

Article

Improved Performance of Dye-Sensitized Solar Cells with TiO₂ Nanoparticles/Zn-Doped TiO₂ Hollow **Fiber Photoanodes**

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Abstract: In this study, dye-sensitized solar cells (DSSCs) were fabricated using double-layer photoanodes consisting of TiO₂ nanoparticles (NPs) and Zn-doped TiO₂ hollow fibers (HFs). The TiO₂ HFs were prepared by co-axial electrospinning and used as the light-scattering layer in the DSSC. The thickness variations of the TiO₂ NP and Zn-doped TiO₂ HF photoanode layers affect the performance of the DSSC, especially the short-circuit photocurrent density. The thickness of the TiO₂ NP layer significantly affected the absorbance of photons and N719 dye molecules in the double-layer photoanode, while that of the Zn-doped TiO₂ HF layer affected the scattering of light, as indicated by the low light transmittance in the photoanode. Conventional DSSCs consist of single-layer photoanodes, and exhibit relatively low efficiency, i.e., 1.293% and 0.89% for TiO₂ NP and Zn-doped TiO₂ HF, respectively. However, herein, the highest efficiency of the DSSC (3.122%) was achieved with a 15 µm NP-5 µm HF photoanode, for which the short-circuit photocurrent density, open-circuit photovoltage, and fill factor were 15.81 mA/cm², 0.566 V, and 34.91%, respectively.

Keywords: double-layer photoanode; dye-sensitized solar cells; nanoparticles; hollow fibers

1. Introduction

Renewable energies such as wind, geothermal, ocean, hydro, biomass, and solar are promising energy resources for meeting the increasing energy demand in the world [1–3]. Sun is the largest source of external energy for our planet. Solar energy is non-toxic, clean, and abundant to satisfy the increasing global energy demand [1]. Solar energy can be directly converted into electrical energy by using solar cells. Third-generation photo-electrochemical solar cells have advantages such as simple processing, environment-friendliness, low cost, and hence find application in a wide range of fields, including dye-sensitized solar cells (DSSCs) [1,4-7]. DSSCs comprise a semiconductor material, electrolytes, transparent conductive oxide (TCO) substrates, counter electrode, and dye sensitizers [4–10]. The semiconductor material used as a photoanode has a very significant influence on the performance of the DSSC [11-13]. TiO₂ is a typically used semiconductor material in DSSCs, and it can provide the highest efficiency among the others obtained with other semiconductor materials such as ZnO, NiO, SnO₂, Nb₂O₅, WO₃, Zn₂SnO₄, and SrTiO₃ [14–17]. This advantage of TiO₂ is attributed to its high photovoltaic performance in the visible region [14] and its ability to maximize the absorption of the dye sensitizer on the surface [18,19]. Extensive efforts have been undertaken to modify the morphology and structure of the semiconductor layer in the DSSC photoanode in order to achieve optimal performance [20]. Nanosized semiconductors have been widely used as a DSSC photoanode owing to their high absorption capability for dye sensitizers and the ability to effectively excite electrons [21-23].

Typically, small-sized semiconductors (<100 nm), in the form of nanoparticles (NPs) and nanopowders, are widely used as the photoanode in DSSCs [24]. Baglio et al. showed that DSSCs in which the photoanode comprised 10- μ m-thick TiO₂ nanopowder layers (particle diameter: 21 nm) yielded an efficiency of 1.44% efficiency. The open-circuit photovoltage (V_{OC}), short-circuit photocurrent density (J_{SC}), and fill factor (FF) were 0.69 V, 4.3 mW/cm², and 50%, respectively [25]. Small-sized nanomaterials possess a large surface area for absorbing dye molecules. However, the high surface area of the photoanode reduces its ability to trap light owing to the large amount of grain boundaries, due to which most of the incoming light (incident light path) is lost [26,27]. On the other hand, large-size semiconductors (>100 nm) can capture a greater amount of the incoming light (incident light path) and scatter more photons in the photoanode; however, their ability to absorb dye molecules is low because of the reduced surface area [26–30].

One way to optimize the characteristics is to use a multilayer structure for the photoanode [31]. A multilayer photoanode comprising a dye-loading layer and a light-scattering layer improved the energy conversion efficiency of DSSCs [29–34]. Kim et al. showed that a multilayer stacked TiO₂ nanoparticle/nanotube photoanode increased the short-circuit photocurrent density by approximately 12.6% [18]. Xie et al. showed that 500–800 nm TiO₂ hollow microspheres had superior light scattering and electron diffusibility to enhance photovoltaic efficiency up to 28.4% [30]. Chava et al. also mentioned that the photoanode based on 150–200 nm TiO₂ hollow nanoparticles for scattering layer increased photovoltaic efficiency from 6.08% to 7.58% [31]. The light-scattering layer in photoanode of DSSC provide a longer electron transfer path and higher charge-collection efficiency for improving photoconversion efficiency [18,27].

In a multilayer photoanode, TiO_2 NPs are typically used as the dye-loading layer to optimize the absorption of dye molecules [15]. This is because an NP semiconductor has a larger surface area compared to materials with other morphologies [15,35]. On the contrary, semiconductors with one-dimensional nanostructures such as nanowires, nanotubes, nanorods, and nanofibers are suitable as a light scattering layer because of the larger particle size and electron transport capability [28,36]. In addition, modification of the nanofiber structure to a hollow fiber (HF) structure increases the scattering of light owing to the branched structure and larger surface area [37].

HF semiconductors can be fabricated by coaxially electrospinning capillaries [37,38], which produces a low-cost and simple system with excellent control of morphology [39]. Studies on the preparation of TiO₂ HFs with excellent electrical properties and non-cracking continuous morphology have been conducted [37]. The addition of zinc to TiO₂ HFs resulted in an increase in the inner and outer diameters of the TiO₂ HFs. Furthermore, the current density of TiO₂ HFs was improved because Zn doping increased the electron mobility. The previous study showed that Zn doping at 0.4% into TiO₂ HF enabled the optimum performance of the DSSC owing to the synergetic effect of the anatase and rutile forms in the TiO₂ semiconductors [37].

The aforementioned advantages of Zn-doped TiO_2 HFs make them suitable for application as a light-scattering layer in DSSCs. However, there has been no systematic study on the use of TiO_2 NPs and Zn-doped TiO_2 HFs as the double-layer photoanode in DSSCs. In this study, the performance of a DSSC with a double-layer photoanode comprising TiO_2 NPs as the dye-loading layer and Zn-doped TiO_2 HFs as the light-scattering layer was investigated. The thickness of each layer was varied in order to analyze its effect on the performance of the DSSC.

2. Results and Discussion

2.1. Photoanode Characterization

Figure 1 shows the X-ray diffraction (XRD) pattern of the TiO₂ NP and Zn-doped TiO₂ HF. The peaks at $2\theta = 25.4^{\circ}$, 37.9° , 48.1° , 53.8° , and 55.0° are in accordance with the (101), (004), (200),

(105), and (211) crystallographic planes of TiO_2 . The size of the crystal in each semiconductor can be calculated by using the Scherrer equation, considering the highest peak, i.e., the (101) peak [37,40].

$$D = \frac{k \cdot \lambda}{B \cdot \cos \theta} \tag{1}$$

where *D* is the diameter of the crystallite TiO₂, λ is the wavelength of the X-ray (Cu K α = 1.5406 Å), and *k* is a constant (~0.9). θ is the angle of diffraction, and *B* is the peak width based on the full width at half-maximum intensity. Equation (1) shows that the crystal size is inversely proportional to the peak width; hence the crystal size of the TiO₂ NP (15.19 nm) is smaller than that of the Zn-doped TiO₂ HF (16.48 nm). Figure 2a shows the morphology of the TiO₂ NP. After sintering, the average grain diameter of the TiO₂, NP becomes approximately 68.8 nm. The morphology of the Zn-doped TiO₂ HF is shown in Figure 2b,c. The average size of the HF semiconductor is 285 nm (outer diameter) and 91 nm (inner diameter). This result suggests that Zn doping causes the diameter of TiO₂ to increase [37], rendering it suitable as a light-scattering layer [26]. Figure 2d shows the cross-section image for the double-layer photoanode that consists of 15 µm TiO₂ NP and 5 µm Zn-doped TiO₂ HF layers.



Figure 1. XRD pattern of TiO₂ NP and Zn-doped TiO₂ HF.



Figure 2. Cont.



Figure 2. SEM images of (**a**) TiO₂ NP, and (**b**) Zn-doped TiO₂ HF; (**c**) TEM images of Zn-doped TiO₂ HF; (**d**) Cross section images of photoanode double layer that consists of 15 μ m TiO₂ NP and 5 μ m Zn-doped TiO₂ HF layers.

Figure 3 is a plot of the optical absorption as a function of the photon energy for TiO_2 NP and Zn-doped TiO_2 HF. Tauc's method for determining the band gap energy of a semiconductor is implemented using the following equation:

$$(\alpha \cdot hv)^2 = c(hv - E_g) \tag{2}$$

where α is the absorption coefficient, hv is the incident photon energy, c is a constant, and E_g is the electronic energy of the optical band gap. The photon energy is determined by h, Planck's constant (6.626 × 10⁻³⁴ Js), and v, the frequency. The frequency can be calculated by the relation $v = c/\lambda$, where c is the speed of light (2.998 × 10⁸ m/s) and λ is the wavelength of light [22]. The band gap energy of the semiconductor can be determined by extrapolating the straight-line section in the $(\alpha.hv)^{1/r}$ vs. hv curve (Figure 3). Anatase TiO₂ is an indirect band gap type; hence, its r is constant, at 2. The results indicate that the band gap energies of TiO₂ NP and Zn-doped TiO₂ HF are 3.19 and 3.23 eV, respectively. The band gap energy of the HF structure in Zn-doped TiO₂ was higher than that of the NP structure.



Figure 3. $(\alpha \cdot hv)^2$ vs. hv curve for TiO₂ NP and Zn-doped TiO₂ HF.

Figure 4 shows the absorption and transmittance of the TiO_2 NP and Zn-doped TiO_2 HF. Using Figure 4, the optical properties of the photoanode layers can be compared. The absorbance of pure TiO_2 NP is higher than that of other photoanodes; hence, TiO_2 NPs can absorb a large quantity of

light entering the photoanode layer. However, the transmittance test results show that the TiO_2 NPs also transmit a large amount of light out of the photoanode. The greater the content of TiO_2 NPs in the photoanode, the higher is the light absorbance; however, the transmittance also increases. Conversely, a high content of Zn-doped TiO_2 HF decreases the light transmittance as well as absorbance. Hence, the scattering of light in Zn-doped TiO_2 HF is better than that in TiO_2 NP, owing to the larger diameter and longer structure than TiO_2 [28]. In this study, the double-layer structure was equally efficient in dye-loading by TiO_2 NP and light scattering by Zn-doped TiO_2 HF.



Figure 4. (a) Absorption and (b) transmittance spectra of TiO₂ NP and Zn-doped TiO₂ HF.

2.2. Performance of DSSCs

Table 1 shows the performance of the DSSCs in terms of the values of V_{OC} , J_{SC}, FF, and efficiency (η) for a typical dye-loading layer composition and thickness of the light-scattering layer in the DSSC photoanode. Figure 5 shows the performance and curves of the photocurrent density versus photovoltage (I-V) for each DSSC. Overall, changes in the photoanode composition of each DSSC do not change the V_{OC} value, which is in the range of 0.55–0.61 V. This is partly because the total thickness of the photoanode in each DSSC is the same. Ito et al. showed that the thicker of photoanode gave the lower photovoltage in DSSC. Thus, the constant total thickness of photoanode in this work produce minor influence in V_{OC} parameter [41]. DSSCs with a single-layer photoanode have a relatively low efficiency, i.e., 1.293% and 0.89% for 20 μ m TiO₂ NP and Zn-doped TiO₂ HF, respectively. However, in this study, the highest DSSC efficiency of 3.122% was achieved by the composition 15 μ m NP-5 μ m HF for the double-layer photoanode. The DSSCs with a conventional TiO₂ NP single layer. The increase in the efficiency of the double-layer DSSC is primarily attributed to the increase in the photocurrent density of the DSSC, which is determined by how many photons are converted into the movement of electrons.

Table 1. Performance parameter of DSSCs with various photoanode layers.

Photoanode	V _{OC} (V)	Jsc (mA/cm ²)	Fill Factor (%)	Efficiency (%)	Dye Loading (mol/cm ²)
20 µm NP	0.553	5.61	41.64	1.293	$8.96 imes 10^{-8}$
15 μm NP-5 μm HF	0.566	15.81	34.91	3.122	$8.17 imes10^{-8}$
10 μm NP-10 μm HF	0.569	12.20	39.34	2.731	$6.46 imes10^{-8}$
5 μm NP-15 μm HF	0.562	9.08	32.11	1.636	$5.84 imes10^{-8}$
20 µm HF	0.612	2.94	49.55	0.890	$4.65 imes 10^{-8}$



Figure 5. I-V curves of DSSCs under irradiation intensity of 100 mW/cm².

The morphology of TiO₂ NP is small and uniform; hence, the NP layer exhibits maximum absorbance for the dye molecules, whereas the morphology of Zn-doped TiO₂ HF is large and long, and hence, it supports optimal scattering [28]. The Zn-doped TiO₂ HF with a diameter of 285 nm played as a scattering layer in the photoanode. It had superior light scattering capability for capturing a greater amount of incident light path. It produced more photons in the photoanode thus increased electron diffusibility. As a result, the DSSC with double layer of photonoda with a scattering layer leaded a higher photovoltaic conversion efficiency [30,31]. The previous study by Nath et al. showed that the use of light-scattering layers in the photoanode improved the incident photon-to-current conversion efficiency (IPCE) of the DSSC up to 32% [27]. By using TiO₂ hollow microspheres with a diameter of 500–800 nm, and Xie et al. reported that light-scattering layers enhanced photovoltaic efficiency from 6.49 to 7.59% [30].

The DSSCs efficiencies in this work were range from 0.890 to 3.122% as shown in the Table 1. Compared with some previous studies [27,30,31], those efficiencies were relatively too low. It caused by the lower fill factor in the solar cell circuit. Fill factor is dominantly influenced by parasitic resistive losses that consists of series and shunt resistance [42]. The electrical resistance in the substrate and the contact resistance between semiconductor and FTO surface gave major influence in series resistance. Thus, it decreased both fill factor and photoconversion efficiency.

The amount of dye molecules that can be absorbed by the semiconductor (dye loading) was measured using the desorption method [43]. Semiconductors containing the absorbed N719 dye were soaked in 0.1 M NaOH with a distilled solvent for 10 min. Dye molecules that separated from the semiconductor dissolved in the NaOH solution. Further, UV-Vis absorption spectra were acquired to measure the concentration of the solution. Figure 6 shows the absorption spectra of a solution that contains the dye for each photoanode composition. The concentration of the dye loaded in the solution was calculated using the Beer-Lambert law.

$$A = \varepsilon \cdot c \cdot l \tag{3}$$

A is the UV-Vis absorbance peak intensity, ε is the molar extinction coefficient of the N719 dye, *c* is the molecular dye concentration, and *l* is the path length of the light beam. The molar extinction coefficient of N719 for 14,100 M⁻¹cm⁻¹ at 515 nm was determined, and the values are listed in Table 1. Table 1 shows that the photoanode with the highest NP content (20 µm NP) had a high dye-loading capability (8.96 × 10⁻⁸ mol/cm²). However, with decreasing thickness of the NP layer, this capability also reduced owing to the decrease in the surface area available for the absorption of the dye molecules. NP structures that are smaller than the HF structure would provide a large surface area and high-density grain distribution.



Figure 6. UV-Vis absorption spectra of the solutions containing dyes adsorbed by various photoanodes.

3. Materials and Methods

3.1. Synthesis and Characteristics of TiO₂ NPs and Zn-Doped TiO₂ HF

The TiO₂ NP (~21 nm particle size) substrate was provided by Sigma Aldrich (St. Louis, MO, USA) and used as received. The Zn-doped TiO₂ HF was synthesized by co-axial electrospinning, as illustrated in Figure 7. A detailed description of the synthesis of Zn-doped TiO₂ HF is provided in an earlier study [37]. The precursor solution used in co-axial electrospinning was prepared by mixing 0.37 g of titanium (IV) isopropoxide (TTIP, 99.9%, Sigma Aldrich-377 996), 1.13 g of polyvinylpyrrolidone (PVP, MW 40,000, Merck-PVP40, Kenilworth, NJ, USA), and 2 g of absolute ethanol (99.5%, 459 844 Sigma-Aldrich), following which it was stirred for 1 h. Subsequently, 0.78 g acetic acid (99.7%, Sigma Aldrich-320 099) and zinc nitrate hexahydrate (98%, Sigma Aldrich-228 737) in a weight ratio of 0.4% to TiO₂ was added to this solution and stirred for 11 h until the solution turned transparent. The precursor solution used as the core (inner side) of the HF layer was prepared by stirring olive oil (Sigma-Aldrich O1514) with a magnetic stirrer for 4 h at 150 °C. The solution was then kept at 25 °C for 25 h in order to remove the foam.



Figure 7. Schematic of co-axial electrospinning to produce Zn-doped TiO₂ HF.

The HF was synthesized by adding 1 mL TTIP solution to the sheath of a syringe pump, where the olive oil solution was supplied to the core of the syringe pump. The diameters of the core and sheath needle syringe pump were 0.3 mm and 0.8 mm, respectively. The syringe pump needle was connected

to the positive terminal of a high-voltage power supply (~15 kV), while a collector in the form of an aluminum plate was connected to the negative terminal. The distance between the terminals was 29.5 cm horizontally. TTIP solution was injected at a rate of 0.6 mL/h, whereas the olive oil solution was injected at the rate of 0.2 mL/h. The difference of volume rate in TTIP and oil solution was caused by the difference of needle diameters for obtaining the continuous hollow fibers. During electrospinning, the collector will collect fibers on the collector surface. The fibers were then sintered at 500 °C for 2 h at a heating rate of 2.5 °C/min and subsequently cooled to 50 °C with a cooling rate of 1.5 °C/min to form the Zn-doped TiO₂ HF [37].

3.2. Counter Electrode

The counter electrode for the DSSC was prepared by depositing platinum on the surface of fluorine-doped tin oxide (FTO, Sigma-Aldrich) by sputtering. FTO with an area of 2×1.5 cm² was placed in a vacuum tube under a pressure of 9.5×10^{-5} Torr (0.012665625 Pa). Platinum was connected to the negative terminal, while FTO was connected to the positive terminal of the high-voltage power supply (404 V, 125 mA). Argon gas (4 mTorr or 0.53328947 Pa) was supplied to the vacuum chamber, by which platinum ions will stick to the surface of the FTO. The FTO in the vacuum chamber was rotated at a speed of 5 rpm to produce a uniformly deposited counter electrode. This sputtering process lasted about 20 min.

3.3. DSSC Fabrication and Testing

FTO (Sigma-Aldrich) was used as the DSSC-assembling substrate. Figure 8 shows the structure of the DSSC fabricated in this study. Semiconductor deposition was performed twice to form a double-layer photoanode. The dye-loading layer was prepared by dissolving 0.24 g TiO₂ (21 nm, Sigma-Aldrich) into 4 mL ethyl alcohol (96%, Merck). TiO₂ NP paste was coated on the FTO surface of area 1×1 cm², to thicknesses of 20, 15, 10, and 5 µm. The photoanode was heated at 100 °C for 10 min to strengthen the bonding and prevent crack formation prior to the second coating.



Figure 8. Structure of DSSCs with double-layer photoanode.

The light-scattering layer was prepared by dissolving 0.24 g of Zn-doped TiO₂ HF into 4 mL ethyl alcohol to form a thick paste. The paste was coated on the TiO₂ NP layer, until the total thickness of the semiconductor was 20 μ m. The layer was then sintered at 500 °C for 1.5 h at a heating rate of 3 °C/min. Upon attaining a temperature of 50 °C, the photoanode was soaked in a solution of 0.3 mM N719 with absolute ethanol solvents (Merck) for 24 h.

Next, the photoanode was assembled with the counter electrode. The electrode had two holes for electrolyte replenishment. The photoanode and counter electrode were combined with a plastic sealant (30 μ m), clamped, and then heated at 115 °C for 8 min to strengthen the bond. An electrolyte solution of 3.3 g sodium iodide (99.95%), 0.523875 g of pure iodine (99.95%), 0.005481 g heteropolyacid (HPA), and 30 mL acetonitrile was injected into the DSSC through the hole in the counter electrode, which was then covered with glass glue. Thus, the DSSC was fabricated. The performance of the DSSC was measured using a solar simulator with an illumination intensity of 100 mW/cm². The current-voltage (I-V) curves were measured using a digital multimeter (Keithley 2401) to obtain the *J*_{sc}, *V*_{oc}, FF, and efficiency of the DSSC.

4. Conclusions

DSSCs with a double-layer photoanode, comprising TiO₂ NP and Zn-doped TiO₂ HF layers, were successfully fabricated. The highest efficiency of the DSSC, i.e., 3.122%, was achieved with the composition 15 μ m NP-5 μ m HF photoanode. The corresponding short-circuit photocurrent density, open-circuit photovoltage, and fill factor were 15.81 mA/cm², 0.566 V, and 34.91%, respectively. The higher content of the NP semiconductor in the photoanode, the greater was the absorbance of the photons and dye molecules. Further, the higher the content of the HF semiconductor in the photoanode, the stronger was the light-scattering effect. Overall, variations in the composition of the NP and HF photoanode layers affected the short-circuit photocurrent density, but not the open-circuit photovoltage of the DSSCs. As a result, the double-layer photoanode using the composition 15 μ m-5 μ m HF NP improved the DSSCs efficiency about 2.41 times higher than that of DSSCs with a conventional TiO₂ NP single layer.

Author Contributions: Z.A. and S.S. designed the concept and methodology for the experiment. S.H. explored the literature summaries. Z.A. and B.S. performed the case study and wrote the paper. Z.A. and S.H. contributed to analyzing the results. S.S. supervised this work.

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