Enhanced efficiency and improved photocatalytic activity of 1 : 1 composite mixture of TiO₂ nanoparticles and nanotubes in dye-sensitized solar cell

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Abstract. TiO₂-based nanotubes (NTs), nanoparticles (NPs) and composite structural film (50% NP + 50% NT film) were synthesized by sol-gel hydrothermal process. Synthetic indigo dye was used as a sensitizer with the unique combination of electrolyte (EMII + BMII + PMII) and with cobalt sulphide as counter electrode. The structure and morphology of the three films, namely, NP, NT and NPNT is studied through X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The absorption spectra and incident photon-to-current conversion efficiency (IPCE) of the three films were compared and found to be higher for NPNT film. The efficiency and photocatalytic activity of three films were evaluated. The composite structure showed improved efficiency (1.72%) than NP (1%) and NT films (0.78%). The photocatalytic activity of the three films were measured using organic dye, methylene blue under UV light radiation. The composite structure showed higher dye absorption and higher rate of reaction with time. This paper certainly proves that there are many rooms to focus on the photoanode configuration, which plays a key role to improve the efficiency of dye-sensitized solar cell (DSSC).

Keywords. Composite mixture; nanoparticle; nanotube; photocatalytic activity; sol-gel process.

1. Introduction

Dye-sensitized solar cell (DSSE) has attracted great interest in academic research and in industrial applications owing to their high energy conversion efficiency and potentially low cost compared with traditional silicon solar cells (O'Regan and Grätzel 1991; Grätzel 2003; Grätzel 2004; El-Etre and Reda 2010). Although, there are many semiconducting metal oxides such as SnO₂, ZnO, CeO₂ and TiO₂, TiO₂ is widely used one in solar cell, because of faster electron injection ratio compared with other oxides (Priti Tiwana *et al* 2011). Intense research has been undertaken on the textural properties of nanocrystalline TiO₂ film, because they play key role in light harvesting in solar cells (Barbe *et al* 1997; Caruso *et al* 2001; Wang *et al* 2001). Photoanode is the most important part of DSSC, so investigations are carried out with great enthusiasm and with more excellent structure for improving the efficiency of DSSC (Law *et al* 2005; Patrocínio *et al* 2008). The current trend in DSSC is the fabrication of mesoporous TiO₂ films with high surface area to accommodate sufficiently more dye absorption as well as to facilitate transport of electrons and electrolyte in DSSC. The key parameter which determines the efficiency of

light harvesting in DSSC is the surface area of TiO₂ material and charge carrier transport in semiconductor electrode. Due to the recombination in TiO₂ semiconductor electrode, the collection of photo-injected electrons compete with recombination, so a high charge collection efficiency is required and that must be faster than recombination rate. In this sense, crystalline nanotubes (NTs) and nanowires (NWs) based on photoelectrode have been investigated to improve electron collection efficiency (Masuda *et al* 2000; Mor *et al* 2005; Zhu *et al* 2007; Weintraub *et al* 2009; Rodriguez-Reyes and Dorantes-Rosales 2011). The reported efficiency of pure TiO₂ nanotubes (TNTs) DSSC are much lower than pure TiO₂ nanoparticles (TNPs). DSSC amounting 2.61% for TNT and 5.2% for TNP (Mor *et al* 2006; Chen *et al* 2008). The main reason is internal surface area of NT-based photoanode is much smaller than that of NP-based photoanode resulting in lower dye absorption and lower photon absorption. But TNP can provide large surface area for dye loading but electron loss is huge, whereas TNT provides higher electron transport capability and stronger light scattering propagation (Imai *et al* 1999; Shankar *et al* 2007; Chen *et al* 2005; Zhu *et al* 2007). Therefore, the composite film of TNT and TNP (TNP + 50% TNT) can be applied as photoelectrode, which is expected to increase the electron collection efficiency, amount of dye

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loading, as well as to reduce the recombination rate (Yang *et al* 2010). Moreover, Ohsaki *et al* (2005) reported the electron lifetime of TNT is 3 times larger than TNP resulting in the improvement of diffusion length. Kuang *et al* (2007) showed template-assisted TNT enrolled 2.7% efficiency and TNT/TNP enrolled 3.2% efficiency.

We synthesized TNP and TNT by sol-gel hydrolysis. In our work, three kinds of films, TNP film, TNT film and TNP/TNT film were prepared by doctor blading technique. The photovoltaic performance and total energy conversion efficiency of these films were studied. The composite NPNT film showed enhanced charge transport. Here, we reported the performance of TNP/TNT DSSC as 1.72% and with TNP 1.00% and with pure TNT 0.78%.

2. Experimental

2.1 Materials

Titanium (IV) isopropoxide ($\text{Ti}(\text{OPr}^3)_4$) used was 99.9% pure liquid from Aldrich, solvents of 99.9% pure ethanol and isopropanol ($\text{C}_3\text{H}_7\text{OH}$) were all Aldrich products and used as supplied. Nitric acid, 10 M of NaOH aqueous solution, 0.1 M HCl were analytical grade. Synthetic indigo dye was purchased from Aldrich.

2.2 Instrumentation

The morphology and structure of synthesized TNT and TNP were characterized by using TEM, Jeol JEM 2100 resolution: 1.4 (lattice)–1.9 Å and X-ray diffraction (X'per PRO) using $\text{CuK}\alpha$ (2.2 kW max.) of $\lambda = 0.15406$ nm in the scan range of $2\theta = 10$ – 90° . The surface morphology of photoanode was characterized by scanning electron microscope (HITACHI model S-3000H). The absorption spectra of the TiO_2 electrode films were measured using a UV-Vis spectrometer (UV-Vis 8153). The UV-Visible absorption spectrum of dye was measured by Perkin Elmer spectrophotometer. QE7 solar cell spectral response system is used to measure IPCE of the electrode. The photocatalytic activity of the samples was investigated through methylene blue dye using UV light radiation. A solar simulator (Poloronoix, K201) furnished with 200W Xenon lamp is used to generate stimulated light of 1 Sun (100 mWcm^{-2}) for photovoltaic measurements of DSSC.

2.3 Preparation of TNP and TNT

The TiO_2 nanoparticle main layer was prepared using the sol-gel method. Nano- TiO_2 was synthesized using titanium (IV) isopropoxide (TTIP), nitric acid, ethyl alcohol and distilled water. The TTIP was mixed with ethanol, and distilled water was added drop by drop under vigorous stirring for 1 h. This solution was then peptized using nitric acid and heated under reflux at 80°C for 8 h. After this period, a TiO_2 sol was prepared. The prepared sol

was dried to yield a TiO_2 powder. This powder was calcined in air at 450°C for 1 h using a furnace to obtain the desired TiO_2 stoichiometry and crystallinity (TNP). TNTs were prepared by hydrothermal process. Five grams of TiO_2 particles prepared by the sol-gel method were mixed with 100 mL of 10 M NaOH aqueous solution, followed by hydrothermal treatment at 150°C in a Teflon-lined autoclave for 12 h. After the hydrothermal reaction, the treated powder was washed thoroughly with distilled water and 0.1 M HCl, subsequently filtered and dried at 80°C for 1 day. To achieve the desired TNT size and crystallinity, the powder was calcined in air at 450°C for 1 h (Fujishima *et al* 2000). The composite mixture film containing TNP + TNT, is also annealed at 450°C . The schematic representations of TNP and TNT are given in figure 1.

2.4 Preparation of photoanode

The indium tin oxide coated glass (ITO, NSG 2.2 mm in thickness), $14 \Omega/\text{square}$ (90% of transmittance in visible region) was cleaned ultrasonically in deionized water, acetone and ethanol for 10 min. The TiO_2 nanoparticles, composite mixture of (TNP + 50% TNT) and TiO_2 nanotubes were coated on ITO plate separately by doctor blading technique. For comparison, 3 photoanodes, one with TNP, other with TNT and third with TNP + TNT were fabricated and the performance was studied. The schematic representation of three photoanodes is shown in figure 2. The thicknesses of all the films were around $10 \mu\text{m}$. All the films were sintered at 500°C for 4 h, then soaked in 20 mM TiCl_4 aqueous solution at 80°C for 15 min and again sintered at 600°C for 30 min.

2.5 Assembly of DSSC

All the three TiO_2 photoelectrodes were immersed in a solution of synthetic indigo dye for 24 h at room temperature to get completely sensitized. The counter electrode cobalt sulphide, was synthesized by coating a drop of 0.35 mm of cobalt sulphide on previously treated ITO plate and heated at 500°C for 30 min. The dye-loaded TiO_2 electrodes (active area 4 cm^2) and counter electrode were assembled into a sealed cell with $50 \mu\text{m}$ thick Surlyn film as a polymer space and sealing agent under the condition of 110°C for 20 min. The electrolyte having the composition of 0.6 M of EMII (1-ethyl-3-methyl-imidazolium iodide), BMII (1-butyl-3-methyl-imidazolium iodide) and PMII (1-propyl-3-methyl-imidazolium iodide), 0.1 M LiI, 0.05 M I_2 in acetonitrile was injected into the cell through the drilled holes on the counter electrode. They were sealed up with a piece of transparent scotch tape.

3. Results and discussion

Figure 3 shows the XRD patterns of NP, NT and NPNT films after annealing at 450°C in air. The peaks of (1 0 1),

Figure 1. Schematic representation for synthesis of TNP and TNT.

Figure 2. Schematic representation of three different photo-electrodes.

Figure 3. XRD analysis of TNP, TNT and TNP/TNT annealed at 450 °C.

(0 0 4), (2 0 0), (1 0 5) and (2 1 1) are typical peaks of anatase TiO₂. From this figure, it could be noticed that the entire three films exhibit highly crystallized anatase

structure without any impurity phase. The crystallite size of TiO₂ nanocrystals, estimated from the full-width at half-maximum of the (1 0 1) peak using the Scherrer equation was 15 nm in diameter, which is in a good agreement with the particle size measured from corresponding SEM image (figure 5).

$$t = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Here λ is the X-ray wavelength used (0.1540 nm), β the broadening of the diffraction line measured as half of its maximum intensity (FWHM) and θ the corresponding Bragg angle.

Figure 4(a) shows the TEM image of the TiO₂ nanoparticles which is grown at 450 °C having uniform spherical structure and with mean diameter of ~15 nm. Figure 4(b) shows the TiO₂ nanotube products with an

average diameter of ~10 nm and the length of ~ (50–100) nm. TEM image shows the pure tube like uniform structure with width around 30–45 nm. No TiO₂ particles exist in this system. Figure 5(a) and (b) shows the SEM image of TiO₂ nanoparticles and TiO₂ nanotubes. Figure 6 shows TEM image of the composite mixture of TNP + 50% TNT in which the particles and tubes are in good adhesion. The spherical morphology of TiO₂ nanoparticles forms a good mechanical strength in which smaller nanoparticles merged and/or connected into larger nanoparticles and tubes. The layers consisting of spherical and tube-shaped particles can be distinguished both in the sketch and in the large-scale micrographs.

Figure 7 shows the absorption spectra of indigo dye, the dye is photochemically active in the UV and visible region. A wide range of photons can be absorbed in the range between 200 and 700 nm. When the dye is attached

Figure 4. TEM images of (a) TNP and (b) TNT.

Figure 5. SEM images of (a) TNP and (b) TNT.

Figure 6. TEM image of composite mixture TNP/TNT.

Figure 7. Absorption spectra of indigo dye.

to TiO₂ surface, the absorption spectra of dye is blue shifted more because of strong interactions between the dyes and the semiconductor surface (Fujishima *et al* 2000). For higher efficiency of DSSCs, the monolayer dye anchoring onto the TiO₂ surface is necessary. One can find the dye with small blue shift values.

The optical properties of the as-prepared TiO₂ nanoparticles, nanotubes and composite mixture were investigated by UV–Vis spectrum. Figure 8 shows the UV–Vis absorbance of the dye-adsorbed TiO₂ films. It can be seen in the figure, in the 250–500 nm wavelength range, the absorbance for the sample containing TNP/TNT was the highest, and the absorbance of the sample containing pure TNT was the lowest. According to Lambert–Beer's law, higher absorbance means a higher dye concentration; a suitable amount of TNT in the film could provide a large

Figure 8. Absorbance spectra of three photoanodes.

Figure 9. IPCE of three photoanodes.

surface area for dye adsorption. Therefore, the TiO₂ layer with the 50% of TNT serves as the active photolayer. It is well known that the photocurrent of a flexible DSSC is correlated directly with the number of dye molecules; the more dye molecules are adsorbed, the more incident light is harvested, and the larger is the photocurrent.

The incident photon-to-current conversion efficiency (IPCE) is defined as the ratio of the number of electrons in the external circuit produced by an incident photon at a given wavelength. In figure 9, the maximum efficiency at the wavelength of 450 nm is in coincidence with the absorption maximum wavelength of the dye. The IPCE peak height at 450 nm for TNP + TNT cell is 45.3%, which is much higher than 30% for TNP cell and 20.2% for TNT cell. Overall in the whole spectral region, TNP + TNT cell exhibits considerable higher IPCE value than

Figure 10. (a)–(d) Photocatalytic evaluation of (NP, NT and (NP + NT)) samples assisted by UV irradiation toward degradation of methylene blue dye.

Figure 11. Current–voltage characteristics of three photoanodes.

the other two samples. Based on the above experimental results and data analysis, the TNP + TNT cell exhibits a combination of the relatively large amount of dye adsorption, low transfer resistance and long electron lifetime and high incident photo-to-current conversion efficiency, and hence, possibly leading to enhanced J_{sc} in DSSCs.

3.1 Photocatalytic activity

The photocatalytic activity of the as-prepared TiO_2 samples can be evaluated by photo-induced degradation of organic dye (methylene blue). Methylene blue can be degraded by an oxidizing agent. But when the methylene blue solution was exposed to the air, the compound cannot be oxidized by dissolved oxygen in water. There was no reaction occurred even under UV irradiation. The concentration of the solution remained fairly constant. This shows that methylene blue is a highly stable

Table 1. Current–voltage characteristics of three different types of photoelectrodes.

Photoelectrode	V_{oc} (mV)	J_{sc} (mA/cm ²)	V_{max} (mV)	J_{max} (mA/cm ²)	FF	η (%)
DSSC-1 (100% NP)	630	9.1	500	8	69.77	1
DSSC-2 (100% NT)	650	6.8	550	5.7	70.93	0.78
DSSC-3 (50% NT + 50% NP)	680	12.8	600	11.5	79.27	1.72

compound. Figure 10 shows the photodegradation behaviours of TNP (B in figure), TNT (A in figure) and TNT + TNP (C in figure) towards 1×10^{-5} M methylene blue dye under UV light irradiation as a function of time. The photocatalytic efficiency was identified by the ratio of absorbance value at the characteristic peaks of dyes before and after photocatalytic reaction (C_0/C). For comparison, UV light was independently used for photodegradation of the selected dye without any TiO₂ particles (T_0 in the figure), and it was found that there was insignificant change in the concentration of dyes before and after being irradiated by UV rays. To evaluate the photocatalytic efficiency, the equation of $-\ln(C/C_0) = kt$ is used (Peng *et al* 2006; Priya and Madras 2006; Lu *et al* 2008; Yun *et al* 2010), where k is the rate constant used as the basic kinetic parameter for the different photocatalysts, and t is the reaction time. The photocatalytic oxidation of organic dyes roughly follows the pseudo-first-order reaction kinetics.

$$r = -\frac{dc}{dt} = kt. \quad (2)$$

Integrating (2) we obtain

$$\frac{\ln C_0}{C} = kt, \quad (3)$$

where C_0 is the initial concentration of MB, C the concentration of MB at irradiation time t , t the irradiation time and k the apparent pseudo-first-order rate constant. To degrade MB completely, C takes 180 min and decrease in concentration is higher when compared with A and B. The composite mixture shows higher photocatalytic efficiency than that of TNP and TNT in this study. This is due to higher surface area. The result may challenge the expectation that the surface area of photocatalyst is one of the most important factors in photocatalytic performance.

3.2 Current–voltage characteristics

The current density–voltage (J – V) characteristics based on the 3 different types of photoelectrodes (NP, NT and NP/NT) are summarized in figure 11 and table 1. The improved J_{sc} of the DSSCs 3 was attributed due to ultrafast and directional electron movement; curtail electron diffusion length and the light scattering effect. The electron transport takes place in three states, from nanoparticles to nanotubes L1, next along nanotubes L2 and

third from nanotubes to nanoparticles L3; the first and last travel distances are very small, so resistance R1 and R3 are also small. For NT/NP film due to large surface area and more scattering centres, more dye absorption is obtained. Such a behaviour in photocurrent density with NT/NP film thickness ratio was observed in previous reports as well (Tan and Wu 2006; Kao *et al* 2007; Zhu *et al* 2007a,b; Wu *et al* 2008). The decrease of light transmittance with NT film thickness was shown in report by Kao *et al* (2007). Our results are consistent with the previous reports (Zhu *et al* 2007a,b; Lin *et al* 2008), where similar dependences of J_{sc} and η on TiO₂ electrode thickness were observed. Although, TiO₂ NP meets the requirement of absorbing dye, it brings about, at the same time, many opportunities for the recombination of photo-injected electrons and the oxidized dye and/or the electron acceptors in the electrolyte. The TiO₂ electrodes such as NTs can enhance the light harvesting, straight pathway electron transport, and also have no serious light loss due to back scattering. Therefore, the design of the TiO₂ NT/NP film balances the surface area and the light scattering; thus, the performance of DSSC with TiO₂ NT/NP electrode is higher than those with NP or NT electrode

$$FF = \frac{I_m \times V_{max}}{J_{sc} \times V_{oc}}, \quad (4)$$

where FF is the fill factor, J_{sc} the short circuit current, V_{oc} the open circuit voltage, I_m the maximum current and V_{max} the maximum voltage

$$\eta = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}}. \quad (5)$$

4. Conclusions

The three photoanodes were prepared using sol–gel hydrothermal synthesis and the corresponding efficiencies and photocatalytic activities are measured. It is observed that DSSC made with composite mixture of NP and NT showed higher efficiency ($\sim 1.72\%$) compared to NP ($\sim 1.00\%$) and NT ($\sim 0.78\%$). Since the surface area of NPNT film is higher than NP and NT film, the dye absorption is higher which leads to high IPCE. Higher absorbance means a higher dye concentration; a suitable amount of TNT in the film could provide a large surface area for dye adsorption. Therefore, the TiO₂ layer with the 50% of TNT serves as the active photolayer. It is

hopeful that the composite structure electrode will play larger potential superiority compared to single structure electrode and can be extended to other composite structures for improving the efficiency of DSSC.

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