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TiO_2 Nanorods Prepared from Anodic Aluminum Oxide Template and Their Applications in Dye-Sensitized Solar Cells

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ABSTRACT

Anodic aluminum oxide (AAO) was used as a template coupled with liquid process for synthesis of TiO_2 nanorods. Immersion setting (IS) was carried out to insert a TiO_2 precursor solution into AAO pore. With the calcination and NaOH treatment to remove AAO, SEM characterization revealed that TiO_2 nanorods with diameter around 100-200 nm were successfully fabricated from AAO commercial templates. The synthesized nanorods mixed with commercial TiO_2 nanoparticles (P-25) with a mixing ratio of 5:95 (by mass) were used as an electrode in a dye-sensitized solar cell (DSSC), The photoelectrodes made with nanorods showed a better performance than the cells used of only pristine TiO_2 nanoparticles. The results from current density-voltage (*J-V*) characteristics of DSSCs showed that short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (*FF*), and power conversion efficiency (*PCE*) are 11.78 mA/cm^2, 0.72 V, 0.55, and 4.68%, respectively. Due to the effects of one-dimensional (1-D) nanostructure, the electron expressway concept was achieved in this research.

Keywords: Anodic aluminum oxide (AAO); Dye-sensitized solar cell (DSC); TiO_2 nanorod

1. INTRODUCTION

Dye sensitized solar cells (DSSCs) have been expected to be candidates substitute to the silicon solar cells owing to the low cost. The highest overall light-to-electricity conversion efficiencies among the DSSCs was over 12% [1]. The interconnected TiO_2 nanoparticles have been mostly used as electrode in DSSCs, due to the large surface area for dye adsorption and electron transportation pathway. While dye molecules on the TiO_2 nanoparticles absorb photon from light, current is produced by electron injection from dye travel to the conduction band of TiO_2. Electrons transport through the TiO_2 nanoparticles to arrive at the electrode.

However, the random contacts between TiO_2 nanoparticles at grain boundaries lead to trapping and recombination of electrons and holes, which limits the efficiency of the DSSCs [2].

Significant attempts have been made to develop well-organized anode materials. These include ordered nanostructured materials, especially, one dimensional (1-D) structured materials [3-4]. In these materials, greater photovoltaic performances may be gained through the development of anode materials with ordered structure effect in the enhancement of electron transport [5]. Ordered TiO_2 nanorods or nanowires are highly interesting candidates to reach this goal [5-7]. There have been numerous methods to grow up TiO_2 nanostructures, including sol-gel process, electrospinning, and anodization of Ti metal [7,8]. However, these methods have limitations in synthesizing highly ordered structures such as uniform TiO_2 nanorods or nanowires with precisely control of dimension and geometry. These factors strongly influence the diffusion of excitons and electrons, and consequently affect overall power conversion efficiency (PCE) of the DSSCs [9].

In this study, anodic aluminum oxide (AAO), containing a uniform 1-D pore was used as a template to fabricate 1-D nanostructured TiO_2. AAO template method is suitable to prepare TiO_2 nanorods and nanowires with uniformly ordered structure [10]. By changing a hole diameter and thickness of AAO or infiltration depth of precursor into AAO, size and aspect ratio of 1-D nanomaterials can be easily controlled [8,10-11]. The aim of this work was to control the fabrication of TiO_2 nanorods by AAO template and apply the nanorods in DSSC applications.

2. EXPERIMENTAL

2.1. Fabrication and characterizations of TiO_2 nanorods

$C_{12}H_{28}O_4Ti$ (tetraisopropyl orthotitanate, TTIP) was used as a TiO_2 precursor and $(CH_3)_2CHOH$ (isopropanol, i-PrOH) was used as a solvent. $C_5H_8O_2$ (acetylacetone: ACA) was used as a chelating agent [12]. The ACA was added to slow down the hydrolysis reaction of TTIP. The composition ratios of TTIP:ACA was 1:1 (by molar), and a ratio of TTIP:(ACA+i-PrOH) was 1:4 (by volume) [10]. Immersion setting (IS) was carried out to insert a TiO_2 precursor solution into AAO pore. After the insertion, the precursor was left in the air for 30 min to allow the hydrolysis reaction to occur. Then, the samples were calcined at 450 °C for 1 h in air. Figure 1 shows a schematic illustration of the fabrication of TiO_2 nanorods from AAO template.

2.2. Template dissolution

After calcinations, samples were immersed in 1 M sodium hydroxide aqueous solution (NaOH aq.) in a centrifuge tube for 1 h to remove AAO template from the samples. The samples were separated into solid phase (TiO_2) and liquid phase by centrifuging at 10,000 rpm. Microstructure of AAO template, synthesized nanorods, and commercial nanoparticles were characterized by a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi High-Tech, Japan).

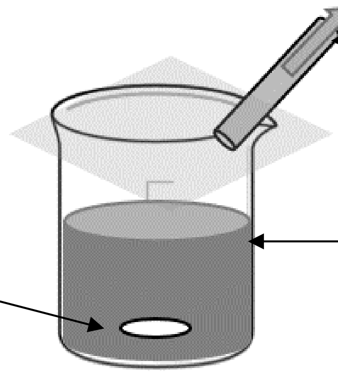

Fig. 1. Schematic illustration of fabrication of TiO_2 nanorods from AAO template.

2.3. DSSC fabrication and characterizations

The obtained TiO_2 nanorods from immersion setting were mixed with pristine TiO_2 nanoparticles, and they were prepared as a paste for fabrication of a DSSC photoelectrode. The ratios of nanorod to nanoparticle in the mixing were 5:95, 10:90, and 15:95. The paste was coated directly on a conducting glass (indium-doped SnO_2 conducting glass, ITO, 10 Ω/sq.) by squeegee technique. The electrode was then calcined at 450 °C for 1 h in air. After the calcination, it was left to cool down to room temperature and then the prepared cell was immersed in an aqueous solution of titanium chloride ($TiCl_4$, 80 mM). After that, the cell was calcined again at 450 ºC for 30 min. Next, the cell was immersed in 0.5 mM solution of ruthenium (II) dye (N719) in *tert*-butylpyridine and acetonitrile. The electrolyte used in this work was composed of dimethylpropyl imidazolium iodide, lithium iodide (LiI), iodide (I_2), and 4-*tert*-butylpyridine in acetonitrile. The current density-voltage (*J*-*V*) curves were measured under simulated solar light (AM 1.5, 100 mW/cm^2).

3. RESULTS AND DISCUSSION

When a commercial 100 nm-grade AAO template was immersed in precursor solution and dissolved in NaOH solution, the 1-D structured TiO_2 nanorods with a diameter and a length of 100-200 nm and 1-2 μm, respectively, were observed. Because the commercial AAO membrane used in this work is normally used as a liquid filter, so its pores are non-uniform [9,12].

The membrane has diameters at the top and the bottom of 100 and 200 nm, respectively, as shown in Fig. 2(a). Therefore, varied diameters of nanorods between 100 and 200 nm were obtained from this method. Apart from TiO_2 nanorods were obtained after dissolution, a formation of some TiO_2 nanoparticles [10] were also revealed in Fig. 2(b).

Fig. 3 demonstrates a SEM image of the photoelectrode fabricated from mixed TiO_2 nanorods/nanoparticles (5:95 by mass fraction), showing some nanorods bridged with small nanoparticles. This morphology is appropriate for a good electron conducting pathway and some bridged nanowires provide the interconnections via anchoring effect, which can help to reduce charge recombination in photocathodes [5,6,13].

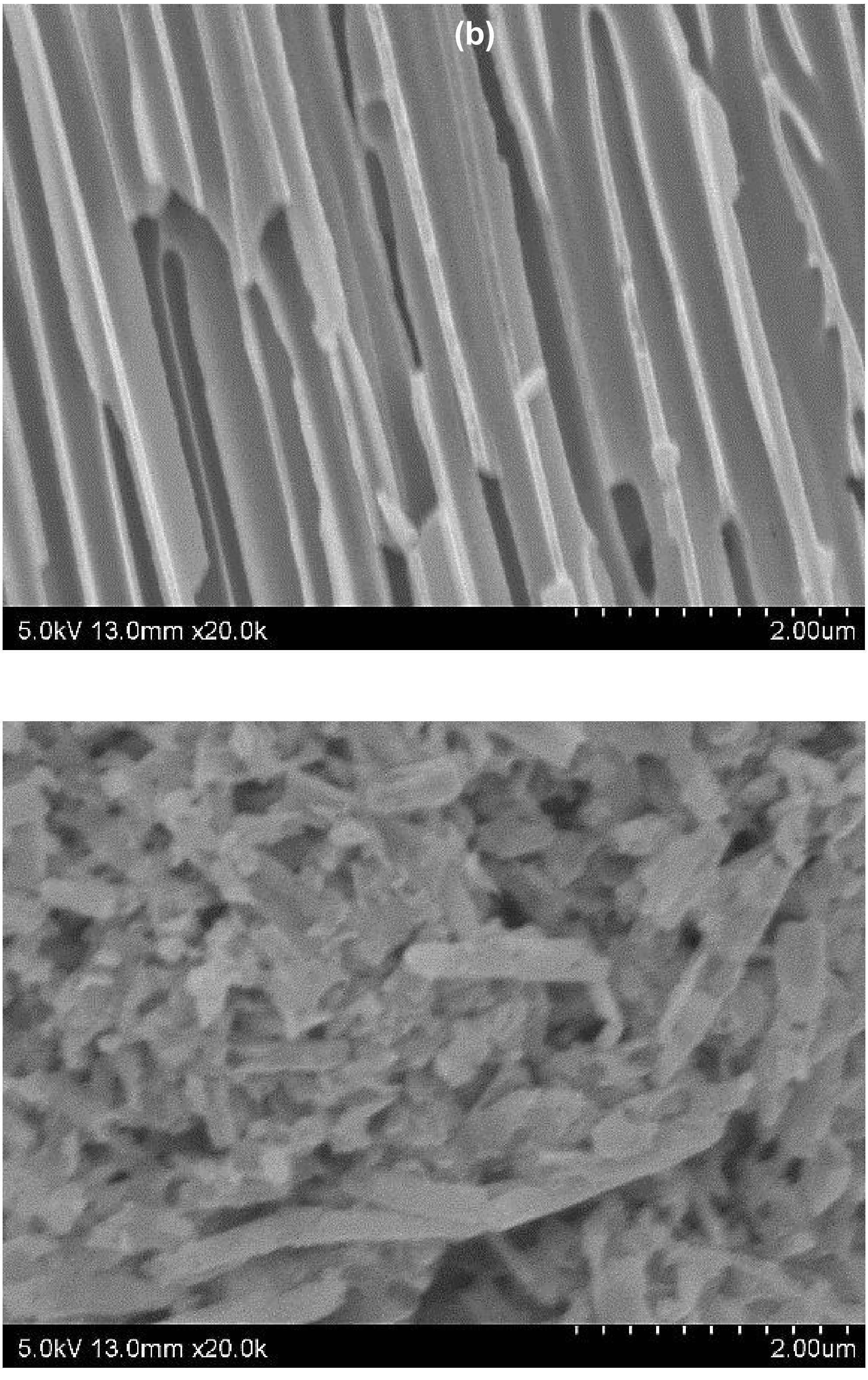

Fig. 2. SEM images of (a) AAO template with 100 nm diameter (side view) and (b) TiO_2 nanorods fabricated from the template.

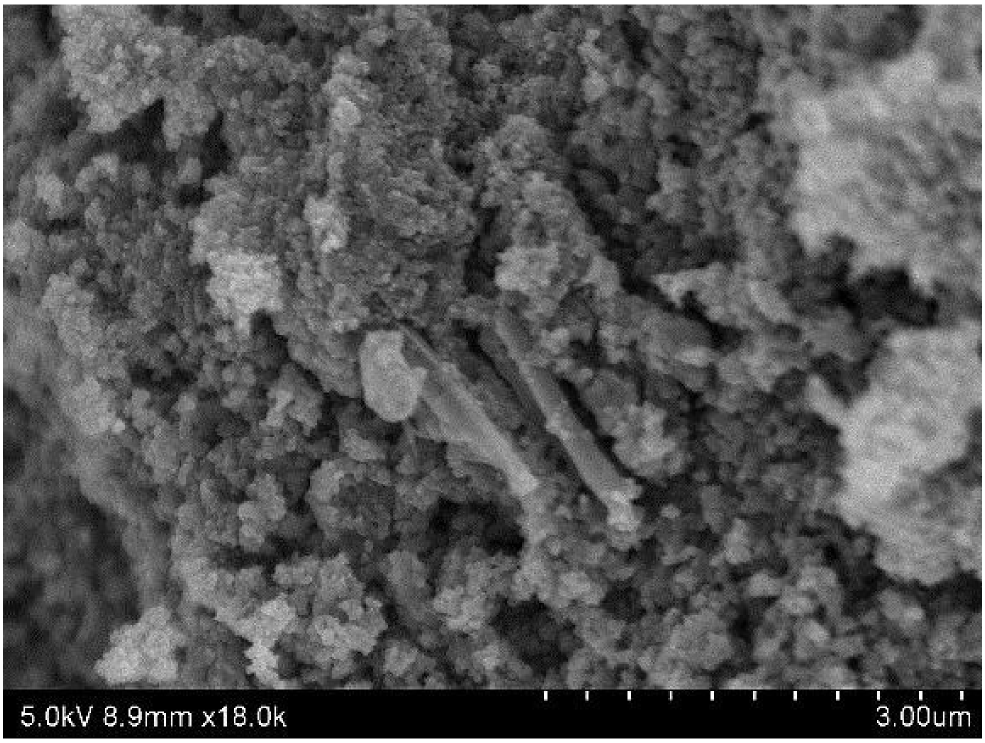

Fig. 3. SEM image of DSSC photoanode fabricated from mixed TiO_2 nanorods/ nanoparticles (5:95 by mass fraction).

Fig. 4 shows *J-V* characteristics of DSSCs fabricated from pristine TiO_2 nanoparticles compared with mixed TiO_2 nanorods/nanoparticles at a ratio of 5:95 (by weight). When the TiO_2 nanorod/nanoparticle electrode was used, *PCE* of the cell increased to 4.68% compared with that of only 4.13% from the system containing pristine TiO_2 nanoparticles.

Although the specific surface area of nanorods is lower than nanoparticles, the photo-generated electron can directly move along the 1-D ordered structure to conducting glass and reduced the possible loss of photoelectron and increase the performance of the cell. On the controversy, the previous work suggested that addition of nanorods into nanoparticles system may decrease the total specific surface area [4-5,6,13]. Therefore, proper content of nanorods supplementary into nanoparticles may completely increase the performance, notable the *PCE*, of DSSCs.

The photovoltaic characteristics of pristine TiO_2 nanoparticles (as reference data) and mixed TiO_2 nanorods/nanoparticles, obtained from the *J-V* curves, are summarized in Table 1. In term of V_{oc}, it was found that addition of nanorods resulted in unchanged value, however, addition of nanorods resulted in increase of J_{sc} and *FF*. This also can be attributed to an electron express way concept [5] caused by the dispersed structure of TiO_2 nanorods. Otherwise, light harvesting effect was improved by mixing nanorods with nanoparticle as electrode used in DSSCs [13].

The highest cell performance could be succeeded from devices with addition of 5% weight nanorods. Over addition of nanorods could decrease the *PCE* because of the decrease of J_{sc} from smaller specific surface area than pristine nanoparticles.

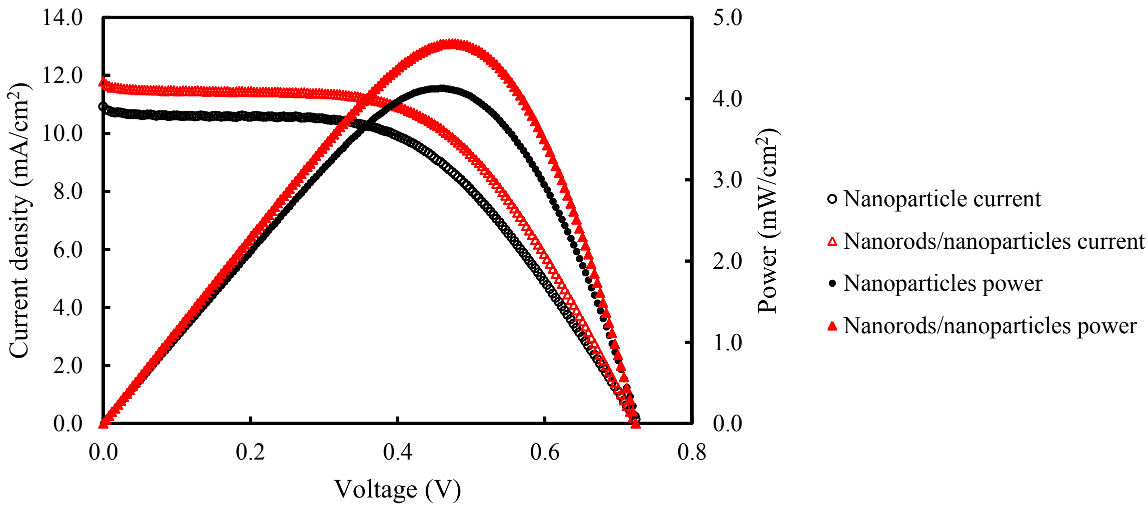

Fig. 4. J-V curves of DSSCs fabricated from (a) pristine TiO_2 nanoparticles and (b) mixed TiO_2 nanorods/nanoparticles (5:95 by mass fraction).

Table 1. Photovoltaic characteristics of DSSC fabricated from pristine TiO_2 nanoparticles and from mixed TiO_2 nanorods/nanoparticles (5:95 by mass).

Sample	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF*	*PCE* (%)
TiO_2 nanoparticles	10.92	0.73	0.52	4.13
Mixed TiO_2 nanoparticles/nanorods	11.78	0.72	0.55	4.68

J_{sc}: short-circuit photocurrent density, V_{oc}: open-circuit photovoltage, *FF*: fill factor.

4. CONCLUSIONS

TiO_2 nanorods were fabricated by AAO template method. The nanorods were applied as a component in a photoanode of DSSC. A DSSC made of mixed TiO_2 nanorods/nanoparticles at a ratio of 5:95 (by weight) showed a better *PCE* than the cell made of pristine TiO_2 nanoparticles. The results from *J-V* characteristics showed that J_{SC}, V_{OC}, *FF*, and *PCE* were 11.78 mA/cm^2, 0.72 V, 0.55 and 4.68%, respectively. These results suggest that a combination of the ordered structure 1-D nanorods and nanoparticles might be very favorable materials use as the electrode for DSSCs.

Acknowledgments

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