Electrospun TiO2 Electrodes for Quasi-Solid State Dye-sensitizedSolar Cell

Mi Yeon Song[1], Young Rack Ahn[1,2], Seong Mu Jo[1], Dong Young Kim[1]*

[1]Optoelectronic Materials Research Center, Korea Institute of Science and Technology, P.O. Box 131 Cheongryang, Seoul 136-791, Korea
[2] School of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea
dykim@kist.re.kr

Introduction

Nanostructured metal oxides have attracted much attention due to their physical properties and dimensionality [1]. In particular, titania nano-materials have been widely investigated for use in applications such as solar cells [2], photocatalysts [3], and gas sensors [4]. Several methods for fabricating one-dimensional (1-D) structured TiO_2 have recently been reported, including template methods [5-6] and surfactant-assisted self-assembling processes [7-8]. Strong alkali treatment has also been found to produce TiO_2 nanotubes [9].

An alternative approach to fabricating 1-D TiO_2 materials is to use an electrospinning method, in which TiO_2 electrodes can be formed directly on various substrates over large areas. The electrospinning process has been widely used in many fields since it was invented by Formhals in 1934 [10]. The electrospinning technique provides a simple, cost-effective approach for producing polymeric and inorganic nanofibers with structures that vary with the processing parameters. In a typical process for inorganic fibers, a sol-gel precursor solution with polymeric binders is extruded from the orifice of a needle under a high electric field. The polymeric binders are easily removed during the calcination of the electrospun composite fibers. Xia *et al.* reported the production of various electrospun TiO_2 nanofibers, including fibers with a diameter of 20 nm, hollow fibers, core/sheath structures, and aligned TiO_2 nanofibers [11-12].

Dye-sensitized solar cells (DSSCs) were first reported by Grätzel *et al.* in 1991 [2, 14], and are an innovative, low-cost alternative to silicon-based solar cells. A typical DSSC comprises a mesoporous nanocrystalline TiO_2 film sensitized by dye molecules and a liquid electrolyte containing an iodide/triiodide redox couple. The nanocrystalline TiO_2 electrode provides a high specific surface area for the adsorption of a large number of dye sensitizers. However, the electron diffusion of nanocrystalline particles is more than 2 orders of magnitude smaller than that in bulk anatase crystals. It has been reported that the use of a network structure of TiO_2 single-crystal-like nanorods instead of TiO_2 nanoparticles results in significant improvements, achieving rapid electron transfer and high efficiency [8]. From the practical point of view, the use of a liquid electrolyte in DSSCs produces both short and long term sealing problems, which has resulted in the search for alternatives, such as quasi-solid or solid solar cells [15-17]. However, the penetration of solid electrolytes into conventional nanocrystalline TiO_2 electrodes is problematic because of their small pores [18]. In this study, a new type of nanorod TiO_2 electrode is shown to enhance the penetration of the quasi-solid electrolyte because of the macroporous structure of the electrospun web.

We report the fabrication of electrospun TiO_2 fibers composed of 1-D aligned fibrils (approx. 20 nm thick) with an islands-in-a-sea morphology similar to that shown in Fig. 1b [13], which were obtained through the phase separation of TiO_2 gel and PVAc during solidification. In this paper, we introduce a new method for producing single crystalline TiO_2 nanorods from electrospun fibers, and use them in an electrode to enhance the photocurrent generation of a quasi-solid state dye-sensitized solar cell.

Experimental

The TiO_2 fibers were electrospun from a solution in dimethyl formamide (DMF) (37.5 mL) of 3 g of poly(vinyl acetate) (PVAc, Mw = 850,000 g/mol), which was synthesized using bulk radical polymerization, 6 g of titanium(IV) propoxide (Aldrich), and 2.4 g of acetic acid as a catalyst. As in typical electrospinning procedures, the precursor solution was loaded into a syringe and connected to a high-voltage power supply. An electric field of 15 kV was applied between a metal orifice and the ground at a distance of 10 cm. The TiO_2 fibers were electrospun directly onto a SnO_2:F coated glass substrate (FTO, 10 cm x 10 cm, TEC-15, Pilkington). The as-spun TiO_2 web was then pressed using pre-heated plates at 120°C for 10 min, because without any pretreatment the electrospun web peels off the substrate during the calcination step. Finally, the pressed TiO_2 electrode was calcined to remove polymers and to develop the anatase TiO_2 nanorods at 450°C for 30 min in air.

In order to prepare the DSSC, the calcined TiO_2 electrode was immersed in ethanol solution 3×10^4 M $RuL_2(NCS)_2$ (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid) (N3, Solaronix) for 24 hours. The dye-absorbed TiO_2 electrode was rinsed with ethanol and dried under nitrogen flow. The gel electrolyte was composed of poly(vinylidenefluoride-*co*-hexafluoropropylene) (PVDF-HFP, Kynar 2801, 0.13 g), 1-hexyl-2,3-dimethylimidazolium iodide (0.13 g), and I_2 (0.008 g) in propylene carbonate (0.75 g) and ethylene carbonate (0.5 g). The mixture was heated at 100°C for 1 h and the resulting hot, highly viscous solution was dropped onto the dye-absorbed TiO_2 electrode. The electrode was pressed with a Pt-sputtered conducting glass as a counter electrode and slowly cooled to room temperature in order to obtain a quasi-solid state electrolyte. The photovoltaic characteristics of the electrode were measured using a Keithley SMU 2400 under the 100 mW/cm^2 irradiation of a Xe lamp (Oriel, 300 W) with a global AM1.5 filter.

Results and discussion

The as-spun TiO_2 fibers have a range of diameters from 200 to 600 nm as shown in the scanning electron microscopy (SEM) image in Fig. 1a. After calcination in air to remove PVAc, each TiO_2 fiber is composed of a bundle structure of about 20 nm thick fibrils, as shown in Fig. 1b. The sheaths and cores of the fibers were found to have an islands-in-a-sea morphology. In the early stages of electrospinning, the TiO_2 sol precursor is converted to TiO_2 gel when the electrospun fibers are exposed to moisture. Liquid-liquid phase separation results in TiO_2-rich and PVAc-rich phases due to the concentration instability that arises after solvent evaporation. The separated phases are elongated during the spinning step, resulting in an aligned fibrillar structure in the fiber-axis direction. Solidification occurs faster in the sheath than in the core due to contact with moisture in the ambient atmosphere.
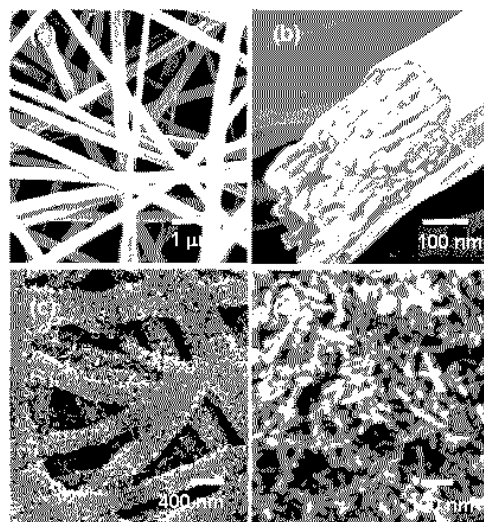

Figure 1. (a) SEM image of as-spun TiO_2/PVAc composite fibers fabricated by electorspinning from a DMF solution. (b) SEM image of a TiO_2 fiber after calcination showing an island-in-a-sea morphology with nanofibrils. (c) SEM image of TiO_2 nanorod electrode which was pretreated with mechanical press at 120 °C for 10 min before calcinations and high-magnification image (d).

To fabricate the electrode used in the DSSC, we pressed the electrospun web directly between pre-heated plates at a temperature

above the glass transition temperature of PVAc. After calcination of the hot-pressed electrode, its morphology was found to be different from that of a TiO_2 web electrode: the original web structure of the as-spun fibers was retained, but each fiber was composed of TiO_2 nanorods, as shown in Figs. 1c and 1d. The fibrils shown in Fig. 1b were broken into nanorods by the mechanical pressure. This approach seems to be a convenient method for preparing TiO_2 nanorods without the separation or purification steps required by other methods.
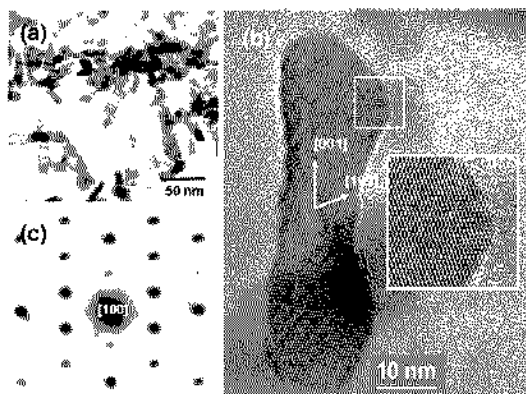

Figure 2. BF TEM and HRTEM images (a and b) and SAED pattern (c) of TiO_2 nanorods prepared by electrospun fibers. The HRTEM and SAED was taken from the zone axis of [100].

The detailed morphology of the TiO_2 nanorods was characterized with a bright field (BF) transmission electron microscopy (TEM) image and a high-resolution TEM (HRTEM) with selected area electron diffraction (SAED), as shown in Fig. 2. Sonication was used to disperse the TiO_2 nanorods in ethanol, which were then mounted on a carbon-coated Cu grid. The widths and lengths of the TiO_2 nanorods were about 15 nm and 60–100 nm respectively, as shown in Fig. 2a. The HRTEM image and SAED pattern show that the electrospun TiO_2 nanorods have a growth direction of [001] and a zigzag shape in the transverse direction. The zig-zag shape is composed of two {101} planes, which is attributed to the lower surface energy (0.44 J/m^2) of the anatase (101) plane than of other planes [19].

Fig. 3 shows the photocurrent density vs. voltage characteristics of a DSSC based on the TiO_2 nanorod electrode (about 12 μm in thickness) with a PVDF-HFP gel electrolyte. The short-circuit current density (J_{sc}), the open-circuit photo voltage (V_{oc}), the fill factor (FF), and the overall conversion efficiency (η) of the TiO_2 nanorod electrode were found to be 14.77 mA/cm^2, 0.7 V, 0.60 and 6.2%, respectively. The successful use of the TiO_2 nanorods in this DSSC indicates that efficient penetration of the highly viscous gel electrolyte into the TiO_2 electrode is occurring through large pores in the web. The well aligned 1-D TiO_2 nanorods may also contribute to better charge transportation because of their reduced grain boundaries compared to those of the nanoparticles. In general, photocurrent (J_{sc}) is generated in the DSSC when a photon absorbed by a dye molecule gives rise to electron injection into the TiO_2 conduction band. The incident photon-to-current conversion efficiency (IPCE) is defined as the number of generated electrons divided by the number of incident photons, and is shown in the inset of Fig. 3. The IPCE spectrum shows that the maximum efficiency was over 60% at 500 nm, and also indicates that efficient light harvesting by the TiO_2 nanorod electrode is occurring for wavelengths longer then 500 nm.
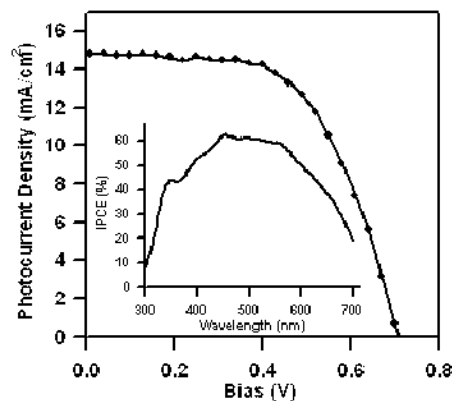

Figure 3. Photocurrent density vs. voltage characteristics of TiO_2 nanorode electrode with PVDF-HFP gel electrolyte at AM1.5 (100 mW/cm^2) illumination. The inset is IPCE spectrum for the same electrode. The TiO_2 nanorod electrode area was 0.16 cm^2.

Conclusions

In summary, we prepared a TiO_2 nanorod electrode for use in DSSCs with the electrospinning method, and demonstrated an enhanced photocurrent generation with a quasi-solid state electrolyte, which arises because of improved contact of the electrolyte with the TiO_2 web electrode.

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