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A Simple Production Method of Mesoporous Titania Nanopowders for Energy Applications

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Abstract

In this study, mesoporous TiO_2 nanopowders with narrow pore size distribution (pore size about 3-4 nm) and higher surface area (about 180 m^2/g) were prepared by hydrothermal method at 130 ^oC for 12 h. Interestingly, the applications (dye-sensitized solar cell and H_2 production from water-splitting reaction) results of the prepared TiO_2 showed higher efficiency than commercial TiO_2 nanoparticles.

Keywords: Mesoporous, TiO_2, Dye-sensitized Solar Cell, Water splitting.

1. Introduction

In the past decade, mesoporous materials have been of great interest as catalysts because of their unique textural and structural characteristics. Much effort has concentrated on the important metal oxides such as TiO_2, SnO_2, VO_2, and ZnO. Amoung them, 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 [1]. 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 [2-7]. In our previous works, mesoporous TiO_2 were synthesized by a modified sol-gel method, however, the prepared mesoporous TiO_2 had surface area about 80 m^2/g [8-10].

In this study, mesoporous anatase TiO_2 nanopowders with narrow pore size distribution (pore size about 3-4 nm) and higher surface area (about 193 m^2/g) has been synthesized, which shows high photocatalytic activity and high performance in dye-sensitized solar cell. The detail microstructure, photocatalytic, and photovoltaic properties will be reported.

2. Experimental Procedure

2.1 Synthesis

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 [11-13]. Subsequently, distilled water 40 ml was added in the solution, and the solution was stirred at room temperature for 5 min. After kept stirring, the solution was put into a Teflon-lined stainless steel autoclave and heated at 130 ^oC for 12 h with stirring condition. After the autoclave was naturally cooled to room temperature, the obtained product was washed with 2-propanol and distilled water, followed by drying at 100 ^oC 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

TiO_2 electrodes were prepared as follows; 1 g of TiO_2 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 SnO_2 conducting glass (FTO, sheet resistance 15 Ω/□, Asahi glass Co., Ltd.) by squeegee technique. After coating, each layer was dried at room temperature and then annealed at 400 ^oC for 5 min. The coating process was repeated to obtain thick films. The resulting films were sintered at 450 ^oC 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 (I_2), and 0.5 M 4-*tert*-butylpyridine in acetonitrile.

The thickness of the TiO_2 films was measured with a Tencor Alpha-step Profiler. Photocurrent-voltage curve was measured under simulated solar light (CEP-2000, Bunkoh-Keiki, AM 1.5, 100 mW/cm^2). The light intensity of the illumination source was calibrated by using a standard silicon photodiode (BS520, Bunkoh-Keiki).

The amount of adsorbed dye was determined by desorbing the dye from the titania surface into a mixed solution of 0.1 M NaOH and ethanol (1:1 in volume fraction) and measuring its absorption spectrum. The concentration of adsorbed dye was analyzed by UV-vis spectrophotometer (UV-2450 SHIMADZU).

2.4 Photocatalytic hydrogen production

Photocatalytic H_2 production reaction was carried out in a closed gas-circulation system (Fig. 1). TiO_2 photocatalyst (0.8 g) was suspended in aqueous methanol solution (800mL distilled H_2O, 80mL 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 deaerated by purging with Ar gas repeatedly. To maintain the reaction temperature during the course of reaction, cooling water 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 Characterization results [17]

Figure 1 shows the X-ray diffraction pattern of the as-synthesized sample. The peaks were rather sharp, which indicated the obtained TiO_2 had relatively high crystallinity, and attributable to the anatase phase.

Figure 2 gives the nitrogen adsorption isotherm and the pore size distribution of the as-synthesized sample. The isotherm shows a typical IUPAC type IV pattern with inflection of nitrogen adsorbed volume at P/P_0 about 0.50 (type H_2 hysteresis loop), indicating the existence of mesopores. The pore size distribution of the sample, as shown in the inset of Figure 2, showed that the as-synthesized sample had average pore diameter about 4-5 nm. The BET surface area and pore volume of sample are about 193 m^2/g and 0.286 cm^3/g, respectively (higher than the previous works (ref. 8-10, 80 m^2/g) about 2 times).

SEM and TEM images of the as-synthesized sample showed nanoparticles size about 5 nm (Figure 3-4).The electron diffraction pattern shown in the inset of (Figure 4) supported that the as-synthesized sample 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 (Figure 5). HRTEM images of the as-synthesized sample with clear lattice fringes, again confirming its high crystallinity.

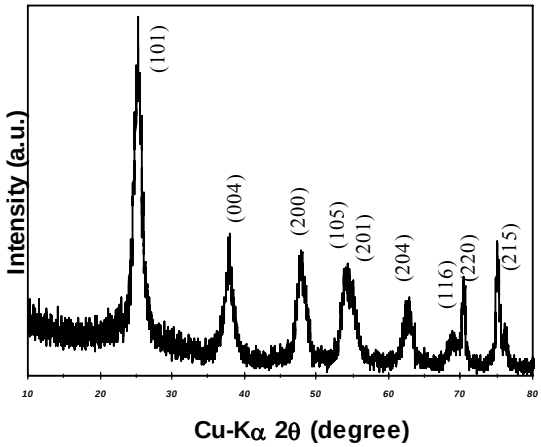

Figure 1. X-ray diffraction pattern of the as-synthesized mesoporous anatase TiO_2 nanopowders.

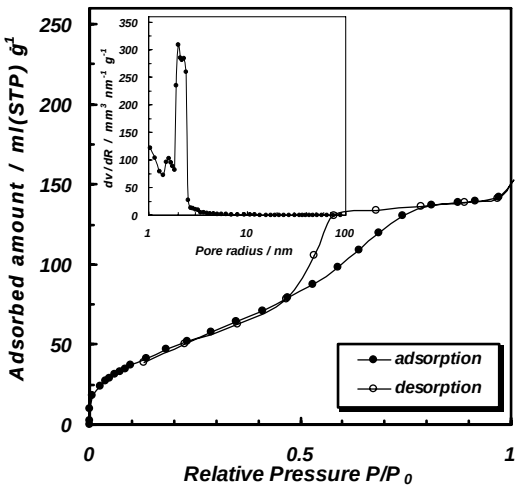

Figure 2. Nitrogen adsorption isotherm pattern of the as-synthesized mesoporous anatase TiO_2 nanopowders, and the pore size distribution of the sample with pore diameter about 4-5 nm (inset).

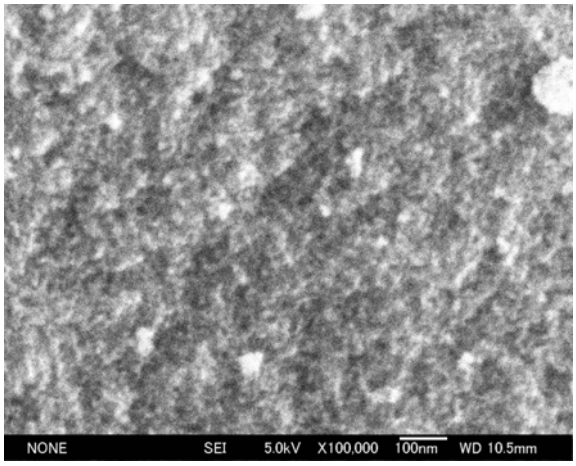

Figure 3. SEM image of the as-synthesized mesoporous anatase TiO_2 nanopowders.

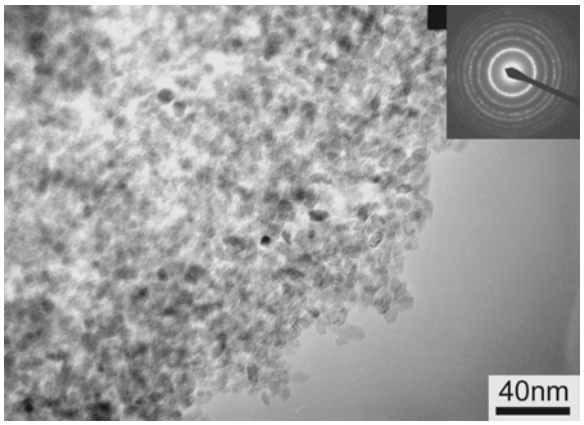

Figure 4. TEM and SAED images of the as-synthesized mesoporous anatase TiO_2 nanopowders.

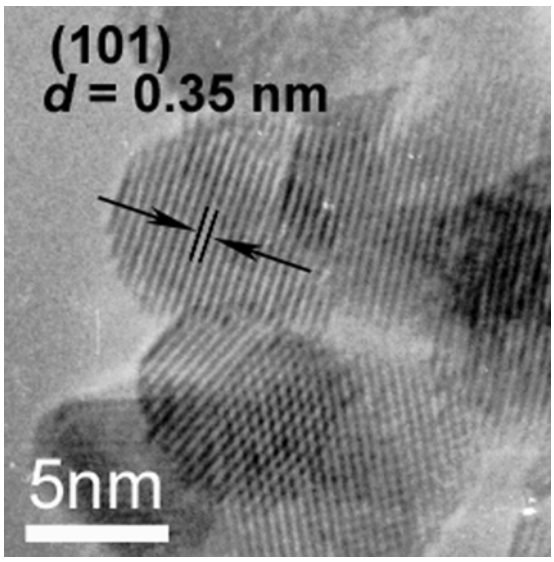

Figure 5. HRTEM of the as-synthesized mesoporous anatase TiO_2 nanopowders.

3.2 Dye-sensitized solar cell results [17]

Table 1 shows the comparison between photocurrent–voltage characteristics of the cell using the mesoporous anatase TiO_2 nanopowders (thinckness = 10.0 μm) and P-25 (thinckness = 13.8 μm). The solar energy conversion efficiency of the cell using the mesoporous anatase TiO_2 nanopowders was about 6.30 % with Jsc of 13.28 mA/cm^2, Voc of 0.702 V and ff of 0.676; while η of the cell using P-25 reached 5.82 % with Jsc of 12.74 mA/cm^2, Voc of 0.704 V and ff of 0.649. Higher current density and efficiency might be attributed to higher amount of adsorbed dye (10.21 x 10^{-8} mol/cm^2 for the mesoporous anatase TiO_2 nanopowders and 5.68 x 10^{-8} mol/cm^2 for P-25), owing to larger surface area of the mesoporous anatase TiO_2 nanopowders (Table 2).

Table 1 The photocurrent-voltage characteristic of a typical dye sensitized solar cells fabricated by the mesoporous anatase TiO_2 nanopowders and commercial TiO_2 nanoparticles (P-25).

Samples	Jsc (mA/cm^2)	Voc (V)	η (%)
Prepared TiO_2	13.28	0.702	6.30
P-25	12.74	0.704	5.82

Table 2 The BET surface area and amount of adsorbed dye of the mesoporous anatase TiO_2 nanopowders (prepared by this study) calcined at 450 ^oC for 2 h and P-25 calcined at 450 ^oC for 2 h.

Samples	**BET surface area (m^2/g)**	**Amount of adsorbed dye (mol/cm^2)**
Prepared TiO_2	101	10.21 x 10^{-8}
P-25	54	5.68 x 10^{-8}

Figure 6 (a, c) depict the nitrogen adsorption-desorption isotherms and pore size distributions of the mesoporous anatase TiO_2 nanopowders calcined at 450 ^oC for 2 h. The isotherms exhibit typical type IV pattern with hysteresis loop, characteristic of mesoporous material according to the classification of IUPAC. A sharp increase in adsorption volume of N_2 was observed and located in the P/P_0 range of 0.70-0.85. This sharp increase can be imputable to the capillary condensation, indicating the good homogeneity of the sample and fairly small pore size since the P/P_0 position of the inflection point is related to the pore dimension. The pore size distribution obtained by BJH approach (Figure 6 (c)) is noticeably narrow, confirming good quality of the sample. In comparison, the isotherm of the P-25 after calcined at 450 ^oC for 2 h is also shown in Figure 6 (b). It can be seen that the isotherm elucidates the typical IUPAC type II pattern, revealing the absence of mesoporous structure in the commercial nanoparticles P-25. The BET surface area of the mesoporous anatase TiO_2 nanopowders and P-25 were around 101 and 54 m^2/g, respectively. Second, electron transport of anatase

structure faster than rutile structure [16]. The crystalline structure of the mesoporous anatase TiO_2 nanopowders calcined at 450 ^oC for 2 h was anatase, while P-25 calcined at 450 ^oC for 2 h was a mixture of anatase and rutile (Figure 7).

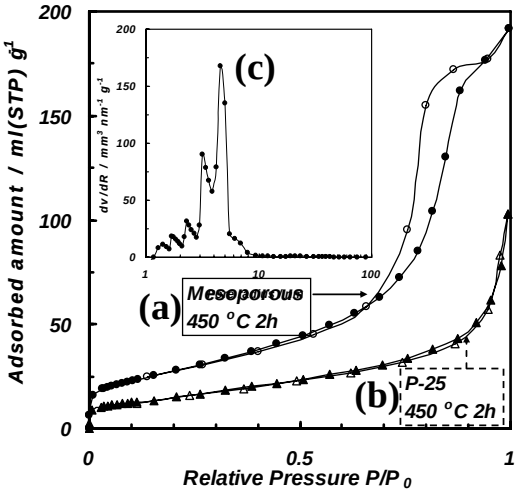

Figure 6 (a) Nitrogen adsorption isotherm pattern of the mesoporous anatase TiO_2 nanopowders calcined at 450 ^oC for 2 h, BET surface are 134 m^2/g), (b) P-25 (450 ^oC for 2 h, BET surface are 54 m^2/g), and (c) the pore size distribution of the mesoporous anatase TiO_2 nanopowders with pore diameter about 6-10 nm.

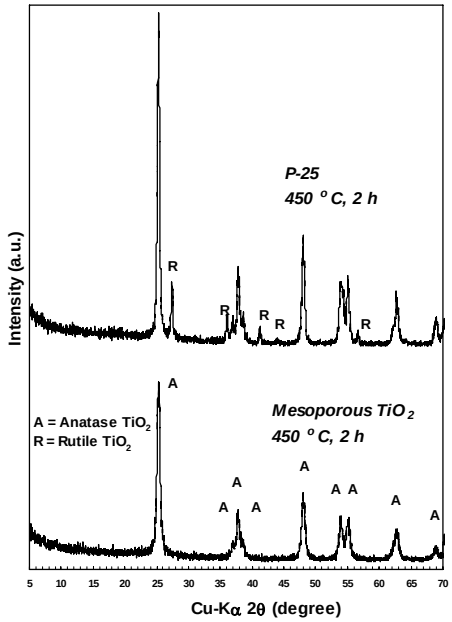

Figure 7. X-ray diffraction patterns of the mesoporous anatase TiO_2 nanopowders calcined at 450 ^oC for 2 h and P-25 calcined at 450 ^oC for 2 h.

3.3 H_2 production from water splitting reaction results [18]

Figure 8 demonstrates the time course of the photocatalytic H_2 production from water splitting reaction over the mesoporous TiO_2 calcined at various temperature and commercial TiO_2 nanoparticles (ST-01). The photocatalytic H_2 evolution activity of the calcined mesoporous TiO_2 samples were higher than the commercial TiO_2 nanoparticles (ST-01). In our previous works, it is obviously revealed that the introduction of mesopore into titania photocatalyst substantially improved the photocatalytic performance [15, 18].

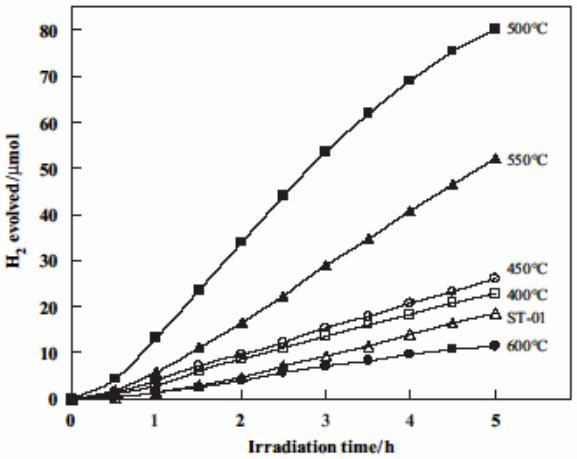

Figure 8. Photocatalytic H_2 production from water-splitting reaction over the mesoporous TiO_2 calcined at various temperatures and commercial TiO_2 (Ishihara ST-01).

5. Conclusion

In summary, high surface area (about 180 m^2/g) anatase TiO_2 with mesoporous structure (pore diameter about 3-4 nm) was synthesized by hydrothermal method at 130 ^oC for 12 h. The η of the cell using mesoporous anatase TiO_2 nanopowders (prepared by this study) was about 6.30 %, while η of the cell using P-25 reached 5.82 %. Mesoporous anatase TiO_2 nanopowders showed higher photocatalytic activity than the commercial TiO_2 (ST-01).This synthesis method provided a simple route to fabricate mesoporous anatase TiO_2 nanopowders with mild condition. The results clearly showed that the mesoporous TiO_2 (prepared by this method) is the promising candidate to serve as an energy-related material.

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