Dye-sensitized solar cells based on composite TiO₂ nanoparticle–nanorod single and bi-layer photoelectrodes

F REZVANI¹, E PARVAZIAN^{2,*} and S A HOSSEINI¹

¹Department of Textile Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran

²Department of Materials Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran

MS received 24 April 2015; accepted 21 March 2016

Abstract. TiO₂ nanoparticle (NP), composite TiO₂ nanoparticle–nanorod (NP–NR) and bi-layer TiO₂ nanoparticle/nanorod (NP/NR) with the optimized diameter of NRs had been prepared as anode layer in dye-sensitized solar cells (DSSCs). Morphology and thickness of anode layers were provided by field emission scanning electron microscope (FE-SEM) and scanning electron microscopy (SEM) devices. Current density–voltage diagrams were prepared by potentiostat and solar simulator devices at air mass (AM) 1.5. It is determined that DSSCs based on composite NP–NR photoelectrode had the best conversion efficiency of 5.07%. Also, the results of the electrochemical modelling of these DSSCs indicated that solar cells based on NP–NR electrode had the highest electron transport time (τ_d) of 312.87 ms, electrons' recombination lifetime (τ_n) of 130.4 ms and the lowest transfer resistance (R_{ct}) as well as transport resistance (R_t) of 22.46 and 9.4 Ω , respectively.

Keywords. Dye-sensitized solar cells; composites; nanostructure; photovoltaic.

1. Introduction

Low cost, non-vacuum and high-energy conversion efficiency have made dye-sensitized solar cells (DSSCs) the most promising alternative to the conventional silicon-based solar cells [1–4]. In a DSSC, the photo-excited electrons of the dye molecules are transferred to the TiO₂ conduction band, which are taken out through an external circuit using an anode electrode (fluorine-doped tin oxide, FTO) and a counter electrode (platinum or carbon sputtered FTO), respectively, in the presence of a liquid or solid redox electrolyte [5–13]. DSSCs have attracted widespread interests since O'Regan and Gratzel [1] made a breakthrough in the efficiency using TiO₂ NP films sensitized with organic dye in 1991. Consequently, 11% efficiency was achieved in 2005 [14,15]. However, owing to the smaller surface-to-volume ratio of TiO₂ nanofibres compared to that of TiO₂ NPs, the photocurrent of devices based on TiO₂ nanofibres is lower than that of DSSCs using TiO₂ NPs. One approach is to extend a thicker TiO₂ nanofibre photoanode. However, the electrons' recombination will increase strongly if the thickness is greater than the electron diffusion length in the photoanode [16]. The light harvesting enhancements of scattering layers such as large NPs, nanowires, nanotubes have been demonstrated experimentally [17–19] and theoretically [20] to improve the photovoltaic performance of DSSCs. Tan *et al* [21] demonstrated that incorporation of 20 wt% of nanowires can enhance the efficiency of DSSCs from 6.7 to 8.6%. Based on the research of Kang *et al* [22], the electron lifetime value

of the NRs within the anode layer is higher than those of the NPs. Adachi *et al* [23] indicated that the current density of DSSCs made of a network of nanowires is more than twice that of NPs DSSCs. However, Wu *et al* [24] lately illustrate with the inconsistent results that the efficiency of the NRs–NPs composite DSSCs as well as NRs DSSCs is lower than that of the NPs DSSCs. Electrospinning is a versatile and economical approach for producing continuous fibres from different materials, such as polymers [25,26], inorganic materials [27–29] and organic–inorganic hybrid compounds [30]. The present study concentrates on fabrication of TiO₂ NP, composite TiO₂ NP–NR and bi-layer TiO₂ NP/NR photoelectrodes for DSSCs. The aim is clarifying the differences in behaviour of electrons within the anode of single- and bi-layer NP/NR composites, using various metallurgical, photovoltaic and electrochemical characterizations.

2. Experimental

TiO₂ nanofibres were prepared by electrospinning method. Electrospinning sol contains polyvinylpyrrolidone (0.3 g, Mw = 1,500,000, Sigma Aldrich, Germany), titanium isopropoxide (0.5 ml, >98%, Merck, Germany), ethanol (3.7 ml, 99.99%, Merck, Germany) and acid acetic (1.2 ml, 99.7%, Merck, Germany). To obtain a yellow clear uniform sol, a magnetic stirrer (IKA®RHbasic2, Germany) was used for 18 h. The solution was electrospun under the voltage of 17 kV, feed rate of 3.4 ml h^{−1} and distance of 13 cm with the rotating drum wrapped in an aluminium foil (50–100 μ m). To remove polyvinylpyrrolidone completely, nanofibres (with the range of 300–600 nm diameter) were placed into the

*Author for correspondence (e.parvazian@ma.iut.ac.ir)

heat-treatment furnace (Carbolite, England) at 600°C for 3 h. Later, TiO₂ nanofibres were ground to NRs in a mortar [8] for about 15 min. All TiO₂ NPs, nanofibres and NRs have anatase phase [19].

Polyethylene glycol (Mw = 4000 g mol⁻¹, Sigma Aldrich, Germany), acetic acid (65%, Merck, Germany), terpineol (Fluka, Germany) and ethyl cellulose powder (5–15 and 30–50 mPas, Aldrich, Germany) were used to prepare TiO₂NR, TiO₂ NP (~35 nm, Sigma Aldrich, Germany) and nanocomposite NR–NP pastes. TiO₂ NR paste was prepared as shown as in figure 1. TiO₂ NP paste was prepared according to reference [31]. The weight ratio of NR:NP was determined to provide NP–NR composite and NP/NR bi-layer electrode. Details about the ratio are discussed in next section. First,

Figure 1. Preparation of TiO₂ nanorod pastes for anode layer of DSSCs.

FTO glasses (15 Ohm per square, 3 × 1.5 × 1.5 cm³, Solaronix, Switzerland) were cleaned in ultrasonic bath with acetone and ethanol (3.7 ml, 99.99%, Merck, Germany) for 15 min. Prepared pastes were printed on these FTO glass substrates by doctor blading method. All provided electrodes have the effective surface area of 0.25 cm². To make porous layers and to remove extra materials, electrodes were placed in a furnace at 450°C for 2 h. Electrodes were immersed in cis-diisothiocyanato-bis (2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis (tetrabutylammonium) or N719 dye solution (0.15 mM in ethanol, Solaronix, Switzerland) for 18 h to prepare photoelectrodes. To remove the extra non-absorbed dye particles, photoelectrodes were immersed in ethanol for 15 min. DSSCs were assembled by using spacer layers (thermoplastic sealant film, Surlyn-50, 50 µm, Dyesol, Australia) between photoelectrodes and platinized counter electrodes. Finally, liquid redox (I⁻/I₃⁻, Sharif Solar, Iran) was injected as electrolyte and spacer layer was heated (up to 125°C for about 2 min) to use as a sealant film.

Field-emission scanning electron microscope (FE-SEM; Hitachi S4160, Japan) and X-ray diffraction device (XPRT-MPD Philips) were used for materials characterizations. Ultrasonic bath (Power sonic 405, Korea) and heat-treatment furnace (Carbolite, England) were used for preparation of TiO₂ NP and TiO₂–multiwalled carbon nanotube pastes. Also, current density–voltage (*J*–*V*) curves and electrochemical impedance spectroscopy (EIS) analysis were achieved by Potentiostat device (ParStat 2273, America) and solar simulator (SolSim; Luzchem, Solar Simulator, Germany) with 1.5 AM radiation.

Figure 2. Field emission scanning electron microscope images for microstructure of photoelectrodes based on TiO₂ nanorods with (a) 193 ± 1, (b) 172 ± 1, (c) 276 ± 1 and (d) 391 ± 1 nm diameter.

Table 1. Open circuit voltage (V_{oc}), short current density (J_{sc}), fill factor (FF) and conversion efficiency of DSSCs based on different TiO₂ nanorod diameters in photoelectrodes.

DSSC code	Thickness of NRs (nm)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	Efficiency (%)
A	193 ± 1	0.65	0.68	0.54	0.23
B	172 ± 1	0.64	0.53	0.52	0.18
C	276 ± 1	0.63	0.41	0.48	0.13
D	391 ± 1	0.44	0.26	0.39	0.05

3. Results and discussion

3.1 NR diameter optimization

The surface morphology related to the anode layer of the TiO₂ NRs with different diameters (193 ± 1, 172 ± 1, 276 ± 1 and 391 ± 1 nm) are shown in figure 2. As shown in table 1, the best photovoltaic performance belongs to the DSSC A; with the NR thickness of 193 ± 1 nm and conversion efficiency of 0.23%. In solar cells A and B, the electrons cannot be transported into the anode layer. On the other hand, the worst conversion efficiency and current density belongs to solar cell D with the maximum NRs diameter 391 ± 1 nm. According to the fill factor parameters, solar cell D had the least power to transport electrons within its anode layer.

3.2 Microstructure of TiO₂ anode layers

To find out the morphologies of TiO₂ NP, composite TiO₂ NP–NR and bi-layer TiO₂ NP/NR anode layers, FE-SEM and SEM images were used. Figure 3a shows the microstructure of porous TiO₂ NP film, which was heated within a heat-treatment furnace at 450°C for 30 min. The average diameter of NPs (35 nm) was carefully calculated with digimizer software. Figure 3b shows the morphology of composite TiO₂ NP–NR film. It should be noted that NR:NP weight ratio is 26% in the composite. The thickness of TiO₂ NP, composite and bi-layer anode films are shown in figure 4. Thickness values are listed in table 2. The role of these morphologies on the performance of DSSC device is discussed in Sections 3.3 and 3.4.

3.3 Photovoltaic characterization

Morphological manipulation can be effective on dye absorbance in photoanode of a DSSC device. To indicate the dye absorbance difference between NP, composite NP–NR and bi-layer NP/NR electrodes, all of them were immersed in dye N719 solution (0.15 ml in ethanol) for 18 h. The bi-layer electrode (figure 5a) had the least dye absorbance. It is because of the compatibility problem between these two layers. It results in empty places, which may cause dye material loss during the immersion process. Therefore, the absorbance problem causes a photoelectrode with light colour. Moreover, it can be noticed that NP electrode (figure 5b) absorbed more

Figure 3. FE-SEM images for the microstructure of (a) anode TiO₂ nanoparticles and (b) composite anode layer TiO₂ NP–NR.

dye molecules. However, the most dye absorbance belongs to composite NP–NR electrode (figure 5c). It means that composite electrode can absorb photons from visible light much more than the others. The difference between these two photoelectrodes is caused by the effect of NRs presence. It helps to improve the effective area on the porous TiO₂ NP–NR active layer.

To compare the photovoltaic behaviour of TiO₂ NRs single-layer, composite NP–NR and bi-layer NP/NR photoelectrodes were prepared. Both composite and bi-layer films had the NR:NP weight ratio of 26%. All devices were characterized under standard test conditions (STCs). STC indicates a temperature of 25°C and an irradiance of 1000 W m⁻² with an air mass 1.5 (AM1.5) spectrum. Also, the specific area of all solar cells was 0.25 cm². According to the current density–voltage curve in figure 6 and the results of table 2, solar cell with the composite photoelectrode has the greatest photovoltaic performance. The conversion efficiency of this particular cell, compared with DSSCs based on TiO₂ NPs, has been enhanced by 39%, because of the presence of TiO₂ NRs as large-sized scattering particles. The presence of these NRs makes larger vacancies in the anode layer and helps to absorb further dye molecules. The more dye particles in the photoelectrode, the more photon absorption in DSSCs. These photons are trapped in anode layer and the probability of generating electrons increases. From table 2, we can notice that

Figure 4. Scanning electron microscope images for thickness of (a) composite TiO₂ NP–NR, (b) TiO₂ NP and (c) bi-layer TiO₂ NP/NR photoelectrodes.

Table 2. Open circuit voltage (V_{oc}), short current density (J_{sc}), fill factor (FF) and conversion efficiency of DSSCs based on TiO₂ NP, composite TiO₂ NP–NR and bi-layer TiO₂ NP/NR electrodes.

TiO ₂ anode	Anode thickness (nm)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	Efficiency (%)
TiO ₂ NP	7.6 ± 0.5	0.69	8.76	0.60	3.65
TiO ₂ NP–NR	7.5 ± 0.5	0.69	11.93	0.61	5.07
TiO ₂ NP/NR	12 ± 0.5	0.65	2.85	0.58	1.10

Figure 5. Different dye absorbance power of photoelectrodes based on (a) TiO₂ bi-layer TiO₂ NP/NR, (b) TiO₂ nanoparticles and (c) composite TiO₂ NP–NR anode layer.

DSSCs based on bi-layer NP/NR photoelectrode have the worst photovoltaic performance. It indicates that the current density is very low. It means that generated electrons had a little chance to get to FTO conductive glass and most of them had recombined to liquid electrolyte. It happens because NRs as a separate layer could not convey the generated electrons to the TiO₂ NPs layer. This phenomenon is discussed in detail along with the results of EIS analysis in Section 3.4.

3.4 Electrochemical modelling of DSSCs

EIS analysis was used to model the inner electrical circuit of the fabricated solar cells under the temperature of 25°C and an irradiance of 1000 W m⁻² with an air mass 1.5 (AM1.5) spectrum. By the theoretical equations in reference [32] and electrochemical modelling software, ZVIEW, electron mobility behaviour in DSSCs based on NP, nanocomposite

Figure 6. J - V curve for DSSCs based on TiO₂ NP, composite TiO₂ NP-NR and bi-layer TiO₂ NP/NR photoelectrodes.

Figure 7. Nyquist curve of DSSCs based on TiO₂ NP, composite TiO₂ NP-NR and bi-layer TiO₂ NP/NR electrodes.

NP-NR and bi-layer NP/NR photoelectrodes were determined. Figure 7 shows the Nyquist curve of these three solar cells. In this diagram, the semi-circle is related to the behaviour of electrons inside the anode porous layer and also the anode/electrolyte interface. It can be seen in table 3 that series resistances in each of these three solar cells are almost equal, because the anode layers were printed in an equal way on similar FTO glass substrates with the same electrical resistance of 15 ohm per square. However, solar cells based on composite NP-NR had decreased in transfer resistance (R_t) and transport resistance (R_{tr}) compared to DSSCs based on TiO₂ NP. This means that electrons entered easily within the composite anode electrode and had transported to conductive glass with the least barriers. Transport and transfer resistances are decreased because of increase in electrons

Table 3. Series resistance (R_s), transfer resistance (R_t) and transport resistance (R_{tr}) of internal circuit for DSSCs based on TiO₂ NP, composite TiO₂ NP-NR and bi-layer TiO₂ NP/NR electrodes.

Anode	R_s (Ω)	R_t (Ω)	R_{tr} (Ω)
TiO ₂ NP	23.37	75.26	12.1
TiO ₂ NP-NR	22.42	22.46	9.36
TiO ₂ NP/NR	22.43	158.4	16.5

recombination. Indeed, TiO₂ NRs had provided new routes for electrons to pass.

In DSSCs based on bi-layer NP/NR photoelectrode, dye molecules cannot absorb through the compact secondary layer. This layer is full of aggregated large-sized NRs, which

Table 4. Chemical capacitance (μC), electron transport time (τ_d), electrons' recombination lifetime (τ_n) and electron diffusion length (L_n) for DSSCs based on TiO_2 NP, composite TiO_2 NP–NR and bi-layer TiO_2 NP/NR electrodes.

Anode	Q (μC)	N	C_μ (mF)	τ_d (ms)	τ_n (ms)	L_n (μm)
TiO_2 NP	122	0.74	3.01	226.53	36.42	7.48
TiO_2 NP–NR	861	0.78	13.93	312.87	130.38	18.61
TiO_2 NP/NR	46	0.77	0.655	103.75	10.80	2.93

are barriers for dye molecules to absorb. The less absorbed molecule dyes, the less photon to electron process in anode layer. On the other hand, this compact secondary layer is a barrier for electrons to transfer into the first layer and most of them recombined, because the transfer resistance (R_t) is too much in this solar cell. The results of table 4 indicate that chemical capacitance of DSSCs based on bi-layer photoelectrode is too low. It demonstrates that the secondary NR layer is an inappropriate layer which traps electrons and causes lots of electron loss. According to table 4, it can be seen that electrons recombination lifetime parameter (τ_n) is enhanced in the composite NP–NR. On the other hand, it is shown that the least electron transport time (τ_d) value belongs to bi-layer solar cell. In other words, electrons pass through the anode layer in this solar cell more rapidly than the other solar cells. Electron diffusion length (L_n) is another parameter that indicates the electrons behaviour in anode layer. The increase in L_n means that electrons can survive and transport in anode layer within longer paths.

4. Conclusion

DSSCs based on single-layer TiO_2 NPs (as a reference cell), single composite TiO_2 NP–NR and bi-layer TiO_2 NP/NR photoelectrodes were fabricated and characterized with FE-SEM, SEM and I–V and EIS analysis. SEM images show the anode thicknesses of 7.45, 7.57 and 12 μm , respectively. The photovoltaic analysis revealed the enhancement in photoelectric conversion efficiency of DSSCs based on nanocomposite TiO_2 NP–NR film. Compared to reference solar cell, the composite solar cell had 36 and 39% increase in current density and conversion efficiency, respectively. Improvement in conversion efficiency is caused by enhancement in dye molecules adsorption in porous composite layer. Also, scattering effect of TiO_2 NRs in composite layer improved the conversion efficiency of the device. On the other hand, the conversion efficiency of bi-layer solar cell is decreased due to incompatibility of two layers. Furthermore, the results for the modelling of inner electrical circuit with the EIS examinations indicate that the generated electrons in DSSCs on composite TiO_2 NP–NR have better situations. In this device, the minimum transport resistance of 9.36 Ω , the minimum transfer resistance of 22.46 Ω , the maximum electron lifetime of 130.38 ms and chemical capacitance of 13.93 mF are obtained. Minimum transport resistance means, electrons can move into porous layer in maximum pace and the maximum diffusion length can be obtained.

References

- [1] O'Regan B and Gratzel M 1991 *Nature* **353** 737
- [2] Noack V, Weller H and Eychmuller A 2002 *J. Phys. Chem. B* **106** 8514
- [3] Chiba Y, Islam A, Watanabe Y, Komiya R, Koide N and Han L Y 2006 *J. Appl. Phys.* **45** 638
- [4] Rhee S W and Kwon W 2011 *Korean J. Chem. Eng.* **28** 1481
- [5] Yoon Y I, Moon H S, Lyoo W S, Lee T S and Park W H 2009 *Carbohydr. Polym.* **75** 246
- [6] Nazeeruddin M K, Pechy P, Renouard T, Zakeeruddin S M, Humphry-Baker R, Comte P et al 2001 *J. Am. Chem. Soc.* **123** 1613
- [7] Tae E L, Lee S H, Lee J K, Yoo S, Kang E J and Yoon K B 2005 *J. Phys. Chem. B* **109** 22513
- [8] Shan C X, Liu Z, Zhang Z Z, Shen D Z and Hark S K 2006 *J. Phys. Chem. B* **110** 11176
- [9] Gratzel M 2003 *J. Photochem. Photobiol. C* **4** 145
- [10] Du S F, Liu H D and Chen Y F 2009 *Nanotechnology* **20** 1
- [11] Yang L and Leung W 2013 *Adv. Mater.* **25** 1792
- [12] Meng L, Li C and dos Santos M P 2013 *J. Inorg. Organomet. Polym.* **23** 787
- [13] Zhang W, Zhu R, Liu B and Ramakrishna S 2011 *Aust. J. Chem.* **64** 1282
- [14] Ghadiri E, Taghavinia N, Zakeeruddin S M, Gratzel M and Moser E 2010 *Nano Lett.* **10** 1632
- [15] Gratzel M 2005 *Inorg. Chem.* **44** 6841
- [16] Laurence P 2009 *Acc. Chem. Res.* **42** 1839
- [17] Jang Y H, Xin X K, Byun M, Jang Y J, Lin Z Q and Kim D H 2011 *Nano Lett.* **12** 479
- [18] Li X, Lin H, Li J B, Li X X, Cui B and Zhang L Z 2008 *J. Phys. Chem. C* **112** 13744
- [19] Parvazian E, Karimzadeh F and Enayati M H 2014 *J. Electron. Mater.* **43** 1450
- [20] Ferber J and Luther J 1998 *Sol. Energy Mater. Sol. C* **54** 265
- [21] Tan B and Wu Y 2005 *J. Phys. Chem. B* **110** 15932
- [22] Kang S H, Choi S H, Kang M S, Kim J Y, Kim H S, Hyeon T and Sung Y E 2008 *Adv. Mater.* **20** 54
- [23] Adachi M, Murata Y, Takao J, Jiu J, Sakamoto M and Wang F 2004 *J. Am. Chem. Soc.* **126** 14943
- [24] Wu J J, Chen G R, Lu C C, Wu W T and Chen J S 2008 *Nanotechnology* **19** 105702
- [25] Madhugiri S, Dalton A, Gutierrez J, Ferraris J J P and Balkus K J 2003 *J. Am. Chem. Soc.* **125** 14531
- [26] Bognitzki M, Czado W, Frese T, Schaper A, Hellwig M, Steinhart M, Greiner A and Wendorff J H 2001 *Adv. Mater.* **13** 70
- [27] Zhan S H, Chen D R, Jiao X L and Liu S S 2007 *J. Colloid Interface Sci.* **308** 265
- [28] Li D and Xia Y N 2003 *Nano Lett.* **3** 555
- [29] Hou H Q and Reneker D H 2004 *Adv. Mater.* **16** 69
- [30] Zhao J G, Jia C W, Duan H G, Sun Z W, Wang X M and Xie E Q 2008 *J. Alloys Compd.* **455** 497
- [31] Ito S, Murakami T N, Comte P, Liska P, Grätzel C, Nazeeruddin M K and Grätzel M 2008 *Thin Solid Films* **516** 4613
- [32] Bisquert J, Fabregat-Santiago F, Mora-Seró I, Garcia-Belmonte G and Gimenez S 2009 *J. Phys. Chem. C* **113** 17278