Simple Preparation of High Specific Surface Area Nanostructured TiO_2 for Dye-sensitized Solar Cells and H_2 Production from Water Splitting Reaction (RMUTT & Kyoto University Cooperative Works)

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ABSTRACT

The principal aim of this study is to prepare the one-dimensional nanostructured TiO_2 by a simple hydrothermal method with high quality (high crystallinity, surface area, thermal stability, photocatalytic activity, and dye-sensitized solar cell). One-dimensional nanostructured TiO_2 was synthesized by hydrothermal method at 80-150 ^{o}C for 12-72 h. The samples were then characterized by XRD, SEM, TEM, HRTEM, and BET surface area. The results clearly showed that the prepared nanostructured TiO_2 was the promising candidate to serve as the materials in dye-sensitized solar cells and H_2 production from water reaction applications.

Key words: One-dimensional, TiO_2, Hydrothermal, Photocatalyst, Dye-sensitized solar cell.

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1. INTRODUCTION

The synthesis and characterization of one-dimensional (1D) nanostructured materials (nanotubes, nanorods, and nanowires/nanofibers) have received considerable attention due to their unique properties and novel applications [1]. TiO_2 and TiO_2-derived materials are of importance for utilizing solar energy and environmental purification. TiO_2 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 TiO_2 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].

The principal aim of this study is to prepare the 1D nanostructured TiO_2 by simple hydrothermal method with high quality (high crystallinity, surface area, thermal stability, photocatalytic activity, and dye-sensitized solar cell). Details of characterization will be given about the structure analysis of nanorods, nanofibers, and nanosheet TiO_2. The results mainly focus on the determination of the shapes, crystalline structure, shape transformation, phase transformation, and specific surface area. Applications (photocatalytic activity, dye-sensitized solar cell, and H_2 production from water splitting reaction) of the prepared 1D nanostructured TiO_2 and commercial TiO_2 nanoparticles will be reported.

2. METHODOLOGY

2.1 Synthesis

2.1.1 TiO_2 Nanorods/nanoparticles [4]

Titanium (IV) butoxide (Aldrich) was mixed with the same mole of acetyacetone (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 150 ^{o}C for 20 h with stirring condition. After the autoclave was naturally cooled to room temperature, the obtained product was washed with HCl aqueous solution, 2-propanal and distilled water for several times, followed by drying at 100 ^{o}C for 12 h.

2.1.2 TiO_2 Nanorods [4]

The nanorods TiO_2 were synthesized by using the same route of 2.1.1 but the hydrothermal temperature was at 170 ^{o}C for 72 h.

2.1.3 TiO_2 Nanofibers [5-6]

The nanofibers TiO_2 were synthesized by hydrothermal method (150 ^{o}C for 72 h) using natural rutile sand as the starting material and calcined at 700 ^{o}C for 4 h (prepared as ref. 5-6).

2.1.4 TiO_2 Nanosheets [7]

The nanosheets TiO_2 were synthesized by using the same route of 2.1.1 but the hydrothermal temperature was at 130 ^{o}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 the scanning electron microscopy (SEM, JEOL JSM-6500FE), the transmission electron microscopy (TEM, JEOL JEM-200CX), and the 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

TiO_2 electrodes were prepared as follows: 1 g of TiO_2 powder was mixed with 0.1 mL of ACA, and was grounded 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 SnO_2 conducting glass (FTO, sheet resistance 15 $\Omega/\square$, Asahi glass Co., Ltd.) by squeegee technique. After coating, each layer was dried at room temperature and then annealed at 400 ^{o}C for 5 min. The coating process was repeated to obtain thick films. The resulting films were sintered at 450 ^{o}C for 2 h in air. Sintered TiO_2 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.

2.4 Photocatalytic hydrogen production

Photocatalytic H_2 production reaction was carried out in a closed gas-circulation system. TiO_2 photocatalyst (1 g) was suspended in aqueous methanol solution (800 ml distilled H_2O, 80 ml methanol) by means of magnetic stirrer within an inner irradiation-type reactor (1100 ml) made of Pyrex glass. A high-pressure Hg lamp (Ushio; UM-452, 450 W) was utilized as the light source. Prior

to the reaction, the mixture was de-aerated by purging with Ar gas repeatedly. To maintain the reaction temperature during the courses of reaction, cooling water (30 ^{o}C) was circulated through a cylindrical Pyrex jacket located around the light source. The gaseous H_2 produced was periodically analyzed by an on-line gas chromatograph (Shimadzu GC-8A, Molecular sieve 5A, TCD, Ar Carrier).

3. RESULTS AND DISCUSSION

3.1 Nanofibers from natural rutile sand [6]

Titanate nanofibers were synthesized by hydrothermal method (150 ^{o}C for 72 h) using natural rutile sand as the starting materials (Fig. 1). TiO_2 (B) and anatase TiO_2 (high crystallinity) nanofibers with the diameters of 20-100 nm and the lengths of 10-100 μm were obtained by calcined titanate nanofibers for 4 h at 400 ^{o}C and 700 ^{o}C (in air), respectively. The nanofibers calcined for 4 h at 500 – 900 ^{o}C maintained nanofiber morphology. Normally, the TiO_2-derived nanotubes after heat-treatment at 400 ^{o}C (anatase phase) were destroyed and changed into particles and the phase transformation from anatase phase TiO_2 to rutile phase TiO_2 begins to appear at 600 - 700 ^{o}C. However, anatase TiO_2 nanofibers, prepared by this method, are stable at 700 – 800 ^{o}C. Therefore, anatase TiO_2 nanofibers can be used at high temperatures. At higher temperature than 900 ^{o}C, they begin to change into rutile-type TiO_2 rod-like structure. The operation of this synthesis method is a simple hydrothermal method and all the reactions of the synthetic process are carried out in aqueous solution.

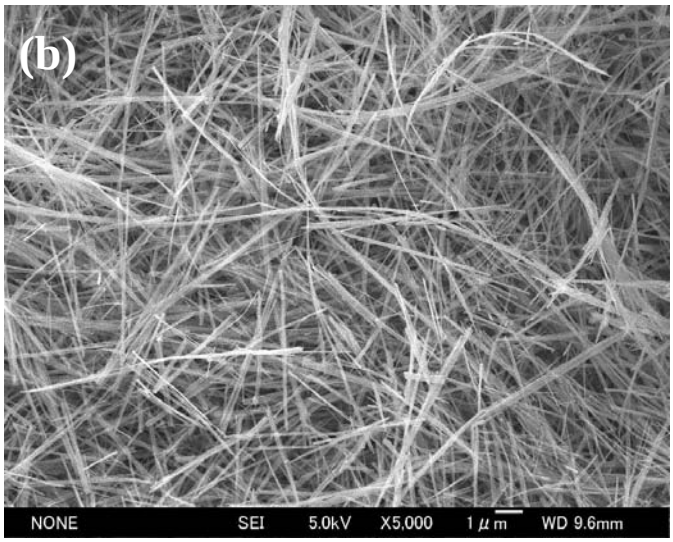
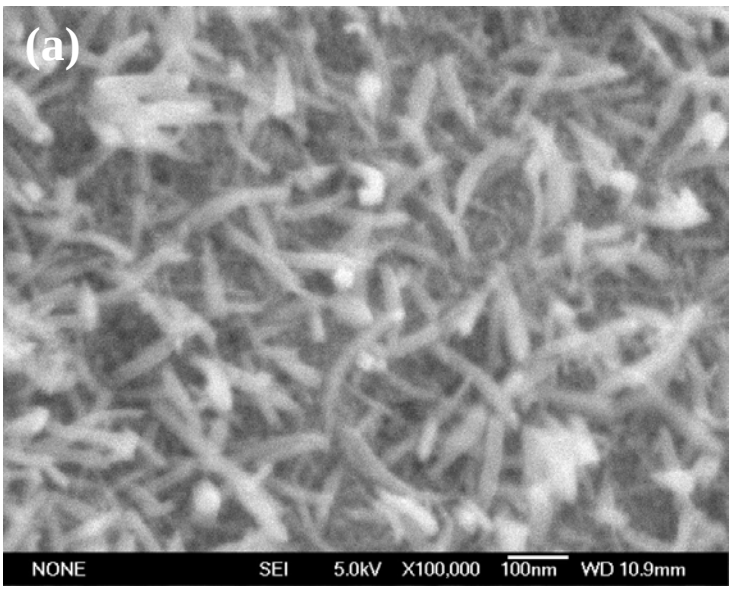


Fig. 1 SEM images of (a) the starting natural rutile sand and (b) the as-synthesized nanofibers [6].

3.2 Nanorods/nanoparticles TiO_2 [4]

Fig. 2 (a) shows SEM image of the as-synthesized nanorods/nanoparticles TiO_2, indicating the rods-like morphology. In addition, it's TEM (Fig. 2 (b)) clearly shows not only nanorods but also nanoparticles. The nanorods in the composite powder had diameter about 10-20 nm and the lengths of 100-200 nm, the nanoparticles had diameter about 5-10 nm. The electron diffraction pattern shown in the inset of (Fig. 2 (b)) supported that the nanorods/nanoparticles composite was anatase-type TiO_2. The lattice fringes of the nanorods and the nanoparticles appearing in the image (d = 0.35 nm) also allowed for the identification of the anatase phase (Fig. 2 (b)). HRTEM image of nanorods/nanoparticles with clear lattice fringes, again confirming its high crystallinity.



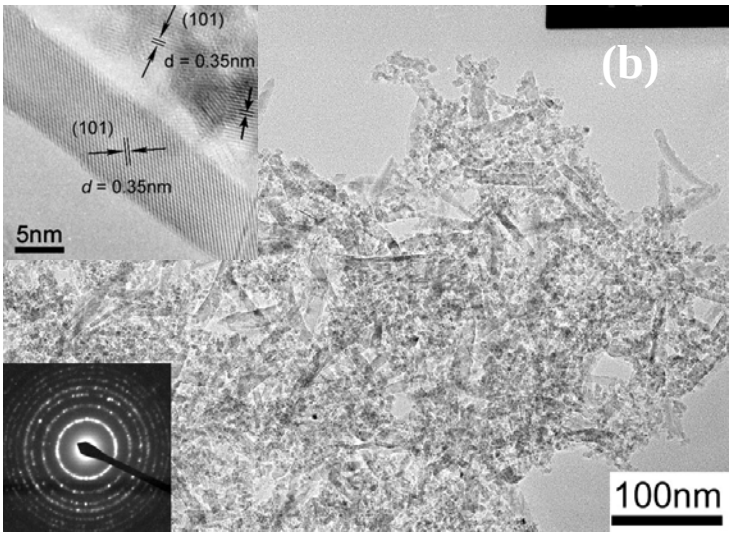
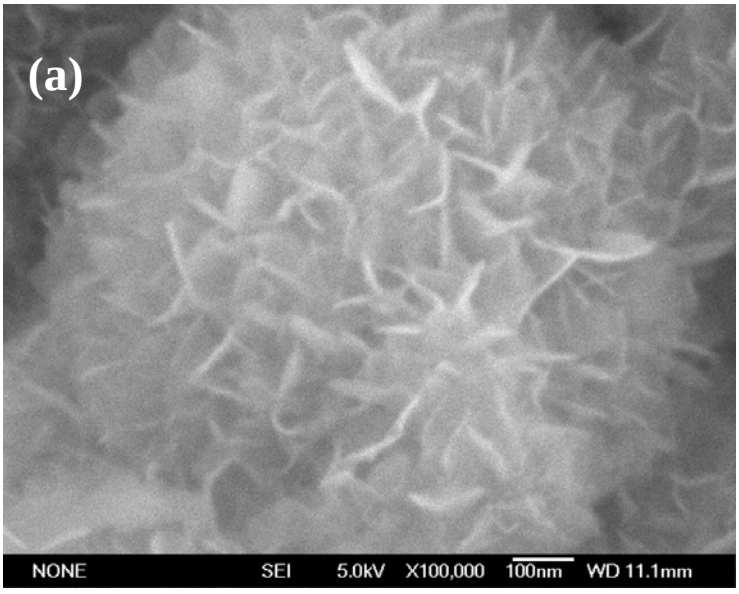


Fig. 2 (a) SEM, (b) TEM, SAED, and HRTEM images of the as-synthesized nanorods/nanoparticles TiO_2 [4].

3.3 High specific surface area nanosheets TiO_2 [7]

SEM image (Fig. 3 (a)) of the as-synthesized sample, indicating the flower-like morphology was 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. 3 (b)). The electron diffraction pattern supported that the nanosheet was anatase-type TiO_2, corresponding to the XRD results (low crystallinity of anatase TiO_2).



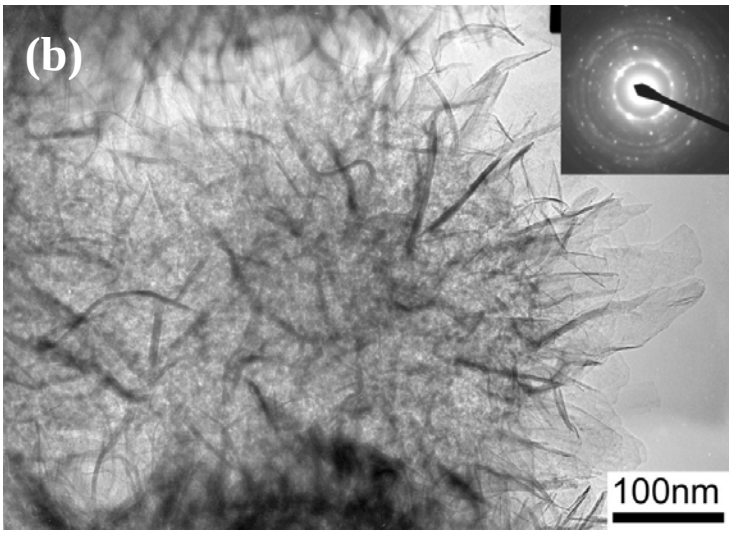


Fig. 3 (a) SEM, (b) TEM and SAED images of the as-synthesized nanosheet TiO_2 [7].

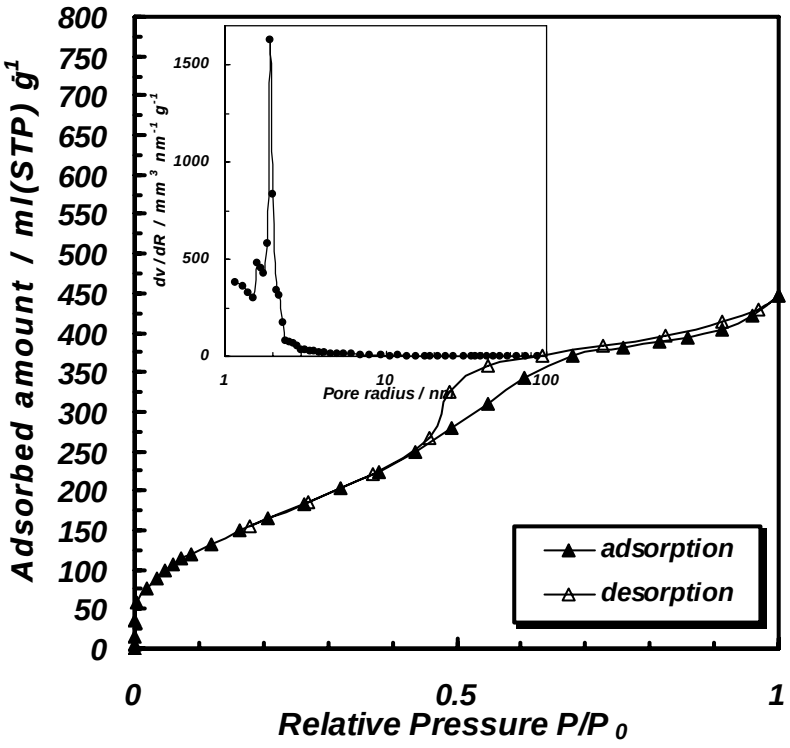


Fig. 4 Nitrogen adsorption isotherm pattern of the as-synthesized nanosheet TiO_2 (BET surface is 642 m^2/g), and the pore size distribution of sample with pore diameter about 3-4 nm (inset) [7].

The nitrogen adsorption isotherm of the as-synthesized nanosheet TiO_2 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. 4). The pore size distribution of the sample showed that the nanosheet TiO_2 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 TiO_2 were about 642 m^2/g and 0.774 cm^3/g, respectively.

3.4 Uniform flower-like nanowires

Flower-like structure titanate and titania on titanium plate substrate composed of nanowires with diameter about 10 nm were synthesized by hydrothermal method at 150 ^{o}C using titanium plate substrate as the starting material. SEM images showed flower-like structure with uniform size about 2 μm (Fig. 5 (a)). The flower-like structure composed of nanowires with diameter about 10 nm (Fig. 5 (b)). Titanate and titania could be controlled by washing process and calcination temperature.

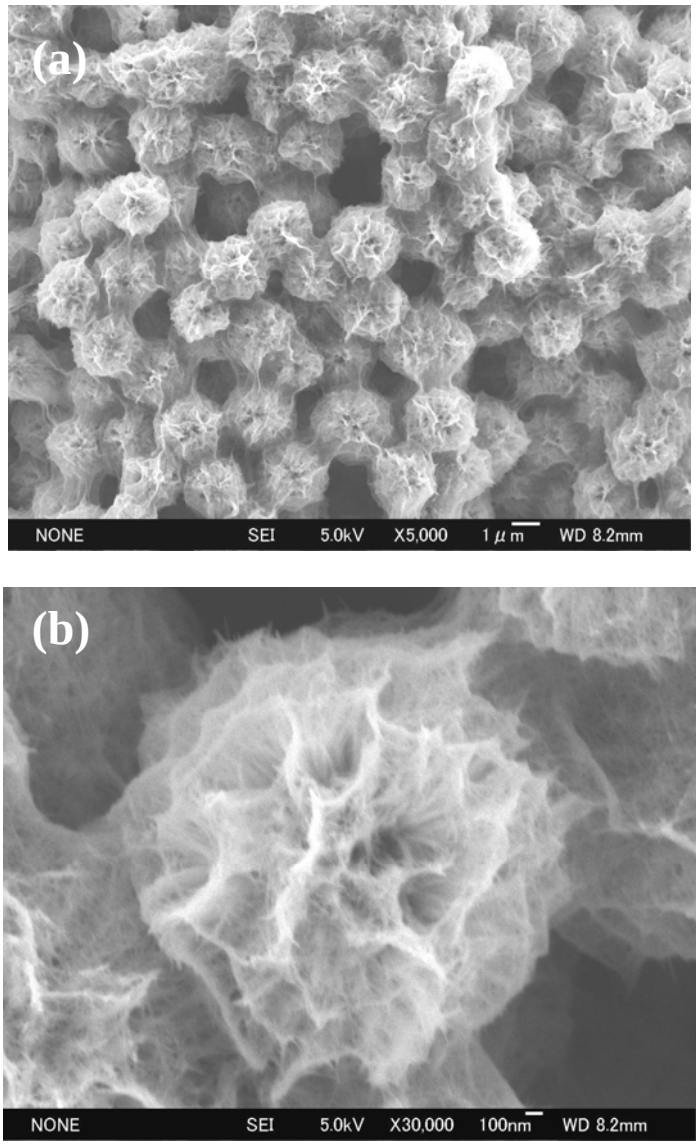


Fig. 5 SEM images of flower-like nanowires titanate (as-synthesized) on Ti plate substrate prepared by hydrothermal method (a) x 5,000 and (b) x 30,000 magnified.

3.5 Applications of the prepared nanostructured TiO_2 [4, 7]

The I_3^- concentration at 60 min of the irradiation period of the nanorods/nanoparticles TiO_2 were about 3.02 x 10^{-4} M (Fig. 6), which is higher than that of other synthesized powders (nanorods TiO_2, nanofibers TiO_2, mesoporous TiO_2) and also that of four commercially available titania nanomaterials,

ST-01, P-25, JRC-01, and JRC-03 which exhibit I_3^- concentration about 2.68 x 10^{-4} M, 1.50 x 10^{-4} M, 0.66 x 10^{-4} M, and 0.25 x 10^{-4} M, respectively. The catalytic activity depended significantly on the specific surface area. Proportionality between BET surface area and catalytic activity indicates that adsorption of I^- on the materials surface is the rate determining step and the introduction of mesopore into the structure of the photocatalyst substantially improved the photocatalytic performance [10, 12].

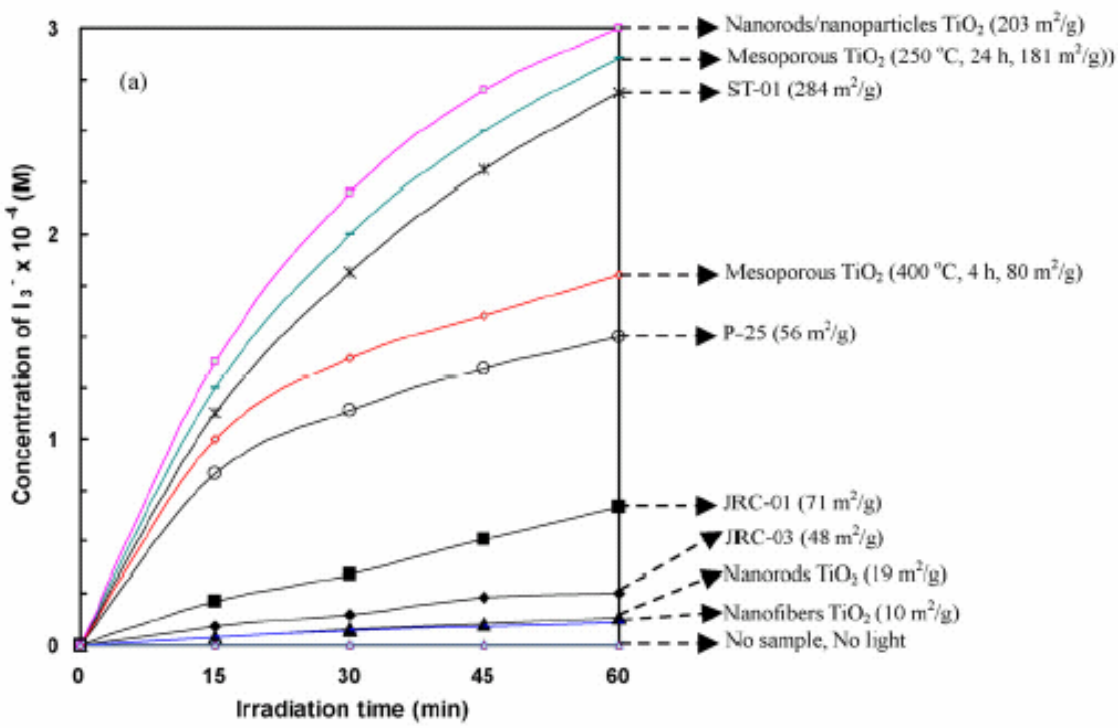


Fig. 6 Photocatalytic activity (I_3^- concentration) of the nanorods/nanoparticles TiO_2 with mesoporous structure (prepared by this study), the mesoporous TiO_2 calcined at 250 °C for 24 h and 400 °C for 4 h (prepared as ref. 8-12), the nanorods TiO_2 (prepared by this study), the nanofibers TiO_2 (prepared as ref. 5-6), and commercial TiO_2 (ST-01, P-25, JRC-01, and JRC-03).

Fig. 7 shows comparison between photocurrent–voltage characteristics of the cell using the nanosheets TiO_2 (thinckness = 8.4 μm) and P-25 (thinckness = 13.8 μm). The solar energy conversion efficiency of the cell using the nanosheet TiO_2 with mesoporous structure was about 7.08 % with Jsc of 16.35 mA/cm^2, Voc of 0.703 V and ff of 0.627; while η of the cell using P-25 reached 5.82 % with Jsc of 12.74 mA/cm2, Voc of 0.704 V and ff of 0.649.

Specific application of 1D nanostructured TiO_2 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 TiO_2 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 cm^2, respectively, were obtained [13]. These results suggest light harvesting nanofibers-combined nanoparticles might be very promising materials for electrode of dye-sensitized solar cells.

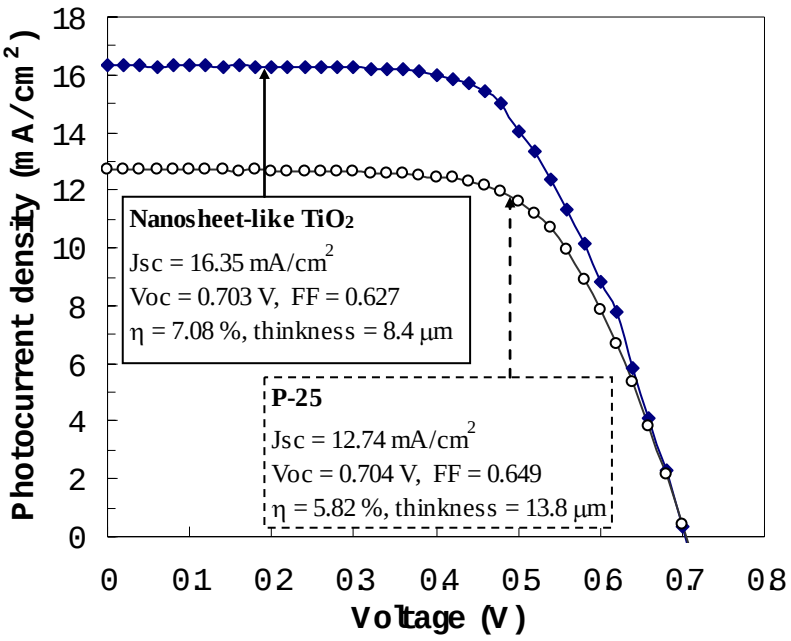


Fig. 7 Photocurrent-voltage characteristic of a typical dye sensitized solar cells fabricated by the nanosheets TiO_2 and the commercial TiO_2 (P-25) [7].

Fig. 8 demonstrates the time course of the photocatalytic H_2 production from water splitting reaction over the nanosheets TiO_2 calcined at 300 ^oC for 12 h and commercial TiO_2 nanoparticles (ST-01, P-25). The photocatalytic H_2 evolution activity of the nanosheets TiO_2 calcined at 300 ^oC for 12 h was higher than the commercial TiO_2 nanoparticles (ST-01, P-25) more than 5 times. In our previous works, it is obviously revealed that the introduction of mesopore into titania photocatalyst substantially improved the photocatalytic performance [10, 12].

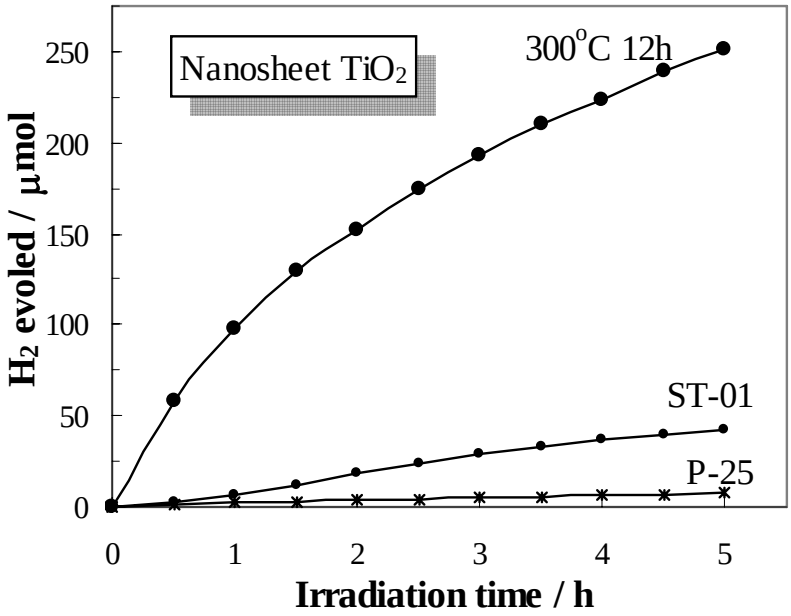


Fig. 8 Photocatalytic H_2 production from water splitting reaction (30 °C) over the nanosheets TiO_2 calcined at 300 °C for 12 h and commercial TiO_2 nanoparticles (ST-01, P-25).

However, the nanosheets TiO_2 prepared by this method were not homogeneous in size with large diameter ranging from 500 nm to 2 μm. So it is meaningful to develop a simple method to synthesize the spherical TiO_2 nanosheets with homogeneous size at rather low temperature.

Recently, we have reported a simple hydrothermal technique for preparation of uniform size flower-like TiO_2 nanosheets [14]. The method combining two-steps: (1) amorphous titania sphere using controlled hydrolysis and (2) flower-like TiO_2 nanosheets by hydrothermal treatment in ammonia solution. Uniform, solid spherical particles were obtained after 24 h aging. The surface of these spheres is relatively smooth with the sizes of 250 to 450 nm. After hydrothermal treatment in ammonia solution, the size of these spheres was not changed too much. However, their surfaces became rough. It was obvious that the hydrothermal temperature was a critical factor. Flower-like nanosheet structure could be obtained for samples prepared at $\geq$ 80 °C. Therefore, it can be preferably concluded that higher temperature was required in order to obtain flower-like nanosheet structure.

Recently, we are also developing polypropylene/TiO_2 composite fibers by using internal mixer and small scale fiber extruder with take up unit, for antibacterial applications (Fig. 9).

Fig. 9 Polypropylene/TiO_2 composite fibers for antibacterial applications.

4. CONCLUSION

In summary, the results demonstrated that the prepared one-dimensional nanostructured TiO_2 could be synthesized by hydrothermal method at 80-150 ^{o}C for 12-72 h. The prepared TiO_2 showed high performance in photocatalytic activity, dye-sensitized solar cells and also higher than commercial TiO_2 nanoparticles. The results clearly showed that the prepared TiO_2 was the promising candidate to serve as the materials in dye-sensitized solar cells and H_2 production from water reaction applications.

5. ACKNOWLEDGMENTS

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