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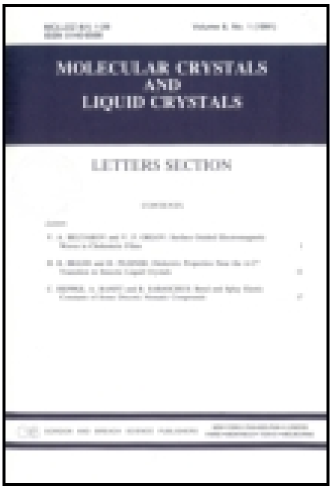

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Synthesis and Characterization of WO_3 Doped TiO_2 Particle/Nanowire Layer in Dye-Sensitized Solar Cells

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Dye-sensitized solar cells (DSSCs) have been intensively studied since their discovery; however, a number of problems remain to be solved in order to enhance their efficiency. In particular, one of the main limiting factors is the electron recombination that occurs due to contact between the transparent conductive oxide and the redox electrolyte. In this work, we report an improvement in the photovoltaic characteristics of dye-sensitized solar cells by using mixtures of TiO_2*,* TiO_2 *nanowires (TNWs), and* WO_3*. DSSCs were constructed by application of* WO_3 *mixed with a composite of varying percentages of* TiO_2 *nanoparticle and TNWs. The addition of* WO_3 *reduces the surface trap states of* TiO_2*, improving its power conversion efficiency by suppressing charge recombination, and increasing the driving force of electron injection. A DSSC fabricated using a* TiO_2*–*WO_3 *mixture was found to have a maximum conversion efficiency of 5.47% owing to the effective prevention of electron recombination. As a result, DSSCs based on* TiO_2*–*WO_3 *mixtures exhibited better photovoltaic performance compared to cells fabricated from pure* TiO_2

Keywords DSSCs; TiO_2; WO_3; TiO_2 nanowire; electron injection

Introduction

Since their discovery in 1991, dye-sensitized solar cells (DSSCs) have been extensively studied as an alternative to silicon-based solar cells, owing to their simple structure, transparency, flexibility, low production cost, and a wide range of applicability. Despite these advantages, the low efficiency of DSSCs compared to silicon-based cells has limited their commercial implementation [1–4]. Consequently, there is a critical need to improve the efficiency of state-of-the-art DSSCs in order to realize next generation solar cells.

In principle, dye-sensitized solar cells are composed of four parts, which are as follows: (1) the TiO_2 electrode film layer, covered by a monolayer of dye molecules, that absorbs solar energy; (2) the conductive TCO (Transparent Conductive Oxides) layer that acts as a support to facilitate charge transfer from the electrode layer; (3) the counter electrode layer

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made of Pt or C; (4) and the redox electrolyte layer for reducing the level of energy supplied from the dye [5, 6]. Thus far, research efforts to improve the efficiency of DSSCs have primarily been focused on improvements in the aforementioned DSSC components [7]. However, in addition to the individual components, the various interfaces that exist in the DSSC architecture such as TCO/TiO_2, TiO_2/dye, dye/electrolyte, and electrolyte/counter electrode, also warrant significant attention. These locations are where recombination of electrons and holes occurs, and a reduction in this recombination is the primary purpose of studies focusing on improving the efficiency of DSSCs. Therefore, maximizing the charge injection and minimizing the recombination of photo-generated electrons and holes are the key factors for realizing high efficiency in solar cells [8]. It has been reported that the efficiency of DSSCs can be improved by surface modification of TiO_2 with insulating oxides, or high band gap semiconductors, to form a blocking layer preventing charge recombination at the TiO_2/dye/electrolyte interface [9–12]. The high conversion efficiency achieved in a DSSC may be attributed to the unique functionality of the TiO_2 porous film, which is usually composed of TiO_2 nanoparticles(TNPs). Sol-gel processing of TiO_2 has generally been the most extensively investigated for DSSC applications. However, significant developments have been made in refining and controlling the stability, and phase formation, of colloidal precursors used for sol-gel processing [13]. Subsequently, researchers have started to explore the use of ordinal TiO_2 in DSSCs, which includes TiO_2 nanowires (TNWs), nanorods, and nanotubes. It has been reported that TNWs can be prepared by hydrothermal treatment of TNPs in a 10 M aqueous solution of NaOH [14,15]. Moreover, the use of TNWs in DSSCs has also been explored as a method to improve electron transport [16,17].

In this work, we have considered the two aforementioned strategies to improve the efficiency of DSSCs. Employing one of these approaches, the use of oxide semiconductors in the form of nanowires is attempted as a novel means of improving the electron transport through the film. Though a higher photoelectrical performance was obtained, we believe that further improvements in the photoelectrical performance of DSSCs could be achieved. In addition, we investigate the effects of TiO_2–WO_3 mixtures on dye-sensitized solar cells, combined with variations in the percentages of the TiO_2 nanoparticle/TNW composite.

Experimental

Titanium(IV) isopropoxide (TTIP, Sigma Aldrich), ethyl alcohol, nitric acid, and de-ionized (DI) water were used as the precursors. As-prepared TiO_2 particles were calcined in air at 450°C for 1 h, using a programmable furnace, to obtain the desired stoichiometry and crystallinity. Subsequently, TNWs were hydrothermally prepared as described by the following procedure: 4 g of TiO_2 particles prepared by sol-gel method were mixed with 500 mL of 10 M aqueous NaOH, followed by hydrothermal treatment at 150°C in a Teflon-lined autoclave for 12 h. After the hydrothermal reaction, the resulting powders were thoroughly washed with distilled water and 0.1 M HCl, then subsequently filtered and dried at 80°C for 24 h. To achieve TNWs of the desired size and crystallinity, the powders were calcined in air at 450°C for 1 h. Following this, the TNPs, and the TNWs prepared by sol-gel and hydrothermal methods, were mixed in the ratio of 10 wt% and ground in a mortar. In addition, a mixed TiO_2 paste was prepared by combining WO_3 particles of 100 nm (Sigma Aldrich) with TNPs, at a WO_3:composite ratio of 1:4 by weight.

The prepared TiO_2 paste was coated onto FTO-glass by the doctor-blade method. Finally, the TiO_2-coated substrate was calcined at 250°C for 15 min, then at 500°C for 15 min, to remove all organic constituents and promote crystal growth.

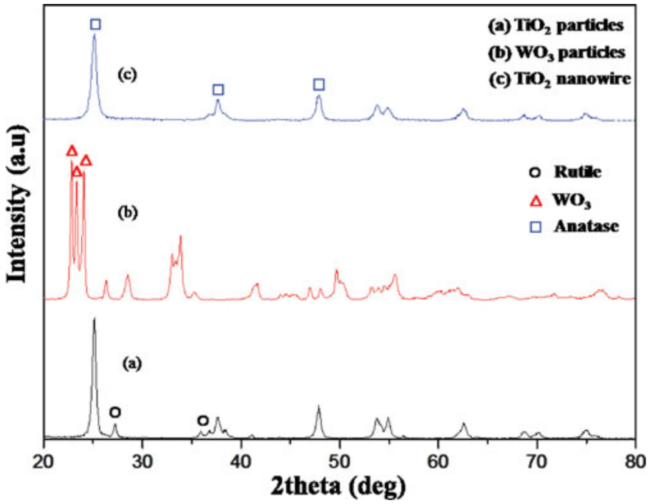

Figure 1. XRD patterns of (a) TiO_2 particles, (b) TiO_2 nanowires, and (c) WO_3 particles.

In addition, a Pt catalyst electrode was prepared by mixing H_2PtCl_6 (5 mM) in isopropyl alcohol, followed by ultrasonic treatment. A counter electrode, which facilitates the redox reaction of electrolyte, was fabricated by spin coating the prepared H_2PtCl_6 solution at 1000 rpm for 30 s, followed by heat-treatment at 450°C for 30 min.

The dye solution to be adsorbed on the electrode films was prepared by mixing 0.5 mM Ru-dye (N719, Solaronix) with ethanol. To facilitate the adsorption of the dye molecules, the prepared TiO_2 electrode films were placed in the dye solution under darkness for 24 h.

Finally, the dye-sensitized solar cell was fabricated by sandwiching the prepared electrode film and counter electrode at 120°C for 10 min, using a hot melt sealant (60°C). The electrolyte (I^-/I_3^-) was injected between the two electrodes, with the inlet then sealed by a cover glass, as shown in Fig 1.

The phase of the particles obtained by hydrothermal treatment at various temperatures was examined by X-ray diffraction (XRD), using a Rigaku D/MAX-2200 diffractometer with a CuKα radiation source. The morphology of the prepared TNW layers was investigated by field-emission scanning electron microscopy (FE-SEM, model S-4700, Hitachi), with the optical transmittance of the prepared TiO_2 electrode films measured using a UV-Vis spectrometer (UV-Vis 8453, Agilent). The conversion efficiency and electrochemical impedance spectroscopy (EIS) of the fabricated DSSCs were measured using an I-V solar simulator (Solar Simulator, McScience). The active area of the resulting cell exposed to light was approximately 0.25 cm^2 (0.5 cm × 0.5 cm).

Results and Discussion

Figure 1(a) shows the XRD pattern of the TNPs synthesized by the sol-gel method, with subsequent heat-treatment at 450°C, and indicates a mixture of anatase and rutile phases. Prominent anatase peaks are seen at (101), (004), and (200), with prominent rutile peaks at (110) and (101). Fig. 1(b) shows the XRD pattern of the tungsten oxide. The XRD pattern of WO_3 shows prominent peaks at (002), (020), and (220), which is consistent with JCPDS(43-1035).

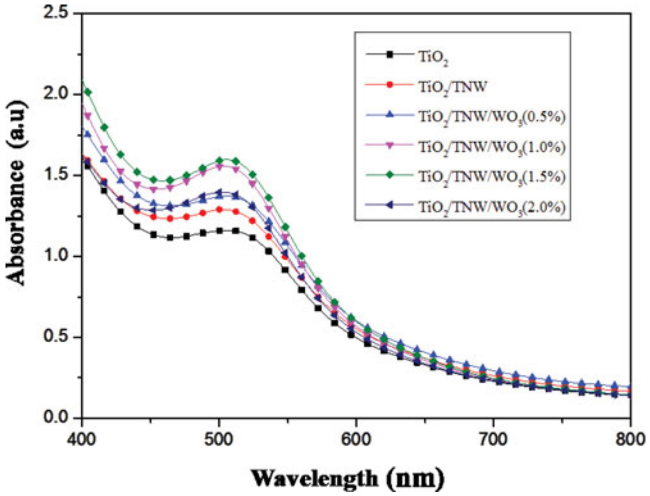

Figure 2. UV-Vis absorbance spectra, showing dye absorption as a function of TiO_2 particle/TNW content and concentration of WO_3.

Fig. 1(c) shows the XRD pattern of the TNW film prepared by hydrothermal treatment at 150°C for 12 h. As a result of the hydrothermal treatment, the TNPs (with mixed anatase and rutile phases) were transformed into their anatase phase. As can be observed from the corresponding XRD pattern, Fig. 1(b), the TNWs possess a highly crystallized anatase structure, without any impurity phases. The absence of rutile peaks in the XRD pattern of TNWs indicates the complete transformation into the anatase phase.

Fig. 2 shows how the UV-Vis absorbance spectra of dye are affected by the use of the TiO_2/TNW/WO_3 mixture. It is known that N-719 dye exhibits absorption peaks, with Fig. 2 showing the absorption spectrum in the wavelength range 400–800 nm when the dye was adsorbed onto TiO_2 electrode films of various compositions (TNW 10 wt.%/WO_3 concentrations of 0.5 wt.%, 1.0 wt.%, 1.5 wt.%, and 2.0 wt.%). As evidenced from Fig. 2, the sample containing 1.0 wt.% WO_3 exhibited the highest absorbance in the 400–500 nm wavelength range, whereas the sample containing 2.0 wt.% WO_3 showed a decrease in absorbance. This could be attributed to the light harvesting of N-719 dye molecules, increased by the light scattering by and the effect of large-sized WO_3 particles [18].

Fig. 3 shows the FE-SEM images of a WO_3 particle, TNPs prepared by the sol-gel method, and TNWs prepared by the hydrothermal method. Fig 3(a) shows TiO_2 particles of size 20 nm, whereas fig 3(b) shows a 100 nm WO_3 particle. The FE-SEM image of TNWs, seen in Fig. 3(c), indicates the formation of uniform, smooth-surfaced, wire-like structures, several hundreds of nanometers in length, and with a diameter of approximately 25 nm. Fig. 3(d) shows the FE-SEM image of the film composed of TNPs, TNWs, and WO_3 nanoparticles, which exhibits a porous structure.

Fig. 4 shows the electrochemical impedance spectroscopy (EIS) analysis of TNWs/WO_3 obtained at various wt.% ratios, which provides information about the electron transport and recombination in DSSCs. The small semicircle is fitted to a charge-transfer resistance (R1) and constant phase, while the large semicircle is fitted to a transfer resistance (R2) and constant phase. As R1 is not affected by the use of TNWs/WO_3, we focused mainly on the variations in R2. The first semicircle is a minimum for the WO_3 (1.0 wt.%), which is related to charge-transfer resistance of FTO/TiO_2 and TiO_2/electrolyte interfaces (R2).

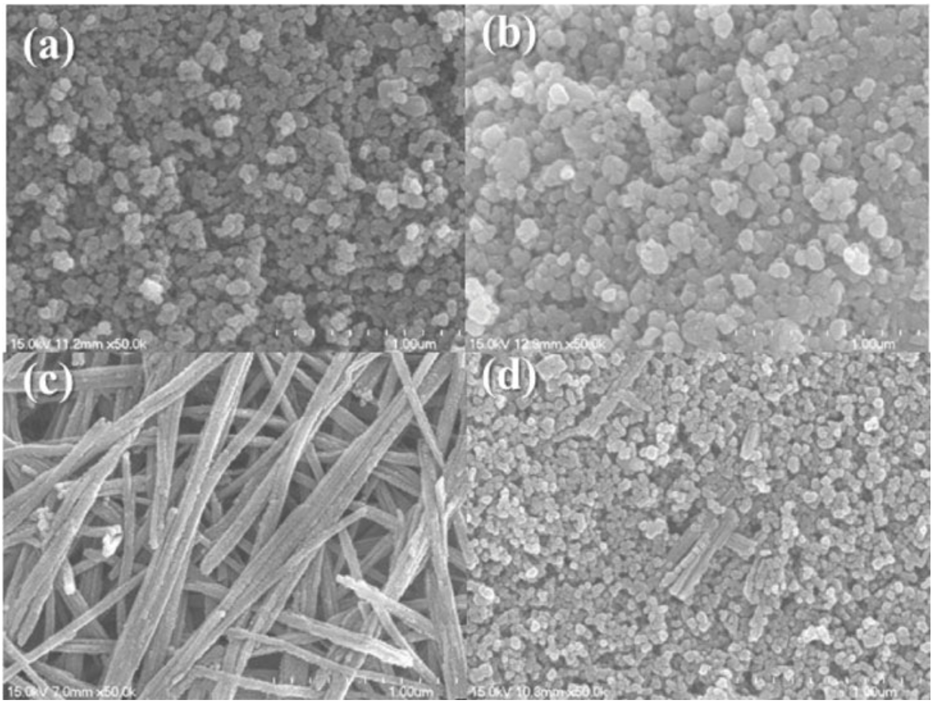

Figure 3. FE-SEM images of (a) TiO_2 particles, (b) WO_3 particles, (c) TiO_2 nanowire, and (d) mixed TiO_2 particles/TNWs/WO_3.

The observed decrease in R2 of WO_3 (1.0 wt.%) indicates reduction in electron recombination and enhancement in the efficiency of electron transport. However, in the case of the WO_3 (2.0 wt.%), R2 increased, as WO_3 (2.0 wt.%), with more trap sites, obstructs the movement of electrons from the nanoporous TiO_2 layer to the FTO electrode [19–22].

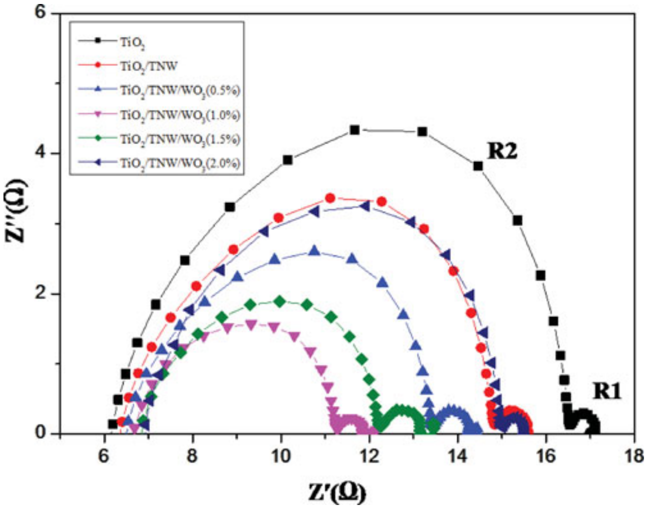

Figure 4. EIS Nyquist plots of TiO_2/TNWs DSSCs with different concentrations of WO_3.

Table 1. The integral photocurrent density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF), and efficiency(η) of DSSCs fabricated using pure TiO_2 particles (bare), and those fabricated using TNW/TiO_2 particles and WO_3 of various compositions

Sample	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	Efficiency (η)
TiO_2	10.08	0.62	65.13	4.10
TNW 10 wt.%	11.91	0.61	63.96	4.69
WO_3 0.5 wt.%	12.09	0.64	65.15	5.06
WO_3 1.0 wt.%	12.07	0.66	68.27	5.47
WO_3 1.5 wt.%	12.20	0.67	65.95	5.43
WO_3 2.0 wt.%	10.41	0.69	65.80	4.79

Fig. 5 shows the current-voltage photovoltaic performance of DSSCs composed of bare TiO_2 particles, TNWs (10 wt.%), and WO_3 (at various concentrations, namely, 0.5 wt.%, 1.0 wt.%, 1.5 wt.%, 2.0 wt.%), under AM 1.5 illumination (100 mW/cm^2). The corresponding photovoltaic parameters of DSSCs are summarized in Table 1. For the composite TNP/TNW (10 wt.%) film, the corresponding DSSC exhibited a high light-to-electric energy conversion efficiency of 4.69%, short-circuit current density of 11.91 mA/cm^2, open-circuit voltage of 0.61 V, and fill factor of 63.96%. These results indicate that the Jsc value increased significantly, based on the effects of the mixed TNWs. The observed increase in Jsc could be attributed to the improved open-circuit voltage of the composite TNP/TNW electrodes, originating from the increased electron lifetime in a one-dimensional electrode, which results in more incident photons being harvested.

The internal resistance decreases as a function of WO_3 content, which confirmed the previous discussion about the blocking effect of WO_3 modification for charge recombination. It can be seen from Table 1 that the presence of WO_3 has different effects on the open-circuit voltage (Voc), the short-circuit current (Jsc) and the overall conversion efficiency (η). The open-circuit voltage of DSSC increases as a function of WO_3 content. One

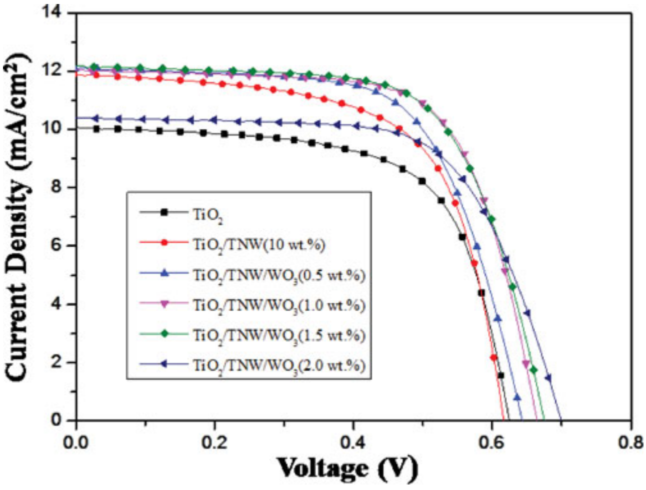

Figure 5. Current-Voltage (I-V) characteristics of TiO_2 films prepared by mixing TiO_2/TNW/WO_3.

of the most important parameters for a solar cell is its photoelectric conversion efficiency, and the DSSC, fabricated using a mixture containing 1.5 wt% WO_3, was observed to have the highest value in this regard, with a photocurrent density (Jsc) of 12.07 mA/cm^2, and a cell conversion efficiency of 5.47%. The open circuit voltage (Voc) of 0.66 V was also higher when compared to the bare cell. The dependence of the overall conversion efficiency (η) on WO_3 content shows the same trend as the short circuit photocurrent. However, higher concentrations of WO_3 (over 1.5 wt.%) reduced the solar cell performance.

Conclusions

In this work, we report for the first time the improvement of photovoltaic performance in dye-sensitized solar cells. TNWs were fabricated by hydrothermal treatment of TiO_2 powder prepared via the sol-gel method. Correspondingly, DSSCs were fabricated with TiO_2 films composed of TNWs and TNPs, with those TNWs prepared by hydrothermal treatment at 150°C exhibiting a pure anatase crystal structure. It was found that the size and the structure of TNWs could be tuned by controlling the temperature of hydrothermal treatment, and that the conversion efficiency of DSSC was highly influenced by the properties of the TNWs.

In addition, DSSCs were constructed by application of WO_3 mixed with a TNP/TNW composite at various percentages. The DSSC prepared without TNW or WO_3 had a short circuit current density (Jsc) of 10.08 mA/cm^2, an open circuit potential (Voc) of 0.62 V, and a cell conversion efficiency of 4.10%. The dye-sensitized solar cell using a WO_3 mixture exhibited the highest measured conversion efficiency of 5.47%, due to an increase in the efficiency of electron transport.

The DSSC composite cell based on WO_3 mixtures with proper weight percentages (i.e. 1.0 wt.%) showed a better photovoltaic performance than the TNP cell. It was observed that efficiency increased, and internal resistance decreased, as a function of WO_3 content. The addition of WO_3 process was, therefore, an effective method for improving the efficiency of TNP-based DSSCs.

Acknowledgments

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