Available online at www.sciencedirect.com
SCIENCE DIRECT
Synthetic Metals 155 (2005) 635–638
SYNTHETIC METALS
www.elsevier.com/locate/synmet

Enhancement of the photocurrent generation in dye-sensitized solar cell based on electrospun TiO_2 electrode by surface treatment☆

Mi Yeon Song [a], Do Kyun Kim [b], Seong Mu Jo [b], Dong Young Kim [a,*]

[a] *Optoelectronic Materials Research Center, Korea Institute of Science and Technology, Seoul 130-650, Republic of Korea*
[b] *Polymer Hybrid Research Center, Korea Institute of Science and Technology, Seoul 130-650, Republic of Korea*

Received 28 June 2004; received in revised form 2 February 2005; accepted 15 August 2005
Available online 7 November 2005

Abstract

We investigated the dye-sensitized solar cell (DSSC) using TiO_2 electrode electrospun directly onto the substrate from a mixture of titanium propoxide and poly(vinyl acetate) in dimethyl formamide (DMF). The electrospun electrode could be penetrated efficiently by a viscous polymer gel electrolyte because of porous structure. The energy conversion efficiency obtained from the DSSC with poly(vinylidenefluoride-*co*-hexafluoropropylene) (PVDF-HFP) gel electrolyte was over 90% of that obtained from liquid electrolyte. In order to improve the short-circuit photocurrent, we treated the electrospun TiO_2 electrode with $TiCl_4$ aqueous solution. The rutile crystal was grown epitaxially on anatase TiO_2 fibers. An additional TiO_2 layer increased the volume fraction of active materials resulting in an increase of sensitizer adsorption. The incident photon-to-current conversion efficiency (IPCE) of $TiCl_4$-treated electrode was higher than the untreated. In particular, the contribution from TiO_2 increases after the surface treatment due to an increase in packing density. The photocurrent of the DSSC with electrospun TiO_2 electrode was enhanced more than 30% after $TiCl_4$ treatment.

Keywords: Electrospinning; Titanium dioxide; Nanofibers; Dye-sensitized solar cell; Gel electrolyte

1. Introduction

The electrochemical photovoltaics have been studied using wide-bandgap semiconductors, such as TiO_2, ZnO, Nb_2O_5, SnO_2, etc. [1–3]. In 1991, Grätzel and co-worker [4] reported the dye-sensitized solar cell (DSSC) using nanocrystalline TiO_2 particles which increased the surface area several hundred times compared to those in compact semiconductor and electrolyte interfaces. The energy conversion efficiency of DSSC reaches over 10%, which is comparable to that of the silicon based solar cell [5]. In organic/inorganic hybrid solar cells, nanorods [6] and nanotubes [7] have been investigated as new electrode materials with a higher degree of order than the random assembly of nanoparticles. Recently, the electrospinning technique has been developed, which provides a simple, cost-effective approach for producing nanofibers within a broad range of diameters, from tens of nanometers to a few micrometers according to the selection of the processing parameters [8–10]. We demonstrated the porous electrode structure based on electrospun TiO_2 nanofibers, in which the energy conversion efficiency, the photocurrent generation with polymer gel electrolyte, was over 90% of the performance in DSSC with liquid electrolyte [11]. However, the volume content of TiO_2 in nanofiber web electrode is still low to maximize the photocurrent generation. In this study, the electrospun TiO_2 nanofibers are treated chemically to increase the TiO_2 volume content by using epitaxial growth of TiO_2 rutile crystal from aqueous $TiCl_4$ solution. The additional rutile layer modified the photocurrent generation of DSSC based on electrospun TiO_2 electrode. The energy conversion efficiency increases 30% after post-treatment.

2. Experimental

TiO_2 fibers were electrospun directly onto a SnO_2:F-coated glass substrate (FTO, 10 cm × 10 cm, TEC-15, Pilkingotn) from mixture containing 3 g poly(vinyl acetate) (PVAc,

☆ Based on presentation at the International Conference on Synthetic Metals, Wollongong, Australia, June 28–July 2, 2004 (ICSM 2004).

* Corresponding author. Tel.: +82 2 958 5323; fax: +82 2 958 5309.
E-mail address: dykim@kist.re.kr (D.Y. Kim).

0379-6779/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2005.08.018

M_W = 850,000 g/mol), 6 g titanium(IV) propoxide (TiP) (Aldrich) and 2.4 g of acetic acid as a catalyst for sol–gel reaction in dimethyl formamide (DMF) (37.5 mL). In a typical electrospinning, the precursor solution was loaded into a syringe connected to a high-voltage power supply (Bertan Model 230). An electric field of 15 kV was applied between a metal orifice and the FTO substrate at a distance of 10 cm. The spinning rate was controlled by a syringe pump (KD Scientific Model 220) at 60 μL/min. Electrospun TiO_2 web was treated with tetrahydrofuran (THF) vapor in a closed chamber for 1 h prior to calcination. The calcination was carried out stepwise at each temperature (duration in min) as: 100 °C (15); 150 °C (15); 325 °C (5); 450 °C (30 min) in air.

To grow TiO_2 rutile crystal epitaxially, TiO_2 web plate was immersed into a 0.1 M titanium tetrachloride ($TiCl_4$) (Aldrich) aqueous solution in a closed chamber for 24 h. The 0.1 M $TiCl_4$ aqueous solution was prepared in the following manner. Firstly, 2 M concentrated $TiCl_4$ solution was prepared by adding directly titanium tetrachloride into a flask containing ice and then, the solution was further diluted to 0.1 M.

The TiO_2 web electrode was immersed overnight in an ethanolic solution containing 3×10^{-4} M of ruthenium dye, $RuL_2(NCS)_2$ (L = 2,2′-bipyridyl-4,4′-dicarboxylic acid) (N3, Solaronix). The electrode was rinsed and dried after its removal from the dye solution. The liquid electrolyte we used consisted of 0.6 M 1-hexyl-2,3-dimethyl-imidazolium iodide (C6DMIm), 0.05 M iodine (I_2), 0.1 M lithium iodide (LiI) and 0.5 M 4-*tert*-butylpyridine dissolved in 3-methoxyacetonitrile. Pt-sputtered SnO_2:F glass was used as the counter electrode. A dye-sensitized solar cell containing a polymer gel electrolyte was characterized; this electrolyte consisted of poly(vinylidenefluoride-*co*-hexafluoropropylene) (PVDF-HFP) (Kynar 2801, 0.13 g), C6DMIm (0.13 g) and I_2 (0.008 g) in propylene carbonate (PC) (0.75 g) and ethylene carbonate (EC) (0.5 g). The typical active area of DSSC was 0.16 cm^2. The photocurrent–voltage characteristics were measured with Keithley 2400 SMU under the global AM1.5, 100 mW/cm^2 irradiation. The incident photon-to-current conversion efficiency (IPCE) was measured using a 350 W Xe lamp light source with a motorized monochromator. Incident light intensity was calibrated using a Newport 818UV photodiode detector. The electrochemical impedance spectra (EIS) were obtained by Solatron FRA 1260 with EG&G PARC Potentiostat/Galvanostat Model 273 with an ac amplitude of 10 mV at the open-circuit voltage (V_{oc}) under illumination.

3. Results and discussion

Nanoporous electrospun TiO_2 electrodes improve the penetration of polymer gel electrolyte effectively. Electrospun TiO_2 web for DSSC in this work shows the well-organized porous electrode structure as shown in Fig. 1a after calcination at 450 °C in air removing PVAc from the as-spun fibers. Several studies have previously reported that treatment of nanocrystalline TiO_2 with $TiCl_4$ solution. Results in a significant improvement in device performance [12]. The nanocrystalline TiO_2 electrode with $TiCl_4$ treatment increased the necking between the nanoparticles of the film, thus, facilitating the

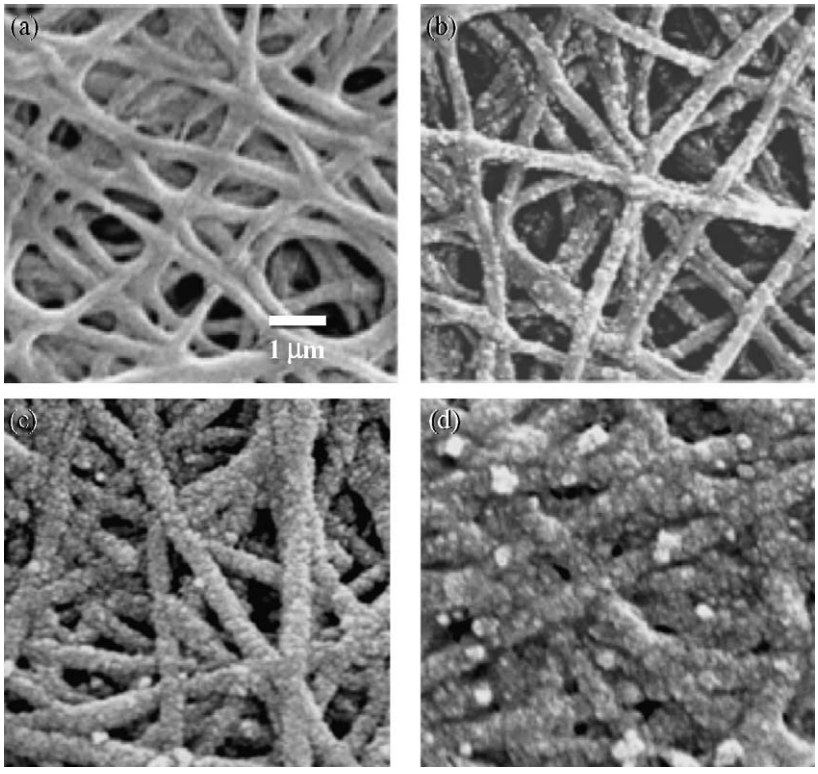

Fig. 1. Scanning electron microscopy (SEM) images of electrospun TiO_2 nanofiber electrodes after $TiCl_4$ aqueous solution treatment for 24 h at different temperatures: (a) without treatment; (b) 20 °C; (c) 40 °C; (d) 60 °C.