

Effect of Nano-TiO₂ Dispersion on PEO Polymer Electrolyte Property

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ABSTRACT: Polymer electrolyte membranes based on poly(ethylene oxide) (PEO) doped with TiO₂ nanoparticles were synthesized by simple solution cast technique. Mesoporous TiO₂ film was prepared by doctor-blade method. The modified polymer membranes and the mesoporous films were characterized by SEM, TEM, AFM, ionic conductivity, and J-V measurements. Dye-sensitized solar cells (DSSC) have been fabricated in which PEO-polymer electrolyte doped with and without nano-TiO₂ were sandwiched between porous TiO₂ and counter electrodes. The

DSSC with nano-TiO₂ doped polymer electrolyte shows better performance (1.68%) in comparison with pristine polymer electrolyte (1.07%), which is due to improved ionic conductivity value in polymer electrolyte system by nano-TiO₂ doping. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2976–2980, 2010

Key words: nanocomposite; nanoporous-TiO₂; polyelectrolyte; PEO-TiO₂; ionic conductivity; dye-sensitized solar cell

INTRODUCTION

In year 1991, Prof. Grätzel reported a new type of solar cell known as dye-sensitized solar cell (DSSC) with relatively better performance and cost effective in comparison with costly crystalline Si solar cell.^{1–3} The overall cell performance in a DSSC depends on many factors like nature of electrodes, dye, sensitizer, electrolyte, etc. The photoactive TiO₂ is commonly used electrode in solar cell. In last decades, porous TiO₂ film has been widely used as photoelectrode due to its high-specific surface area that allow the maximum adsorption of large dye molecules. As far as synthesis of photoelectrode is concerned, the doctor-blade method is frequently used as it gives uniform crack free film.^{1,2} For an efficient DSSC, electrolyte also plays an important role. The electrolyte with proper redox couple can influence the re-reduction of the oxidized state and electron transfer kinetics at the counter electrode.^{4,5} Also, it has influence on the formation of ion-pair with dye. The electrolytes reported in DSSC are solid as well as liquid. With liquid electrolyte, like volatile acetonitrile, the maximum reported efficiency is ~ 11% using I⁻/I₃⁻ redox couple. The significant problems

with liquid electrolytes are leakage, corrosion, evaporation of solvent, poor long-term stability, etc. These limitations restrict the large-scale production of DSSC. In last decade, the liquid electrolyte is replaced with solid electrolyte. The popular solid electrolytes are gel and polymer electrolytes.^{4,6–9} But, the polymer electrolytes are more attracted in science community due to its superiority over gel electrolytes. The gel electrolyte still retains a significant volume of liquid encapsulated in the pores, which gives a large increase in vapor pressure as the temperature is raised and therefore the sealing of such cells still remains a problem.¹⁰ PEO-based solid polymer electrolytes have shown its importance in DSSC. It has good mechanical stability, excellent complexation nature, presence of polar groups, and low T_g . These properties attracted most of the researchers in developing efficient DSSC.^{11–15} The main disadvantage is its low-ionic conductivity (σ) at ambient condition and it is associated with its high crystallinity. The popular alternate to reduce crystallinity are addition of inorganic additives and/or plasticizers.^{15–17} Doping plasticizers to reduce crystallinity is well-known phenomenon; addition of too much plasticizer reduces the mechanical properties of the film.¹⁷ For efficient DSSC, the concentration of additives should be optimum.

In the present study, we have reported the preparation and characterization of PEO-TiO₂ based nanocomposite polyelectrolyte system for DSSC applications. The added nanoparticles of titania (nano-TiO₂) powder (particle size <25 nm) into polymer

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electrolyte matrix (PEO : KI/I₂) have significant effect on the ionic conductivity.^{18,19} The structural and photoelectrochemical properties of the resulted composite polyelectrolyte are evaluated in details. The preparation of porous TiO₂ electrode using doctor-blade method for fabrication of DSSC is also presented. The performance of the fabricated DSSC have been compared with those without nano titania and the implications have been discussed.

EXPERIMENTAL

Development of polymer electrolyte films containing nano-TiO₂ powder

Poly (ethylene oxide) (PEO, $M_w = 1 \times 10^6$), potassium iodide (KI), iodine (I₂, 99.99%), nano-TiO₂ powder (TiO₂, particle size <25 nm) were purchased from Aldrich Chemical. All chemicals used in this study were dehydrated before use. As a first step, a viscous solution of PEO : KI/I₂ (75 : 25 : 2.5 wt %) complex was obtained using acetonitrile as solvent to which nano-TiO₂ of desired weight ratio were added. These resultant solutions were vigorously stirred at 50°C for ~ 5 h and the final viscous homogenous solutions were poured into polypropylene Petri dishes. The solvent was allowed to evaporate slowly and a solvent-free polymer salt complex film doped with nano-TiO₂ was obtained. These films were dried in ambient condition for about a week followed by vacuum drying to remove the traces of the solvent.

Fabrication of porous TiO₂ film and DSSC assembly

Opaque, thin-nanostructured TiO₂ film was prepared by doctor-blade technique on conductive glass substrates. In this method, first of all, a blocking layer of Ti (IV) bis (ethyl acetoacetato)-diisopropoxide solution (2 wt % in 1-butanol) was spread on FTO conducting glass (Pilkington, sheet resistance 30 Ω/cm²) surface by spin coating (1000 rpm at 30 s). The TiO₂ colloidal paste (Ti-nanooxide D, Solaronix) was then spread onto the conducting FTO glass substrate using doctor-blade and sintered at 500°C for 30 min, which give porous films of thickness ~ 10 μm. The thickness of this TiO₂ film was controlled by scotch tape having thickness ~ 50 μm. The porous TiO₂ film deposited onto FTO was sensitized overnight with dye solution in which 0.5 mM of 535 bis-TBA (Solaronix, Switzerland) dye was dissolved in distilled methanol while the Pt-counter electrode was prepared by spin-coating H₂PtCl₆ solution (0.05 mol dm⁻³ in isopropyl alcohol) onto the conductive glass and then sintering at 400°C for ~ 30 min. Finally, the polymer electrolytes (~ 400 μL) containing nano-TiO₂ and pristine polymer electrolytes were spread on the surface of the

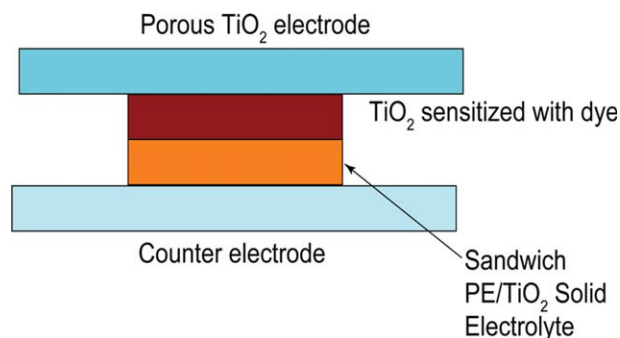


Figure 1 Preparation method of DSSC showing fabricated DSSC assembly. The polymer electrolyte (PE)-TiO₂ composite solid film is sandwiched between electrodes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sensitized TiO₂ electrode following two-step casting method as shown in Figure 1. In this method, first a dilute solution of electrolyte (~ 200 μL) was spread on porous sensitized TiO₂ electrode followed by remaining 200 μL concentrate solution (Fig. 1). The platinized SnO₂ counter electrode was pressed against the TiO₂ electrode. An external clamp was used to maintain the mechanical integrity of the DSSC. The fabricated DSSC assembly was vacuum-dried for 4 h and cell performances were evaluated without any special sealing. The active area of present cell was 0.25 cm².

Measurements

The surfaces features of porous TiO₂ film was observed using scanning electron microscopy (SEM, model JSM-5600 LV, JEOL, Japan) operated at an accelerating voltage of 10 kV. The morphology of TiO₂ nanoparticles was further investigated by transmission electron microscope (TEM, JEOL-4000EX) operating at 200 kV. For taking TEM micrographs, the TiO₂ film was scratched from the substrate and lifted on TEM-platinum grid. Atomic force microscopy (AFM) images of these films were obtained using multimode nanoscope IV (Digital Instruments, Canada) operated in tapping mode with a scan rate of 1 Hz. AFM images were recorded using phosphorous doped silicon (Si) tip with spring constant 28–80 N/m and having resonant frequencies between 262 and 307 kHz. To evaluate the ionic conductivity values of the polymer electrolyte films, we have used complex impedance spectroscopic technique. In this method, the polymer film was sandwiched between stainless steel die with an active area 3.14 cm². The ionic conductivities (σ) of these polymer films were obtained from bulk resistance by a.c. complex impedance analysis using a Solartron (SI 1287) interfaced with 1252A FRA and frequency range between 40 Hz and 40 KHz.

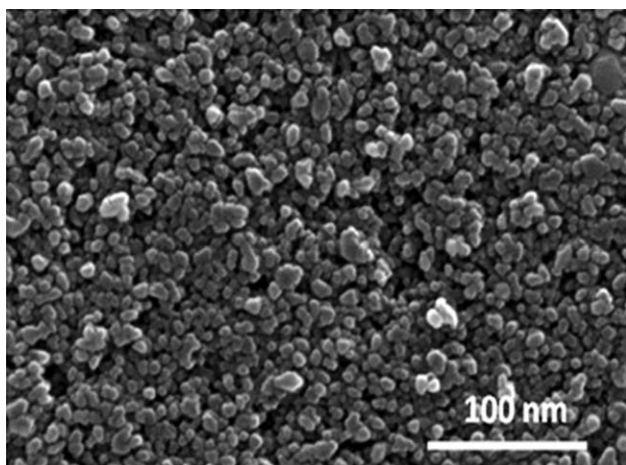


Figure 2 The top view scanning electron micrograph (SEM) of mesoporous TiO₂ film.

The photovoltaic tests of the DSSC were carried out by measuring the current density-voltage characteristics (J-V curve) at AM 1.5 illumination (100 mW cm⁻²) employing a source measure unit (Keithley Model 2400) equipped with 1000 W Xenon lamp (solar simulator model Oriel, 91193).

RESULTS AND DISCUSSIONS

In the present study, we successfully prepared the nanocomposite polyelectrolyte system by dispersing the nano-TiO₂ powder into the PEO matrix at room temperature. We observed there was no precipitation and/or phase separation of the either component during preparation. The polyelectrolyte system with different composition of dispersed nano-TiO₂ was prepared to optimize the optimum concentration of nano-TiO₂ to achieve the maximum DSSC performance. The optimization was carried out by measuring the conductivity of the system after fabrication of device as discussed in "Experimental" section with nanoporous TiO₂ film electrode. In the first step, the nano porous TiO₂ film electrode was prepared by doctor-blade method and detail characterized by SEM, TEM, and AFM

Surface profile of mesoporous TiO₂ film

SEM measurement

Figure 2 shows the SEM images of the mesoporous TiO₂ film. Surface morphology of film shows the interconnected TiO₂ nanoparticles with average particle size 25–30 nm. The particles are randomly oriented/distributed throughout the surface resulting very high surface area. Additionally, the film shows porous nature. The nanoporous TiO₂ film provides a large surface area for adsorption of photoactive molecules and good communication with the redox cou-

ple. Such a highly porous film was proven to greatly enhance the photo-to-current conversion efficiency of the dye-sensitized semiconductor solar cells. Some randomly distributed larger clusters could also be seen. These may be due to the agglomeration of the smaller particles. The surface is predominantly rough which has been quantitatively estimated by AFM and discussed below.

TEM measurement

Figure 3 shows the TEM micrograph of the mesoporous TiO₂ film scratched from the surface of FTO conducting glass. It is well known that anatase TiO₂ shows much better performance in DSSC in comparison with rutile TiO₂. The prevalent structures of the anatase nanoparticles of TiO₂ are square-bipyramidal, pseudocubic and stab like.^{1,2,5} In present case, we observed same shape/size particles of TiO₂ interconnected with each other. The average particle sizes are ~ 27 nm which is in good agreement with our SEM measurement.

AFM measurement

Figure 4 shows the two-dimensional AFM images of TiO₂ films taken under tapping mode. The observed particle-size distributions of TiO₂ were about 40–60 nm, which is much greater than the crystallite sizes calculated from the SEM or TEM results. The increase in the crystallite sizes of TiO₂ particles in AFM is due to the aggregation of the primary crystallites. It was also clear that the surface morphology of porous TiO₂ film shows rough nature with average roughness of 34.5 nm. Such a high roughness of TiO₂ adsorbs the large number of dye molecules as well as provide better wetting of polymer

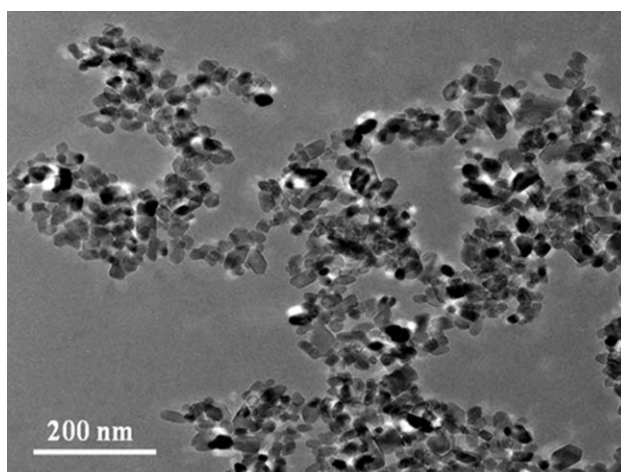


Figure 3 TEM photographs of porous TiO₂ film scratched from FTO conducting substrate.

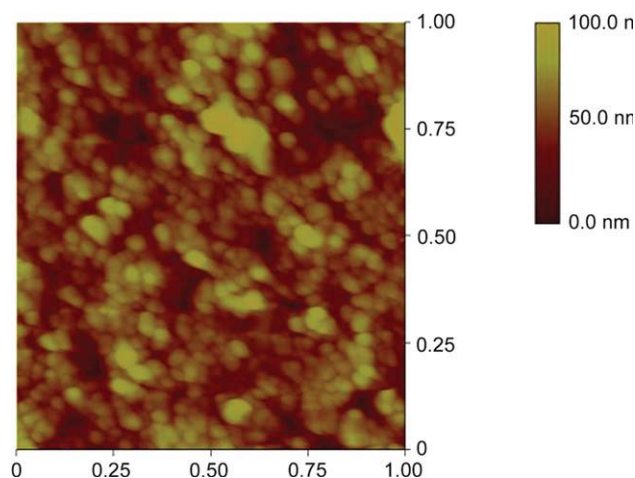


Figure 4 Two-dimensional AFM image of mesoporous TiO₂ film deposited onto the surface of FTO substrate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

electrolyte, which may enhance overall DSSC performance.¹⁵

Effect of nano-TiO₂ dispersion on the ionic conductivity of polymer electrolyte films

The ionic conductivity (σ) was evaluated from the complex impedance plots and using the relation $\sigma = G \times l/A$, where l and A are the thickness and area of prepared polymer film and G is the conductance value of sample ($G = 1/R$). The value of bulk resistance (R) is obtained from the first intercept on the real-axis of the impedance data in the complex impedance plot. The calculated values of ionic conductivities are presented in Figure 5 against the amount of titania dispersed in the polymer matrix. It is clear that conductivity of the polymer electrolytes with nano-TiO₂ dispersoid is always greater than the host polymer (PEO : KI/I₂). The addition of nano-TiO₂ in

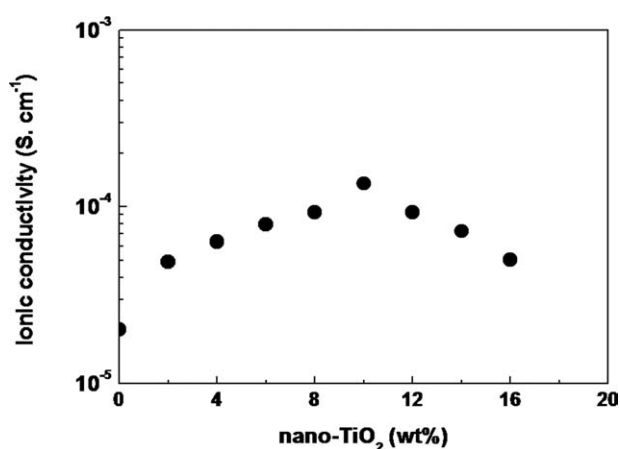


Figure 5 The ionic conductivity versus composition plot in nano-TiO₂ doped PEO : KI/I₂ solid polymer electrolyte system.

polymer electrolyte matrix increases the ionic conductivity and it attains a maxima at 10 wt %, where σ value is $1.35 \times 10^{-4} \text{ S cm}^{-1}$ and then decreases.

For a heterogeneous or nanostructured system, ionic conductivity is contributed from both bulk and interfacial transport. This enhancement in conductivity is similar to the conductivity enhancement reported in literatures for polymer-solid composite electrolyte systems.^{18–21} The filler particles, because of their large surface area, prevent the recrystallization of PEO and increase its amorphicity, which is suitable for DSSC application.^{22,23} Thus the regions permitting the ions to migrate gets enhanced and hence the conductivity. Additionally, the highly charged surfaces of the particles also add up as the conductive path. At a particular concentration of such segments, the paths link up and the percolation threshold is achieved. In our case, the threshold is obtained for x wt % for which maximum conductivity is obtained. As shown in Figure 5, it is clear that the conductivity of our polymer electrolyte film with 10 wt % nano-TiO₂ is maximum and hence this film has been chosen in present DSSC application.

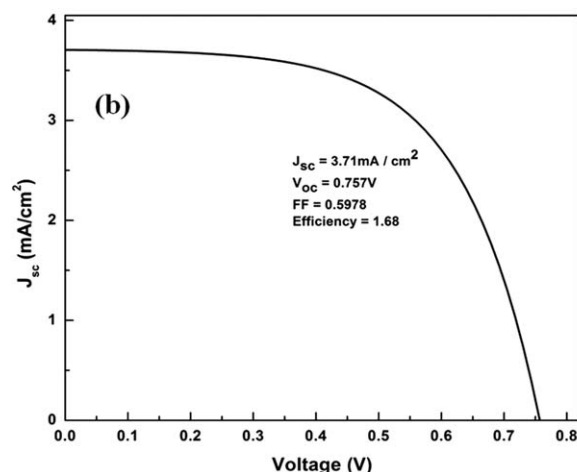
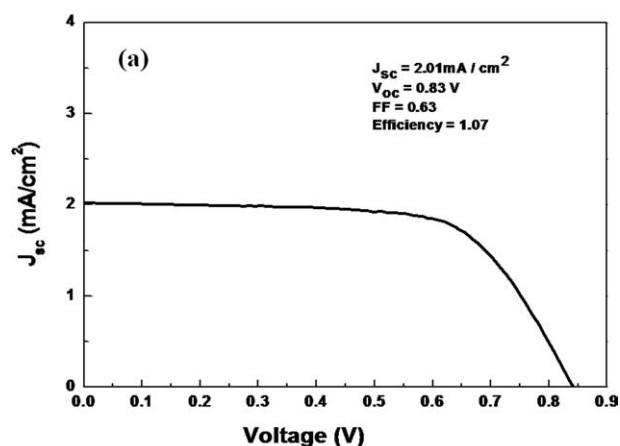


Figure 6 Photovoltaic curves (J - V) of the DSSC with (a) PEO : KI/I₂ and (b) PEO : KI/I₂ + 10 wt % nano-TiO₂ solid polymer electrolyte at 100 mW cm^{-2} light intensity.

Effect of nano-TiO₂ dispersion on the DSSC performance

Figure 6 shows the DSSC performance of polymer electrolyte with and without nano-TiO₂. It is clear that polymer electrolyte film without nano-TiO₂ [Fig. 6(a)] shows efficiency of 1.07% while the polymer electrolyte film containing 10 wt % nano-TiO₂ shows [Fig. 6(b)] improved efficiency of 1.68%. This enhancement in efficiency is possible since σ of nano-TiO₂ doped polymer electrolyte film is greater (1 order of magnitude) than without nano-TiO₂ dispersed film. Additionally, dispersion of nano-TiO₂ provide more amorphous matrix (more conductivity) in which I⁻/I₃⁻ can easily move and penetrate inside the voids of nano-TiO₂ and shows better efficiency.^{22,23}

CONCLUSIONS

The optimization of PEO-polymer electrolyte (PEO : KI/I₂) was achieved by the addition of nano-TiO₂ particles. The ionic conductivity of the polymer electrolytes was improved by the incorporation of nano-TiO₂ and the maximum 1.35×10^{-4} S cm⁻¹ conductivity observed at 10 wt % nano-TiO₂ concentration. A mesoporous TiO₂ film has been successfully developed for DSSC application using doctor-blade method. The DSSC with nano-TiO₂ doped polymer electrolyte (maximum σ) shows improved efficiency of 1.68% in comparison with DSSC without nano-TiO₂ (1.07%). This improvement in efficiency is due to better ionic conductivity value of polymer electrolyte with nano-TiO₂ dispersion.

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