than the pure  $\text{TiO}_2$  film, in which case the amount of dye loading was increased, and  $J_{sc}$  and  $\eta$  were also increased. The



**Table 1 Photocurrent-voltage characteristics of DSSCs using TiO<sub>2</sub> with different amounts of ZrO<sub>2</sub> nanofibers**

Sample	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	η (%)
Pure TiO <sub>2</sub>	0.68	11.5	0.62	4.9
3 wt.% ZrO <sub>2</sub> nanofiber-doped TiO <sub>2</sub>	0.69	14.9	0.60	6.2
5 wt.% ZrO <sub>2</sub> nanofiber-doped TiO <sub>2</sub>	0.69	15.9	0.60	6.5
7 wt.% ZrO <sub>2</sub> nanofiber-doped TiO <sub>2</sub>	0.69	14.7	0.59	6.0

V<sub>oc</sub>, open-circuit photovoltage; J<sub>sc</sub>, short-circuit photocurrent density; FF, fill factor; η, light-to-electricity conversion efficiency; TiO<sub>2</sub>, titania; ZrO<sub>2</sub>, zirconia.

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

#### Author details

<sup>1</sup>Department of Electrical Engineering, Chonnam National University, Gwangju, 500-757, South Korea <sup>2</sup>Southwestern Research Institute of Green Energy Technology, Mokpo-si, Jeonllanam-do, 530-400, South Korea

#### 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<sub>2</sub> 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.

Received: 9 September 2011 Accepted: 2 February 2012

Published: 2 February 2012

#### References

1. O'Regan B, Grätzel M: A low-cost, high-efficiency solar cell based on dye-sensitized colloidal titanium dioxide films. *Nature* 1991, **353**:737-740.
2. Nazeeruddin MK, Kay A, Rodicio I, Humphry R, Muller E, Liska P, Vlachopoulos N, Grätzel M: Conversion of light to electricity by cis-X<sub>2</sub>bis (2,2'-bipyridyl-4,4'-dicarboxylate (ruthenium(II) charge transfer sensitizers) X = Cl-, Br1, I-, Cn-, and SCN-) on nanocrystalline titanium dioxide electrodes. *J Am Chem Soc* 1993, **115**:6382-6390.
3. Hore S, Vetter C, Kern R, Smit H, Hinsch A: Influence of scattering layers on efficiency of dye-sensitized solar cells. *Sol Energy Mater* 2006, **90**:1176-1188.
4. Park K, Gu H, Jin EM, Dhayal M: Using hybrid silica-conjugated TiO<sub>2</sub> nanostructure to enhance the efficiency of dye-sensitized solar cells. *Electrochimica Acta* 2010, **55**:5499-5505.
5. Ito Seigo, Kitamura Takayuki, Wada Yuji, Yanagida Shozo: Facile fabrication of mesoporous TiO<sub>2</sub> electrodes for dye solar cells: chemical modification and repetitive coating. *Solar Energy Mater Solar Cells* 2003, **76**:3-13.
6. Jin EM, Park K, Yun J, Hong CK, Hwang M, Park B, Kim K, Gu H: Photovoltaic properties of TiO<sub>2</sub> photoelectrode prepared by using liquid PEG-EEM binder. *Surface Rev Lett (SRL)* 2010, **17**:15-20.
7. Park KH, Jin EM, Gu HB, Shim SE, Hong CK: Effects of HNO<sub>3</sub> treatment of TiO<sub>2</sub> nanoparticles on the photovoltaic properties of dye-sensitized solar cells. *Mater Lett* 2009, **63**:2208-2211.
8. Chou Chuen-Shii, Yang Ru-Yuan, Yeh Cheng-Kuo, Lin You-Jen: Preparation of TiO<sub>2</sub>/nano-metal composite particles and their applications in dye-sensitized solar cells. *Powder Technol* 2009, **194**:95-105.
9. Fabregat-Santiago F, Bisquert J, Garcia-Belmonte G, Boschloo G, Hagfeldt A: Influence of electrolyte in transport and recombination in dye-sensitized

solar cells studied by impedance spectroscopy. *Solar Ener Mat Solar Cells* 2005, **87**:117-131.

10. Koide Naoki, Islam Ashraf, Chiba Uasou, HAn Liyuan: *J Photochem Photobiol A: Improvement of efficiency of dye-sensitized solar cells based on analysis of equivalent circuit. Chem* 2006, **182**:296-305.

doi:10.1186/1556-276X-7-98

Cite this article as: Wang et al.: Increases in solar conversion efficiencies of the ZrO<sub>2</sub> nanofiber-doped TiO<sub>2</sub> photoelectrode for dye-sensitized solar cells. *Nanoscale Research Letters* 2012 **7**:98.

Submit your manuscript to a SpringerOpen® journal and benefit from:

- Convenient online submission
- Rigorous peer review
- Immediate publication on acceptance
- Open access: articles freely available online
- High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at ► [springeropen.com](http://springeropen.com)