

High Specific Surface Area Nanosheets TiO₂ Electrode for Dye-sensitized Solar Cells

Sorapong Pavasupree^{1,*}, Jaturong Jitputti², Navadol Laosiripojana³, Supachai Ngamsinlapasathian², Yoshikazu Suzuki², and Susumu Yoshikawa²

¹Department of Materials and Metallurgical Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Klong 6, Pathumthani, 12110, Thailand

²Institute of Advanced Energy, Kyoto University, Uji, Kyoto, 611-0011, Japan

³JGSEE, King Mongkut's University of Technology Thonburi, Bangmod, Bangkok, 10140, Thailand

Abstract— In this study, high specific surface area nanosheets TiO₂ with mesoporous structure were synthesized by hydrothermal method at 130 °C for 12 h. The nanosheets structure were slightly curved and approximately 50-100 nm in width and several nanometers in thickness. The as-synthesized nanosheets TiO₂ had average pore diameter about 3-4 nm. The BET surface area and pore volume of the sample were about 642 m²/g and 0.774 cm³/g, respectively. The solar energy conversion efficiency (η) of the cell using the nanosheets TiO₂ was about 7.08 % with J_{sc} of 16.35 mA/cm², V_{oc} of 0.703 V and FF of 0.627; while η of the cell using commercial nanoparticles TiO₂ (P-25) reached 5.82 % with J_{sc} of 12.74 mA/cm², V_{oc} of 0.704V and FF of 0.649. Using one-dimensional (1D) nanostructured TiO₂ composite concept could improved the efficiency of dye-sensitized solar cells (η =8.1-10.3%). From the results clearly showed that the high surface area nanosheets TiO₂ (prepared by this method) was the promising candidate to serve as a material in dye-sensitized solar cell.

Keywords— TiO₂, Nanosheets, Dye-sensitized Solar Cell

1. INTRODUCTION

The synthesis and characterization of nanostructured materials (nanotubes, nanorods, nanowires, and nanosheet) have received considerable attention due to their unique properties and novel applications [1]. TiO₂ and TiO₂-derived materials are of importance for utilizing solar energy and environmental purification. TiO₂ has been widely used for various applications such as a semiconductor in dye-sensitized solar cell, water treatment materials, catalysts, gas sensors, and so on [2]. Functional properties of TiO₂ are influenced by many factors such as crystallinity, particle size, surface area, and preparation. Hydrothermal synthesis has become one of the most important and promising new material fabrication method for nanoscale materials and nanotechnology [3]. In the view point of surface area, nanosheet and nanotubes (from nanosheet rolling technique) TiO₂ (or titanate) offered high surface area (about 100-400 m²/g) [4-5]. In our previous works, nanofibers TiO₂ were synthesized by hydrothermal and post heat-treatments from natural rutile sand, however, nanofibers TiO₂ had rather low surface area (10-20 m²/g) [6-7]. The author's group preliminary reported that the mesoporous nanorods or nanowires/nanoparticles composite structure (hydrothermal method at 150 °C for

20-72 h) showed better photovoltaic conversion effect in dye-sensitized solar cell [8].

In this study, high surface area nanosheet TiO₂ with mesoporous structure (with much higher surface area, 642 m²/g) has been synthesized, which shows high performance in dye-sensitized solar cell.

2. METHODOLOGY

2.1 Preparation

Titanium (IV) butoxide (Aldrich) was mixed with the same mole of acetylacetone (ACA, Nacalai Tesque, Inc., Japan) to slowdown the hydrolysis and the condensation reactions. Subsequently, distilled water 40 ml was added in the solution, and the solution was stirred at room temperature for 5 min. After kept stirring, ammonia aqueous solution 28 % (Wako Co., Ltd., Japan) 30 ml was added in the solution, then the solution was put into a Teflon-lined stainless steel autoclave and heated at 130 °C for 12 h with stirring condition. After the autoclave was naturally cooled to room temperature, the obtained product was washed with HCl aqueous solution, 2-propanol and distilled water for several times, followed by drying at 100 °C for 12 h.

2.2 Characterization

The crystalline structure of the samples was evaluated by X-ray diffraction (XRD, RIGAKU RINT 2100). The microstructure of the prepared materials was analyzed by scanning electron microscopy (SEM, JEOL JSM-6500FE), transmission electron microscopy (TEM, JEOL JEM-200CX), and selected-area electron diffraction (SAED). The Brunauer-Emmett-Teller (BET) specific surface area was determined by the nitrogen adsorption (BEL Japan, BELSORP-18 Plus).

2.3 Dye-sensitized solar cell measurement

TiO₂ electrodes were prepared as follows; 1 g of TiO₂ powder was mixed with 0.1 mL of ACA, and was ground mechanically. During vigorous stirring, 5 ml of mixture of water and ethanol (1:1, in vol %) was added and 0.4 ml of polyoxethylene (10) octylphenyl ether (Triton x-100) was added to facilitate spreading of the paste on the substrate. The obtained colloidal paste was coated on fluorine-doped SnO₂ conducting glass (FTO, sheet resistance 15 Ω/\square , Asahi glass Co., Ltd.) by squeegee technique. After coating, each layer was dried

at room temperature and then annealed at 400 °C for 5 min. The coating process was repeated to obtain thick films. The resulting films were sintered at 450 °C for 2 h in air. Sintered TiO₂ electrodes were soaked in 0.3 mM of ruthenium (II) dye (known as N719, Solaronix) in a t-butanol/ acetonitrile (1:1, in vol %) solution. The electrodes were washed with acetonitrile, dried, and immediately used for measuring photovoltaic properties. The electrolyte was composed of 0.6 M dimethylpropylimidazolium iodide, 0.1 M lithium iodide (LiI), 0.05 M iodide (I₂), and 0.5 M 4-tert-butylpyridine in acetonitrile.

3. RESULTS AND DISCUSSION

SEM images (Fig. 1 (a-b)) of the as-synthesized sample, indicating the flower-like morphology composed of nanosheets. The flower-like structure had diameter about 500 nm to 2 μm. The nanosheet structure was slightly curved and approximately 50-100 nm in width and several nanometers in thickness (Fig. 1 (c)). The electron diffraction pattern supported that the nanosheet was anatase-type TiO₂, which corresponding to the XRD results (low crystallinity of anatase TiO₂).

The nitrogen adsorption isotherm of the as-synthesized nanosheet TiO₂ showed a typical IUPAC type IV pattern with inflection of nitrogen adsorbed volume at P/P₀ about 0.45 (type H2 hysteresis loop), indicating the existence of mesopores (Fig. 2). The pore size distribution of the sample showed that the nanosheet TiO₂ with narrow pore size distribution had average pore diameter about 3-4 nm. The BET surface area and pore volume of the as-synthesized nanosheet TiO₂ were about 642 m²/g and 0.774 cm³/g, respectively.

Since the high surface area result of the nanosheet-like TiO₂, we have tried to apply the nanosheet-like TiO₂ for the electrode in dye-sensitized solar cell application. Commercially available nanoparticles TiO₂ powder, P-25 (Nippon Aerosil Co., Ltd., Japan) was selected for comparative study of photovoltaic properties.

Fig. 3 shows comparison between photocurrent-voltage characteristics of the cell using the nanosheets TiO₂ (thickness = 8.4 μm) and P-25 (thickness = 13.8 μm). The solar energy conversion efficiency of the cell using the nanosheet TiO₂ with mesoporous structure was about 7.08 % with J_{sc} of 16.35 mA/cm², V_{oc} of 0.703 V and FF of 0.627; while η of the cell using P-25 reached 5.82 % with J_{sc} of 12.74 mA/cm², V_{oc} of 0.704 V and FF of 0.649.

High current density is attributed to the following reasons. First, higher amount of adsorbed dye (13.94 × 10⁻⁸ mol/cm² for nanosheet-like TiO₂ and 5.68 × 10⁻⁸ mol/cm² for P-25), owing to larger surface area of the nanosheet-like TiO₂, although after the nanosheet-like TiO₂ calcined at 450 °C for 2 h, the nanosheet-like changed to nanorods/nanoparticles composite with mesoporous structure (pore diameter about 4-6 nm, BET surface area around 134 m²/g). The BET surface area of P-25 calcined at 450 °C for 2 h (particles diameter about

30-50 nm without mesoporous structure) was about 54 m²/g. Second, electron transport of anatase structure faster than rutile structure [9]. The crystalline structure of the nanosheet-like TiO₂ calcined at 450 °C for 2 h was anatase, while P-25 was a mixture of anatase and rutile. Third, incorporation of nanorods and nanoparticles also improved the performance of dye-sensitized solar cells as the recently reported by ref. [10].

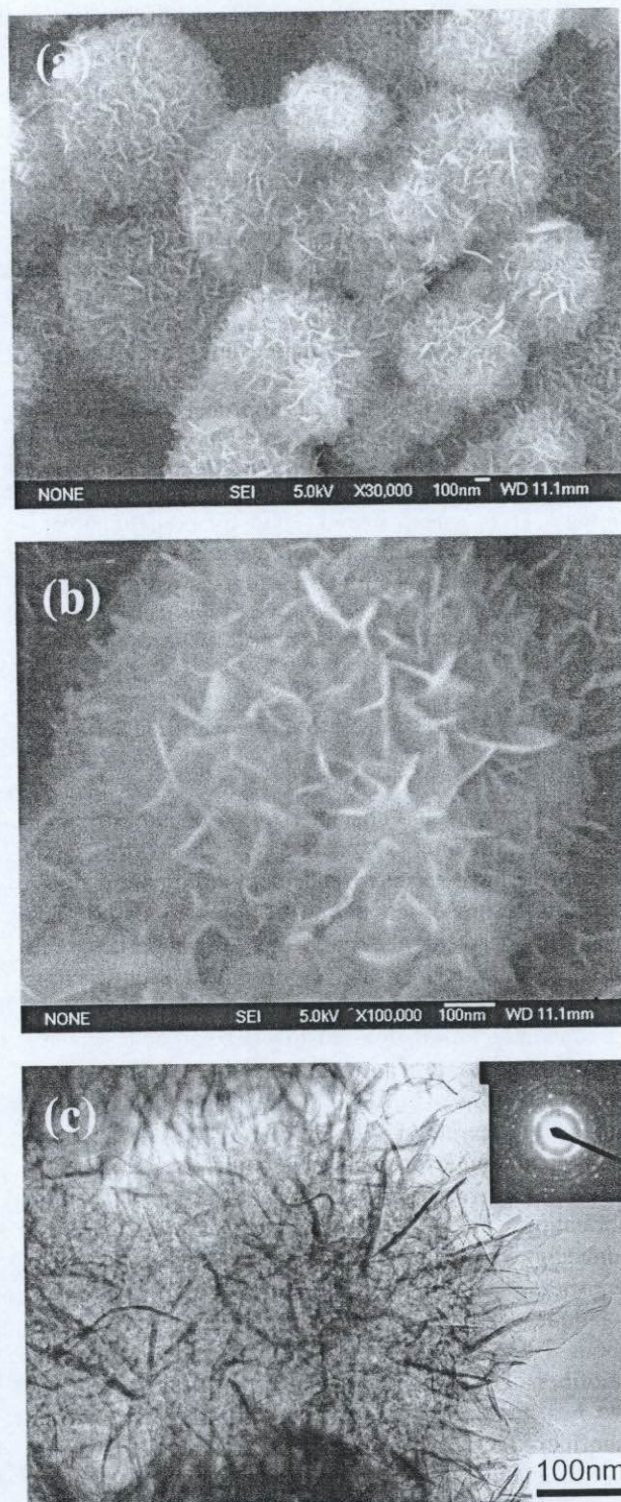


Fig. 1 (a-b) SEM, (b) TEM and SAED images of the as-synthesized nanosheets TiO₂.

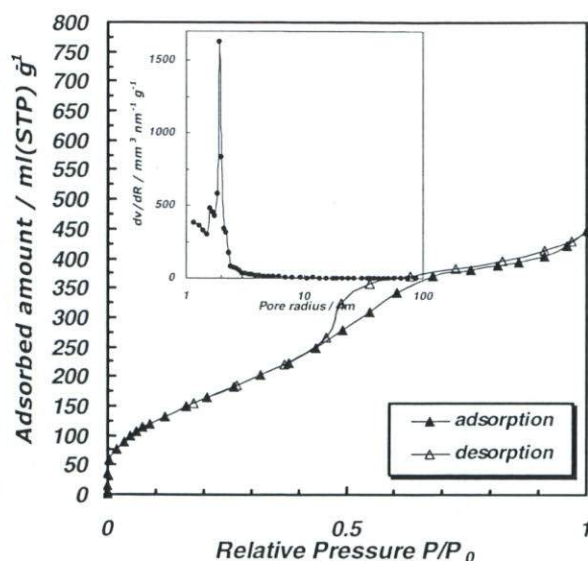


Fig. 2 Nitrogen adsorption isotherm pattern of the synthesized nanosheet TiO₂ (BET surface area 642 m²/g), and the pore size distribution of sample with pore diameter about 3-4 nm (inset).

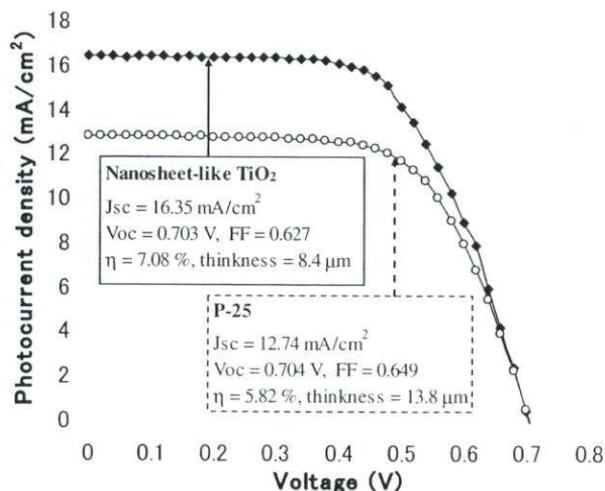


Fig. 3 The comparison between photocurrent-voltage characteristic of a typical dye sensitized solar cells fabricated by the nanosheets TiO₂ and the commercial TiO₂ nanoparticles (P-25).

The η of dye-sensitized solar cell fabricated from the nanosheet-like TiO₂ (prepared by this study) higher than the η of dye-sensitized solar cell fabricated from the TiO₂ (ST-01)-derived nanotubes ($\eta = 3.1\%$) [11], from the TiO₂ (P-25)-derived nanotubes ($\eta = 2.9\%$) [12]. The J_{sc} and V_{oc} also higher than recently reported of the TiO₂ nanorods as additive to TiO₂ film for improvement in the performance of dye-sensitized solar cells [10].

Specific application of 1D nanostructured TiO₂ using 1D nanostructured composite concept (nanoparticles and nanofibers) are being developed in our cooperative works in order to improve the electron transport and enhance the light confinement leading to higher conversion efficiencies of dye-sensitized solar cells.

Anatase TiO₂ nanofibers (by electrospun) were directly fabricated on thick nanoparticles-electrode through electrospinning and sol-gel techniques, and applied for dye-sensitized solar cells. IPCE of 85% at the wavelength of 540 nm and conversion efficiencies of 8.14 and 10.3% with area of 0.25 and 0.0515 cm², respectively, were obtained [13]. These results suggest light harvesting nanofibers-combined nanoparticles might be very promising materials for electrode of dye-sensitized solar cells.

4. CONCLUSION

In summary, high surface area (about 642 m²/g) nanosheets TiO₂ with mesoporous structure (pore diameter about 3-4 nm) were synthesized by hydrothermal method at 130 °C for 12 h. The η of the cell using nanorods/nanoparticles TiO₂ (from the nanosheet calcined at 450 °C for 2 h) was about 7.08 %, while η of the cell using P-25 reached 5.82 %. Using one-dimensional (1D) nanostructured TiO₂ composite concept could improved the efficiency of dye-sensitized solar cells ($\eta=8.1-10.3\%$). The results clearly showed that the high surface area nanosheets TiO₂ (prepared by this method) was the promising candidate to serve as an material in dye-sensitized solar cell.

5. ACKNOWLEDGEMENT

This research was financially supported by the Thailand Research Fund (MRG5180124) and Textiles Collaborative Research Consortium (NANOTEC, Thailand).

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