Current Applied Physics 13 (2013) 252–255

Contents lists available at SciVerse ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Synthesis of nanobranched TiO_2 nanotubes and their application to dye-sensitized solar cells

Soon Hyung Kang [a,*], Wonjoo Lee [b], Yoon-Chae Nah [c], Kug-Seung Lee [d], Hyun Sik Kim [e]

[a] Department of Chemistry Education, Chonnam National University, Gwangju 500-757, Republic of Korea
[b] Advanced Material Research Lab, Samsung Advanced Institute of Technology, Samsung Electronics, Yongin-si, Gyeonggi-do 449-712, Republic of Korea
[c] School of Energy, Materials, and Chemical Engineering, Korea University of Technology and Education, Cheonan-si, Chungnam 330-708, Republic of Korea
[d] Texas Materials Institute, University of Texas at Austin, Austin TX 78712, United States
[e] Honam Petrochemical Corporation, Daejeon 305-726, Republic of Korea

A R T I C L E I N F O

Article history:
Received 23 May 2012
Received in revised form
25 June 2012
Accepted 18 July 2012
Available online 7 August 2012

Keywords:
TiO_2 nanotube
Nanobranches
Dye-sensitized solar cells
Rutile TiO_2
Electron transport

A B S T R A C T

Nanobranched TiO_2 nanotubes (TONTs) were synthesized by a sol–gel dipping method for the formation of seed layer, followed by a solution-phase deposition process. The different concentrations of seed solution influence the density of nanobranches on the top surface of TONT, achieving complete surface coverage of nanobranches in 10 mM $TiCl_4$ seed solution relative to 5 mM $TiCl_4$ seed solution. With a control sample of bare TONT, the nanobranched TONTs were explored as a photoanode for dye-sensitized solar cells (DSSCs). In the 5 mM $TiCl_4$ seed solution, the nanotree-shaped branches were sporadically formed on the top surface of TONT, with little effect on the photocurrent-voltage (J–V) properties, while in the 10 mM $TiCl_4$ seed solution, J_{sc} and fill factor increased, which may have been on account of the increased surface area and light scattering effect from rutile nanobranches, whereas the fill factor may be also increased by the electron transport property, leading to the degraded charge recombination. Accordingly, the nanobranched TONT showed 33% improved efficiency compared to bare TONT.

1. Introduction

Since 7% efficient dye-sensitized solar cells (DSSCs) consisting of approximately 20 nm-sized TiO_2 nanoparticles was reported [1], considerable effort have been devoted to develop suitable photoanode materials and to design their nanostructure to suppress the charge recombination, which is regarded as a main obstacle for achieving efficiency above 15%. Up to now, early efforts have been mainly focused on studying the metal oxide nanoparticles (NP) films on account of offering vast surface area for dye adsorption, leading to efficiency of above 12% [2]. However, one of the barriers to produce more efficient DSSCs has been the fast charge recombination in the large surface area and grain boundaries between nanoparticles, where photoinjected electrons move through trapping/detrapping events [3]. Accordingly, to minimize the charge recombination in the photoanode of DSSCs, one-dimensional (1-D) TiO_2 nanoparticles (*e.g.* nanorod, nanotube, nanowire *etc.*) have been anticipated to give improved electron transport rate [4,5]. 1-D TiO_2 nanoparticles have been enormously examined because of their unique shape-dependent electronic and optical properties, as well as their accepted applications in a wide variety of electrochemical and photoelectrochemical devices [6,7]. In particular, electrochemically anodized TiO_2 nanotubes (TONT) has been widely employed as a photoanode for DSSCs on account of easy, inexpensive, and reproducible technique. But, the low surface area resulting from wide pore size of about 100 nm lowers the efficiency [8]. Hence, varied approaches to increase the actual surface area for dye loading have been surveyed toward the post-treatment exploring of $TiCl_4$ and other metal oxides [9,10]. Here, a novel 1-D nanostructure called nanobranched TONT is suggested to facilitate the combinational effect to increase the surface area as well as to enhance the electron transport. Sometimes, the modification of nanotube structure leads to the loss of electron transport, because of providing the additional grain boundaries. However, the nanobranch of this architecture may provide the enough surface area without any loss of electron transport owing to a single crystalline property.

* Corresponding author. Tel.: +82 62 530 2497; fax: +82 062 530 2499.
E-mail address: skang@jnu.ac.kr (S.H. Kang).

1567-1739/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cap.2012.07.024

2. Experimental details

2.1. Synthesis of nanobranced TiO_2 nanotube

Two-step TONT was developed in an electrolyte of 0.25 wt% NH_4F using ethylene glycol containing an extremely small amount of water, as reported elsewhere [11]. Herein, the electrochemical anodization was performed for 30 min in a two-step process to fabricate 7.1 (±0.3) μm thick TONT, and subsequently thermally treated in 450 °C for 3 h. Afterward, the seed layer for the synthesis of nanobranches was deposited on the TONT by dipping in the aqueous solutions of 5 mM and 10 mM $TiCl_4$ for 30 min in a 70 °C oven, followed by annealing in air at 450 °C for 30 min. The seeded TONT were put in the aqueous solution composed of deionized (DI) water (10 mL), HCl (0.03 mL), and $TiCl_3$ solution (0.01 mL) for 2 h in a 80 °C oven. Finally, the sample was thoroughly cleaned with DI water and subsequently annealed at 450 °C for 1 h under air.

2.2. Fabrication of dye-sensitized solar cells

DSSCs utilizing TONT photoanode were fabricated as already described in a previous literature. Briefly, the nanobranched TONT films and bare TONT as a control sample together were put in an anhydrous ethanol solution containing Ru-complex dye (Ru 535-bisTBA (N719), Solaronix) for over 12 h. The electrode was then rinsed with anhydrous ethanol and dried under nitrogen gas. Pt catalysts as the counter electrode were prepared by spreading a drop of 3 mM H_2PtCl_6 in 2-propanol on fluorine-doped tin oxide (FTO) glass and heating it to 350 °C for 15 min in ambient air. The dye-adsorbed TiO_2 photoanode was assembled using thermal adhesive films (thickness: 60 μm) in a Sandwich-type cell with a counter electrode. Finally, a drop of electrolyte composed of 0.8 M 1-hexyl-2,3-dimethylimidazolium iodide and 50 mM iodine in methoxypropionitrile was injected into the cell.

2.3. Characterization

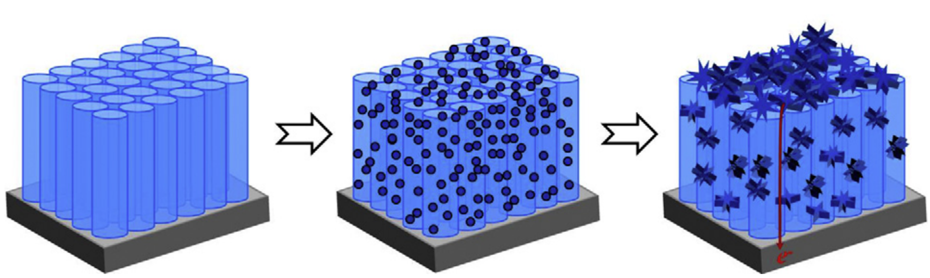
A field-emission scanning electron microscope (FE-SEM, JEOL JSM-7000F), transmission electron microscope (TEM, JSM-5400, JEOL) and X-ray diffraction (XRD, Scintag DMS-2000 diffractometer using Cu Kα radiation) were used to confirm the surface structure and crystallinity of the samples. The J–V curves were obtained by measurements under the irradiation of one sun condition (100 mW/cm^2 with AM 1.5 G).

3. Results and discussion

3.1. Characterization of nanobranced TiO_2 nanotube film

The overall synthesis procedure is illustrated in Scheme 1, involving a fabrication of two-step TiO_2 nanotubes by electrochemical anodization, a deposition of TiO_2 seed layer by sol–gel dip-coating technique, and the synthesis of TiO_2 nanobranches by solution-phase method on the TONT surface. Finally, the single crystalline rutile nanobranches were applied to the entire area of TONT. In general, the formation of seed layer is a starting point to grow a certain material, being an essential step for the synthesis of a material. Considering that the orientation of ZnO seed layer directly determines the orientation of the nanorods, that is to say, the aligned ZnO seed layer makes the aligned ZnO nanorod on the substrate, while a powder formed ZnO seed layer rests at all angles on the substrate [12], in the similar fashion, the TiO_2 seeds on the high aspect-ratio TONT substrate exist preferentially at all angles because the $TiCl_4$ treatment is facilitated as a seed solution that forms the powder formed TiO_2 nanoparticles [13]. Upon this substrate, the TiO_2 nanorods concurrently grow at all angles, finally forming the nanobranched TiO_2 structure. This scheme presents that the nanobranched TONT can provide direct pathways for fast electron transport.

Fig. 1 summarizes the surface- and cross-sectional view of TONT and nanobranched TONT. Two-step TONT (Fig. 1(a) and (d)) showed unique morphological properties, where nanotubes with a uniform surface structure are not separated independently but are joined to each other by sharing a wall. A diameter of approx. 80 nm (±10) depending on the intrinsic surface morphology of Ti substrate was achieved. Basically, the seed layer provides the starting point for the synthesis of a certain material and should be formed with constant size and uniform distribution as possible. Upon the 1-D nanostructure as a base material, $TiCl_4$ treatment was chosen for uniform coating on the entire surface of TONT. The concentration of $TiCl_4$ solution affects the density of the formed seed layer, therefore, the effect on the seed layer of 5 mM and 10 mM $TiCl_4$ solutions was investigated. The nanobranched TONT made from 5 mM $TiCl_4$ solution, shown in Fig. 1(b) and (e), exhibits scattered distribution of nanotree-shaped branches having diverse sizes on the top of the TONT surface. From the side-view of this image, the distribution of various sized nanotrees in a hemispherical form was again confirmed on the surface of TONT. This imperfect distribution of nanotrees may have resulted from the insufficient supply of Ti precursors in the low concentrated $TiCl_4$ seed solution. On the other hand, the increase of $TiCl_4$ solution in the seed solution can provide enough sources to form the TiO_2 seed particles throughout the entire surface area of TONT, leading to the complete coating of nanobranches throughout the TONT. Also, on the top of the surface, large sized nanotrees were also formed that could bring about a light scattering effect [14]. Furthermore, the specifically directing crystalline plane in the nanobranches was also observed to indicate the single crystalline properties of the nanobranches. Also, to confirm the conformal coating of nanobranches through the inner pores of TONT, the TEM measurement was performed, shown in Fig. 2. Though the inner pores of TONT, it was noticed that unspecified shaped TiO_2 materials were coated instead of nanotrees



Scheme 1. Simple experimental procedure to make nanobranched TONT on the Ti substrate. Nanobranched TONT may enhance the electron transport property due to the 1-D structural property of nanobranches without any loss of electrons.