204% enhanced efficiency of ZrO_2 nanofibers doped dye-sensitized solar cells

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Zirconia (ZrO_2) nanofibers added mesoporous titania (TiO_2) photoelectrode has been synthesized for dye-sensitized solar cells to enhance the efficiency of cell. The ZrO_2 nanofibers had reduced the resistance of the photoelectrode as well as enhancement of the absorption spectra in the ultraviolet (UV), visible, and near infrared (IR) region. The internal resistance of the photoelectrode is one of the important factor to affects the power conversion efficiency directly. The ZrO_2 nanofibers provide the more photon harvest and optimal electron pathway. Finally, about 200% increases in conversion efficiency has been achieved. © *2010 American Institute of Physics*. [doi:10.1063/1.3459958]

Developing materials and fabrication process of dye-sensitized solar cells (DSSCs) have been challenging and has great interest to provide an alternative to conventional silicon solar cells for sustainable energy. A typical DSSC is inexpensive, semitransparent and flexible,[1,2] and which is an assembly of sensitized dye, a dye-immobilized nanocrystalline photoelectrode as a dye absorber, an electrolyte, and counter electrode.[3]

Performance of DSSC depends on several factors, such as the band gap of TiO_2, particle size, surface morphology, porosity, thickness of the photoelectrode, etc.[1,2] Improvement of absorption of the solar spectrum has been investigated mainly by adding different types of dopants such as transition metal elements, nonmetal element; nitrogen, sulfur, boron, carbon nanotubes, and etc.[4–14] Metal oxides (ZnO_2, SiO_2, La_2O_3, and etc.) have also been introduced to improve the thermal stability and photocatalytic effect.[15,16]

ZrO_2 has unique properties; a high refractive index, wide optical band gap, low absorption and dispersion in the visible and near infrared spectral regions.[17–20] In the past, the addition of ZrO_2 to TiO_2 was reported to improve the stability of the phase, surface area, and finally the photocatalytic effects.[21–23] Jing *et al.* reported that ZrO_2 nanofibers (diameter ≈ 200 nm) have been synthesized by sol-gel process, calcinations of the zirconium oxide/poly(vinyl pyrrolodone) (PVP) composite nanofibers and electrospinning technique.[24] The specific surface area is 30 m^2/g and crystal phase is monoclinic.

In this paper, we have reported interface and/or internal resistance of the ZrO_2 doped cells by examining the alternating current (ac) impedance, conductivity and resistances, and photocurrent-voltage curves.[25]

The photoelectrode was fabricated using precleaned fluorine-doped tin dioxide (FTO, Pilkington Conducting Glass TEC8, $\sim 9\ \Omega/cm^2$) by squeeze printing. The TiO_2 paste was prepared by mixing TiO_2 (Degussa, P-90) with polyethylene glycol, acetyl acetone, H_2O, triton X-100, HNO_3, and ZrO_2 nanofibers. The concentration of the ZrO_2: 0, 3, 5, 7, and 9 wt % were the ratio of the mixed TiO_2 paste and ZrO_2. The mixed solution was stirred well for 30 min. The coated photoelectrode was treated to 450 °C for 30 min at a heating rate of 5 °C/min.

The obtained TiO_2 film was immersed in 0.5 mmol ethanol solution of [bis(isothio-cyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II)-bis-tetrabutyl ammonium] (N719 dye, Solaronix) for 24 h and dried in a vacuum oven. The thickness of the printed TiO_2 film was 10 μm, and the active area of the photoelectrode was 0.5×0.5 cm^2. On the other hand, the counter electrode was prepared to the similar process of the fabrication for photoelectrode. Pt-Sol (Solaronix, Pt catalyst/SP) coated onto the FTO glass using a squeeze printing method. The coated paste was heat treated at 450 °C for 30 min at a heating rate of 5 °C/min. The sheet resistance of the substrate and platinized counter electrode were measured by using the four-dot method (Chang Min Co.).

The electrolyte solution consist of 0.3 M 1,2-dimethyl-3-propylimidazolium iodide, 0.5 M LiI, 0.05 M I_2, and 0.5 M 4-t-butylpyridine in 3-methoxypropionitile. The ac impedance spectra were measured by the symmetric thin-layer cells. The photocurrent-voltage performances of the cell were measured using a solar simulator under the illumination of a Xe lamp (100 mW cm^{-2}) on the 0.25 cm^2 active area.

Figure 1 shows the UV-vis-IR absorption spectra of the N719 dye, undoped and 7 wt % of ZrO_2 nanofibers doped photoelectrode. The absorption spectra show much enhanced redshift which indicates that the more photon energy could be harvest. The effective spectrum ranges from 370 to 1000 nm. This spectrum covers UV-visible-IR region. The effect of ZrO_2 nanofibers doped system is similar to that of tandem cell structure. The atomic force microscope (AFM) images of the pristine and 7 wt % of ZrO_2 nanofiber added photoelectrode are also shown the inlet of the Fig. 1. Based on the AFM, the scan area was 1.0×1.0 μm^2, the gain size mean of TiO_2 surface is estimated to be around 25 nm.

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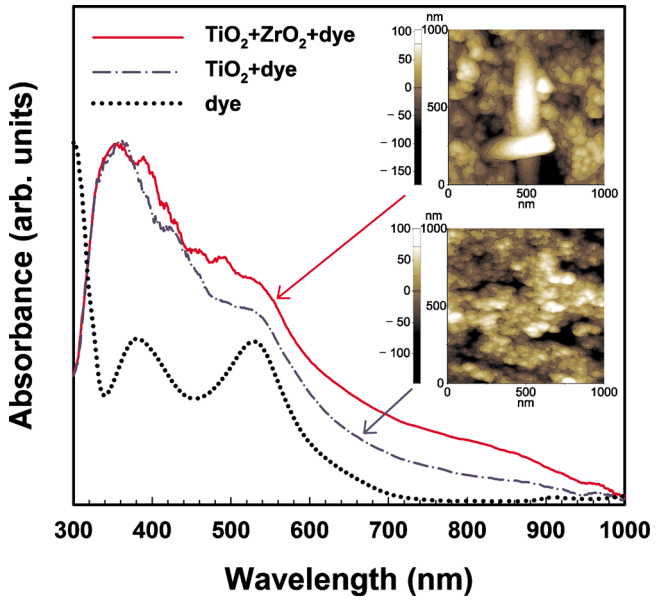

FIG. 1. (Color online) UV-vis-IR absorption spectra of N719 dye (dotted line), TiO_2+N719 dye (dashed line) and TiO_2+ZrO_2+N719 dye (solid line), and AFM images of the ZrO_2 nanofiber-doped and undoped dye-sensitized solar cells.

Figure 2 shows electrochemical impedance spectroscopy (EIS) measurements for 5, 7, and 9 wt % of the ZrO_2 nanofiber-doped photoelectrode. In these observations, the Nyquist plots of the impedance characteristics were obtained from the dependence of the real axis resistance (Z' or Z_{re}) and imaginary axis resistance (Z'' or Z_{im}) along with the angular frequency. The diameter of the semicircle at high frequency illustrated in the spectra shows the charge-transfer resistance (R_{ct}) of the samples, indicating the electrocatalytic activity for tri-iodide reduction.[26,27] The results show a significant effect on the internal resistance of the solar cell, and consequently can affect the fill factor (FF) and conversion efficiency. The results show a very good consistence with

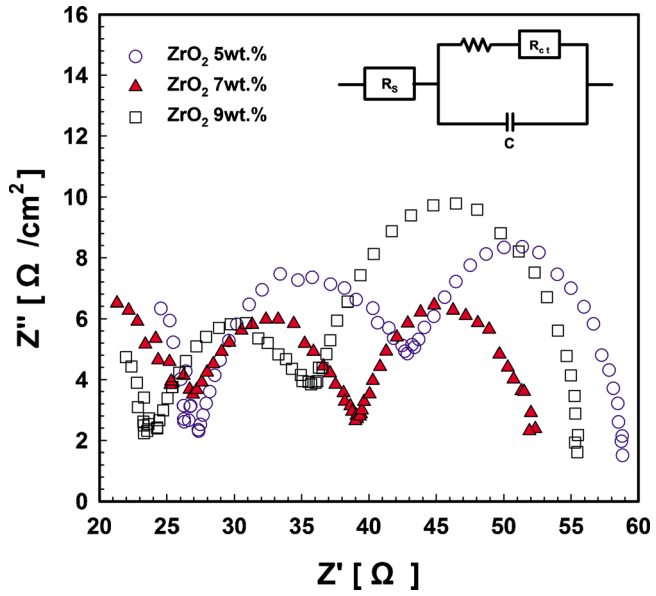

FIG. 2. (Color online) The Nyquist plot of the impedance characteristics between Z_{re} and Z_{im} with the angular frequency ($\omega=2\pi$ f) of the 5, 7, and 9 wt % of ZrO_2 nanofiber-doped photoelectrode.

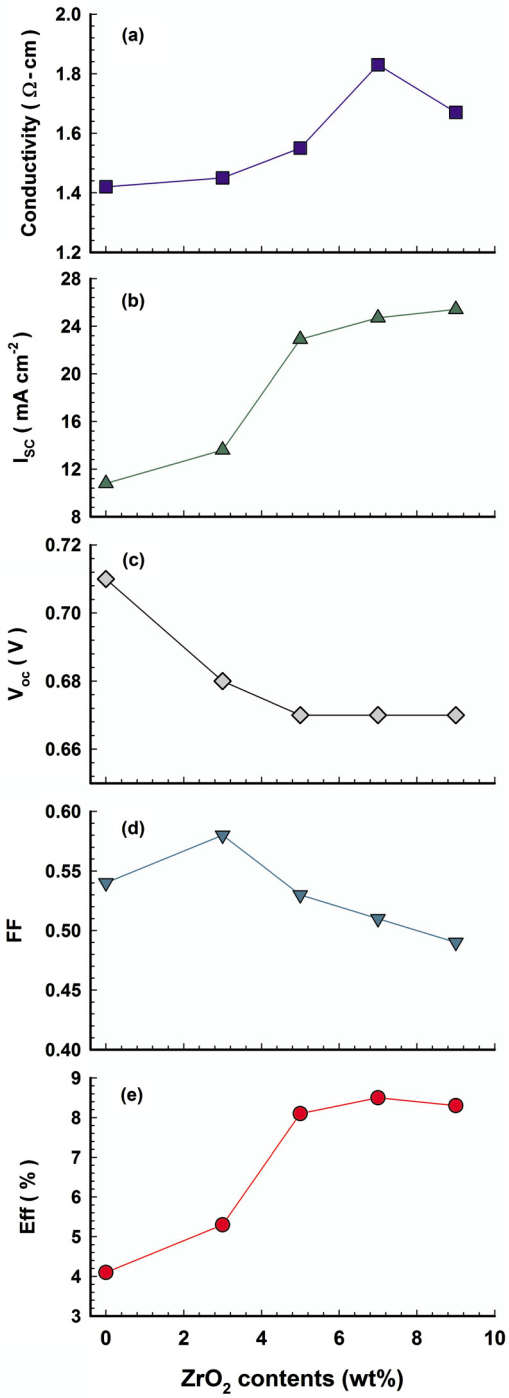

FIG. 3. (Color online) The values of conductivities (a) and photocurrent-voltage properties of the ZrO_2 nanofiber-doped dye-sensitized solar cells; short circuit current (b), open circuit voltage (c), FF (d), and efficiency (e).

conductivity, resistances, and cyclic voltammetry (CV) observations.

The bulk resistance (R_s) of the 5 wt %, 7 wt %, and 9 wt % ZrO_2 doped TiO_2 electrodes are 22.97×10^{-3} Ω, 24.52×10^{-3} Ω, and 23.45×10^{-3} Ω, respectively. The charge transfer resistance (R_{ct}) of the 5 wt %, 7 wt %, and 9 wt % devices are 13.15×10^{-3} Ω, 7.58×10^{-3} Ω, and 12.96×10^{-3} Ω, respectively. The R_{ct} represent mainly by the distance between the counter-electrode and photoelectrode, as well as, the effective area of the electrode. The R_s and R_{ct} could refer the adhesion properties between the substrate and Pt particles. Finally, the ZrO_2 nanofiber doped sys-

tem showed improvement of charge transferring property. The surface and/or interface of the cell is an important factor for charge transport of the short circuit current and life time of electron in the open circuit voltage.

The conductivity and resistance were measured using a four point probe measuring system (Chang min CMT-series) and resulted were averaged after seven times repetition for same condition. Figure 3(a) gives the values of conductivities: pristine (1.42×10^{-9} Ω-cm), 3 wt % doped (1.45×10^{-9} Ω-cm), 5 wt % doped (1.55×10^{-9} Ω-cm), 7 wt % doped (1.83×10^{-9} Ω-cm), and 9 wt % doped (1.67×10^{-9} Ω-cm). The 7 wt % of ZrO_2 nanofiber-doped sample shows the lowest resistance and highest conductivity.

The photocurrent-voltage properties of the devices obtained with the standard measurement condition. The photoelectric effects are shown from Figs. 3(b)–3(e). The best efficiency came from 7 wt % ZrO_2 nanofibers doped device; with a short circuit current density (J_{sc}) of 24.7 mA/cm^2, an open circuit voltage (V_{oc}) of 0.67 V, a FF of 51% and an overall power conversion efficiency (η_{eff}) of 8.3%. The efficiencies of pristine and doped samples (0 wt %, 3 wt %, 5 wt %, and 9 wt %) were 4.1%, 5.3%, 8.1%, and 8.3%, respectively. The increased value of I_{sc} from 10.8 $mAcm^{-2}$ to 24.7 $mAcm^{-2}$ and the value of Voc 0.67V make poor fill factor (0.52).

The FF marked the best with 3 wt % of the ZrO_2 nanofibers doped device, and then gradually dropped. The open circuit voltage was hardly altered by the insertion of ZrO_2 nanofibers. But, the short circuit currents were increased from 10.8 to 25.4 mA with the proportional to the concentration ZrO_2 nanofibers. This suggests that the insertion of ZrO_2 nanofibers gives (1) optimal electron pass way by reducing the surface and/or interface resistance, (2) porosity, which made by ZrO_2 nanofibers, it gives many absorption site to the dye. The optimal porosity of the concentration of ZrO_2 could be achieved with 7 wt %, which is close relating to the conductivity data, FF, and η_{eff}.

In conclusion, ZrO_2 nanofibers were introduced into the photoelectrode of a dye sensitized solar cell. 204% enhanced efficiency was achieved to the concentration 7 wt % ZrO_2 nanofibers. Doped ZrO_2 nanofibers had contributed toward (1) redshift and much enhancement of the absorption spectra from UV to near infrared region just like tandem cell structure, (2) reduction in the resistance of the surface and/or interface of the photoelectrode, and (3) porosity, which made by ZrO_2 nanofibers, it gives many absorption site to the dye. The internal resistance of the photoelectrode is one of the important factor to affects the power conversion efficiency directly. ZrO_2 nanofibers could play an important role in the realization of high efficiency dye-sensitized solar cells.

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