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Application of mesoporous anataseTiO₂ microspheres for dye sensitized solar cell on flexible titanium metal photo anode

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ABSTRACT

In the preset study dye-sensitized solar cells (DSSC) have been fabricated on a flexible titanium metal foil substrate with mesoporous anatase Titania microsphers (TMS) as the electron transport layer for photo anode. These microspheres perform dual function of light scattering and efficient dye absorption. A light to electricity conversion efficiency of 2.93% is achieved with illumination through the counter electrode. Additionally electrochemical impedance spectroscopy (EIS) is used to analyze the electron transport processes occurring at the various interfaces. Copyright © 2013 VBRI press.

Keywords: Dye sensitized solar cell; titanium foil; titania microspheres.



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Introduction

Dye-sensitized solar cells (DSSCs) have been investigated extensively due to their advantages of low cost, easy scale-up and use of flexible panels compared with silicon solar cells [1–5]. DSSCs consist of a fluorine-doped tin oxide electrode (FTO) coated with a film of titanium dioxide, a sensitizing dye, an electrolyte and a counter electrode. When a light photon is absorbed by a dye molecule, the electrons are excited from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. The excited electron is injected into the conduction band of the TiO₂ film, and the oxidized dye is reduced back by a redox species in the electrolyte. The oxidized form of the redox species is converted back to the reduced state by gaining electrons at the counter electrode via the external electronic circuit.

Now days, light-weight flexible DSSCs have attracted attention because of their applications in powering mobile devices. The FTO glass substrate has been replaced by the light weight substrates that can be categorized into polymer substrate such as polyethylene naphthalate coated with indium-doped tin oxide (ITO/PEN) and metal foil substrate such as titanium or stainless steel [6-8]. Polymer substrate cannot be heated above a certain temperature. Ti is an appropriate choice as far as the stability is concerned because of its surface oxidation to TiO₂, which is compatible with DSSCs. Additionally the recombination

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from TiO₂ surface to the electrolyte is significantly lesser than that from FTO [9-10]. In fact, TiO₂ is commonly used as recombination blocking layer on other substrates and it improves the cell performance especially at low light intensities [11-13].

Recently TiO₂ microspheres composed of nanoparticles have become attractive for high efficiency DSSCs on glass substrate [14]. These are promising photo anode material alternatives to the traditional randomly assembled nano particles [15]. The primary building blocks comprising the microspheres provide a high surface area for dye adsorption when used for assembling photo anodes. Secondary construction units of sub micrometer microspheres provide the photo anode with a strong light scattering ability, potentially overcoming the intrinsic weak absorption of Ru–complex dye sensitizers in the near–infrared region [14, 16].

In the present study, DSSCs are assembled using flexible photo anodes of Ti/TMS. As the cells are illuminated through the counter electrode, the conversion efficiency is expected to be low due to the light absorption by electrolyte species and the light reflection by platinum film in the counter electrode [17, 7]. Grätzel and coworkers reported a 4% difference in efficiency between front and back side illuminated cells [7]. Therefore it is imperative that the photo anode material should have high surface area which imparts maximum dye absorption, good electron transport and light scattering ability. To achieve a high efficiency, TMS are used as the photo anode material on flexible Ti substrate and it is fabricated by simple doctor blade technique. The thickness of TMS layer is optimized to achieve the highest efficiency and it is compared with cells made of nano particles. Furthermore, to see the effect of backside illumination, cells made on glass substrate are studied for front and backside illumination and compared with cells made on Ti substrate. Electrochemical impedance spectroscopy (EIS) is used as a diagnostic tool to quantitatively evaluate the photovoltaic parameters of DSSCs on flexible photo anode, since EIS has been widely employed to study photo electrochemical processes occurring in DSSCs [18].

Experimental

Materials

All chemicals, titanium (IV) isopropoxide (TIP, 97%, Sigma-Aldrich), hexadecylamine (HDA, 90%, Sigma-Aldrich), absolute ethanol (>99.7% Merck), potassium chloride (AR, Oxford Laboratory), ammonia solution (25%, SDFCL), titanium foil (Sigma Aldrich, 0.25mm thickness, 99.7% trace metal basis), cis-bis (isothiocyanato) bis(2,20bipyridyl-4,40-dicarboxylato) ruthenium(II) bistetrabutyl ammonium, (N719 dye), platisol, surlyn (all from Solaronix) acetonitrile (99%, SDFCL) triton X100(SDFCL), 1-methyl propyl imidazolium iodide, lithium iodide, iodine, tert-butyl pyridine (all from Sigma Aldrich) and tertbutanol(99.0%, SDFCL) were used as received. Deionised water (14.2 M Ω cm) was used for preparation of solutions.

Synthesis of TMS

TMS were synthesized using the procedure reported [14]. Briefly, amorphous TMS were synthesized by a sol gel method in the presence of HDA dissolved in ethanol, titanium iso propoxide as the TiO₂ precursor. In order to obtain the mesoporous TMS with a highly crystalline framework, a hydro-thermal process was used. About1.6 g of the air dried amorphous TMS were dispersed into a mixture of ethanol and de-ionized water (2:1 ratio), followed by the addition of 1ml, 25% ammonia solution. The mixture was sealed within a Teflon-lined autoclave (50 ml) and heated at 160 °C for 16 h. The solid product was collected by filtration, washed with ethanol and dried in air at room temperature.

Fabrication of photo anode

To prepare the DSSC photo anodes, 1.5 g of the TMS was first dispersed in a mixture of 10 ml ethanol and sonicated for 30 min to form slurry. A drop of Triton X100 surfactant was added and again sonicated for 5 min. A titanium foil substrate (2 x 2 cm²) was washed with a detergent solution and ethanol in ultrasonic bath and then coated with the TMS slurry using doctor blade technique. The coated electrode was allowed to dry at room temperature and heated to 350 °C for 0.5 h and allowed to cool to room temperature. The coating, heating and cooling cycle was repeated to get the desired thickness. In addition, all the electrodes were treated with TiCl₄ solution (0.1 M in ice cooled water) followed by annealing at 500 °C [19].

DSSC fabrication

The electrodes were cooled to 80 °C and sensitized with N719 dye by soaking in a 0.5mM solution in acetonitrile/tert-butanol(v/v, 1:1) for 24 h. The sensitized films were rinsed with ethanol to remove excess dye remaining on the surface and then air-dried at room temperature. For the preparation of counter electrodes, a platinum catalyst was painted on FTO glass substrates (2 cm * 2 cm) and fired at 400°C for 30 min. This procedure provided a quasi-transparent activated platinum layer on FTO glass and reduced the over potential for iodide / triiodide redox couple. The electrolyte contained 0.6 M 1methyl propyl imidazolium iodide, 0.1M lithium iodide, 0.05M iodine and 0.5M tert-butyl pyridine in acetonitrile. The dye-covered TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell using surlyn polymer foil as the spacer. The gap between the electrodes was filled with the electrolyte. For comparison, DSSCs were made with TMS coated glass substrate in place of flexible Ti substrate.

Characterization and measurements

The crystalline phases of the TMS were determined by X-ray powder diffraction (Bruker D8 Advance diffractometer) by using Cu K α radiation. The morphologies of the samples were studied by a field emission scanning electron microscope (FESEM; SIRION). Micro structure was examined using transmission electron microscope and high-resolution transmission electron microscope (TEM

and HRTEM; TECHNAI F30). The thickness of TiO_2 coatings was measured using Dektak-150 surface profilometer. Nitrogen adsorption – desorption isotherms were measured at -196 $^{\circ}$ C using Micromeritics surface area analyzer ASAP 2020. The standard multi-points Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area. The pore size distributions of the materials were derived from the adsorption branches of the isotherms based on the Barett–Joyner–Halenda (BJH) model.

Photocurrent measurements of the cells were performed with a Keithley model 2420 source meter under illumination (AM1.5, 100mW/cm²) using a solar simulator (Newport Class 3A). The electrochemical impedance spectra (EIS) were recorded using an impedance analyzer (Solartron Analytical, 1255B) connected with a potentiostat (Solartron Analytical, 1287) under illumination. EIS spectra were recorded over a frequency range of 0.1-100 kHz at 298 K. The applied bias voltage and ac amplitude were set at open circuit voltage (Voc) of the DSSCs and 10 mV, respectively. The electrochemical impedance spectra were analyzed using Z-View software (Solartron Analytical).

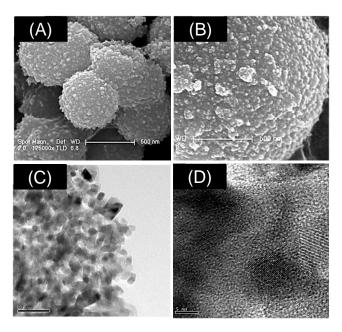


Fig. 1. Scanning electron microscope image of TiO_2 microspheres synthesized by combined sol gel and solvo thermal method (A) magnified image of one of the spheres showing the nano particles (B) TEM image of the TMS (C) HRTEM image shows the inter particle growth (D).

Results and discussion

Structural analysis of TMS

The titania microspheres self-assembly is achieved by the presence of hexadecylamene (HDA) as a structure-directing agent in the sol gel method. The hydrothermal treatment in presence of ammonia decides the porosity, crystallite size and surface area of the sol-gel synthesized spheres. The detailed formation mechanism of these self-assembled mesoporous material is described in the literature [20].

Fig. 1 (A) and (B) illustrate the morphology of the as prepared TMS. The size of these spheres ranges from 400-800 nm with a rough surface consisting of nano particles. Since their size is comparable to wavelength of visible light they have the ability to scatter light, which is essential to get high efficiency DSSCs. The TEM and HRTEM images clearly show that the spheres are made of densely packed nano crystals with a size varying from 12-15nm. Also the nanoparticles have multiple contacts with neighboring grains which is expected to reduce the grain boundary effects for electron transport [14].

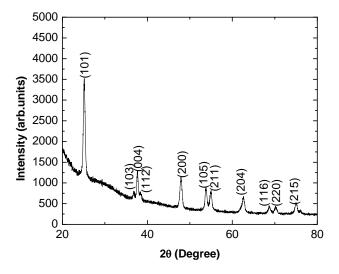


Fig. 2. XRD pattern of TiO₂ microspheres.

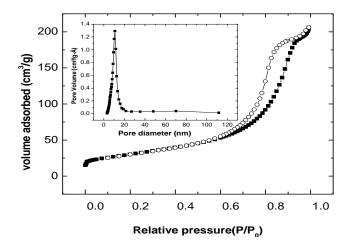


Fig. 3. Nitrogen absorption- desorption isotherms for TiO_2 microspheres. Inset shows the pore size distribution.

Fig. 2 shows the XRD pattern of TMS. All peaks correspond to anatase tetragonal phase of TiO_2 are observed and the pattern agrees well with the standard pattern reported (JCPDS file No. 21-1272). There is no impurity peaks, indicating a high purity of the TMS prepared in the present study. The specific surface area and pore size distribution is measured from nitrogen absorption- desorption isotherm and the results are shown in **Fig. 3**. There is a hysteresis in adsorption-desorption isotherm at relatively high partial pressures indicating porous nature of the sample. The BET surface area of 108

 m^2/g is obtained from the adsorption isotherm which is almost double that of P25 TiO₂. From BJH curves a pore diameter of 12 nm is obtained. Thus the high surface area enhances the dye loading capability of these TMS and the porous nature aids in electrolyte penetration.

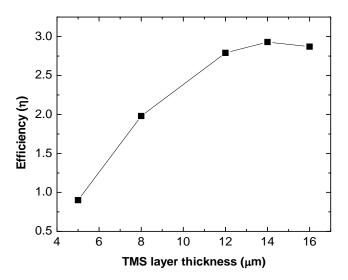


Fig. 4. Variation of efficiency with TiO₂ microsphere layer thickness for reverse illuminated DSSC on flexible Ti substrate.

Table 1. Summary of the photovoltaic properties of different DSSCs fabricated in the present study.

Thickness	V _{oc} (V)	FF	J _{sc}	Efficiency
			(mA cm ⁻²)	(%)
5	0.608	49	3.02	0.90
8	0.640	52.6	5.87	1.98
12	0.658	54.6	7.74	2.79
14	0.653	54.4	8.26	2.93
16	0.645	55.6	8.01	2.87
P25 TiO ₂	0.656	49.5	4.14	1.35

I-V characteristics

The performance of the cells was characterized by measuring the current-voltage curves under 100 mW/cm^2 . **Fig. 4** and **Table 1** show the variation of power conversion efficiency with TMS layer thickness for reverse illuminated DSSC on flexible Ti. The overall conversion efficiency η of the photovoltaic cell is calculated from the integral photocurrent density (J_{SC}), the open-circuit photo voltage (V_{OC}), the fill factor of the cell (ff), and the intensity of the incident light (I_{Ph}),

$$\eta = (J_{sc} * V_{oc} * FF) / I_{Ph}$$

where FF is defined as (voltage at the maximum power point * current at the maximum power point)/(J_{sc} * V_{oc}) [21]. In case of reverse illuminated cells, optimization of thickness is very important. If the thickness is too high it unnecessarily increase the length of electron pathways, and thus decrease V_{oc} and FF. As shown in **Fig. 4** maximum efficiency of 2.93% is obtained at a thickness of $14\mu m$ and further increasing the thickness does not improve the

efficiency. In fact the conversion efficiency gets saturated around $12-16 \mu m$ thickness.

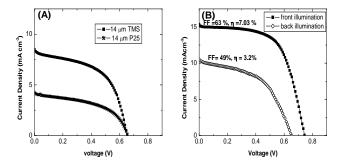


Fig. 5. (A) J-V characteristics of DSSC made on flexible Ti with $14\mu m$ thick TMS layer under $1 \, Sun(100 \, mW/cm^2)$ along with that of P25 TiO₂ nano particles on Ti substrate and (B) J-V characteristics of DSSC on glass substrate with front and back side illumination.

Fig. 5 (A) shows the J-V characteristics of high efficiency cell. For comparison DSSC made of P25 nanoparticles of similar thickness have been made on Ti substrate and it provided an efficiency of 1.35 %, which is 55 % lower compared to TMS based cells. Although the voltage is comparable to microsphere based DSSCs, the current density is halved, indicating the superiority of TMS for reverse illuminated DSSC. To see the effect of substrate, DSSCs were fabricated on glass substrate using TMS and the J-V characteristics for the same are shown in **Fig. 5** (**B**) for front and back side illumination. With front side illumination the photovoltaic parameters are V_{OC}; 0.75 V, J_{SC} ; 15.6 mA/ cm², FF; 0.63 and η ; 7.03%, whereas with back-side illumination the corresponding values are 0.66 V, 10.1 mA/ cm², 0.49, 3.2% respectively. These data indicate that backside illumination for glass DSSC has caused a reduction of about 50% in the total efficiency due to the absorption of a partial amount of light by the electrolyte as well as the light reflection by the counter electrode. The n values of both glass and Ti based DSSCs with back illumination are nearly the same. Also the fill factor for DSSC on titanium substrate is high compared to glass based cell illuminated through counter electrode which may be due to the lower sheet resistance of Ti foil compared to FTO glass as pointed out by Kinji et.al [22]. This quality makes titanium a good candidate for large area flexible cell fabrication.

EIS analysis

Further we have employed EIS to study the electron transport properties of these cells. Two semicircles, including a small one at high frequency and a large semicircle at low frequency, were observed in the Nyquist plots of EIS spectra (**Fig. 6** (**A**)). The one at high frequency is assigned to electrochemical reaction at the platinum electrode, and the larger one at low frequency is attributed to charge transfer reactions at the TiO_2 /dye/electrolyte interface [23-24]. These data were analyzed with a nonlinear least squares fitting program using Z view software. From the high frequency arc it is clear that the impedance of electron transfer at the platinum counter electrode is high for solution deposited transparent platinum and the values is being 45 Ω . The high impedance

implies an inferior catalytic activity of counter electrode. As a result the reduction of I₃ ions decreases, leading the electrolyte to be rich in I₃- ions. Consequently the conduction band electrons have to encounter a much higher resistance to reach the external circuit. This is obvious from the shape of the second semicircle. It is slightly deviating from a true semicircle, which is an indication of the existence of a higher transport resistance [25]. Also according to bode phase plot (Fig. 6 (B)) the electron life time can be extracted as $\tau = \frac{1}{2\pi f}$, where f is the peak frequency of the low frequency arc, which is having a value of 11Hz. Thus the electron life time is found to be 14.4 ms. The low value of electron life time indicates the increased probability of recombination of generated electrons back to the electrolyte. As a consequence of the existence of a higher transport resistance along with a low electron life time the dark current enhanced which leads to lower conversion efficiency. Hence additional precautions are essential to reduce the leakage current.

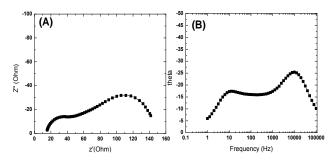


Fig. 6. (A) Nyquist plot of DSSC made of $14\mu m$ layer thickness of TMS on flexible titanium photo anode and (B) Bode plot.

We feel that in the present study the large size of TMS might have caused the exposure of titanium substrate directly to the electrolyte, which is rich with electron acceptors. Hence we focus on the optimization of electrolyte components and the use of a compact layer made of nanoparticles of TiO₂ to improve the efficiency still further.

Conclusion

In summary we have fabricated DSSCs on Ti metal foil substrate using TiO_2 microspheres as the supporting matrix for dye absorption. A solar to electricity conversion efficiency of 2.93% is obtained which is almost 54% higher compared to cells is made of P25 TiO_2 nano particles. EIS spectroscopy analysis has revealed a higher charge transport resistance and lower electron life time in these cells, leading to the leakage of photo current. Therefore further optimization is underway to increase the efficiency by the reduction of the leakage current in TMS based flexible dye solar cell.

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