Mesoporous anatase TiO2 nanopowder was synthesized by hydrothermal method at 130 °C for 12 h. The samples characterized by XRD, SEM, TEM, SAED, HRTEM, and BET surface area. The as-synthesized sample with narrow pore size distribution had average pore diameter about 3-4 nm. The specific BET surface area of the as-synthesized sample was about 193 m²/g, higher than the previous works (ref. 8-10, 80 m²/g) about 2 times. Mesoporous anatase TiO2 nanoparticles (prepared by this study) showed higher photocatalytic activity than the nanorods TiO2 (prepared as ref. 6), nanofibers TiO2 (prepared as ref. 3-4), mesoporous TiO2 (prepared as ref. 8-10), and commercial TiO2 nanoparticles (P-25, JRC-01, and JRC-03). The solar energy conversion efficiency (η) of the cell using the mesoporous anatase TiO2 was about 6.30 % with Jsc of 13.28 mA/cm², 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/cm², Voc of 0.704 V and ff of 0.649.

Keywords: Mesoporous, Anatase, TiO2, Hydrothermal, Photocatalytic Activity, Dye-sensitized Solar Cell

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 TiO2, SnO2, VO2, and ZnO. Among them, 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 [1]. 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 methods for nanoscale materials and nanotechnology [2-7]. In our previous works, mesoporous TiO2 were synthesized by a modified sol-gel method, however, the prepared mesoporous TiO2 had surface area about 80 m²/g [8-10].

In this study, mesoporous anatase TiO2 nanopowders with narrow pore size distribution (pore size about 3-4 nm) and higher surface area (about 193 m²/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. METHODOLOGY

2.1 Synthesis

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 [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 °C for 12 h with stirring condition. After the autoclave was naturally cooled to room temperature, the obtained product 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 °C for 12 h with stirring condition. After the autoclave was naturally cooled to room temperature, the obtained product 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 °C for 12 h with stirring condition. 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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/□, 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-butylypyridine in acetonitrile.

The thickness of the TiO2 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/cm²). 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).

3. RESULTS AND DISCUSSION [17]

3.1 Characterization results

Fig. 2 shows the X-ray diffraction pattern of the as-synthesized sample. The peaks were rather sharp, which indicated the obtained TiO2 had relatively high crystallinity, and attributable to the anatase phase.

Fig. 3 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/P0 about 0.50 (type H3 hysteresis loop), indicating the existence of mesopores. The pore size distribution of the sample, as shown in the inset of Fig. 3, 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 m²/g and 0.286 cm³/g, respectively (higher than the previous works (ref. 8-10, 80 m²/g) about 2 times).

SEM and TEM images of the as-synthesized sample showed nanoparticles size about 5 nm (Fig. 4 (a-b)). The electron diffraction pattern shown in the inset of (Fig. 4(c)) supported that the as-synthesized sample was anatase-type TiO2. 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. 4(d)). HRTEM images of the as-synthesized sample with clear lattice fringes, again confirming its high crystallinity.

Fig. 5 shows the summarized results (SEM, TEM, SAED, and BET surface area) of the prepared TiO2 nanopowders (nanorods TiO2, nanofibers TiO2, mesoporous TiO2) and commercial TiO2 nanopowders (P-25, JRC-01, JRC-03).

The BET surface area of the nanorods TiO2 (Fig. 5 (a), anatase structure with diameter 60-80 nm and the lengths of 300-600 nm), the nanofibers TiO2 (Fig. 5 (b), anatase structure with diameter 20-100 nm and the lengths of several ten micrometers), and mesoporous TiO2 (Fig. 5 (c), anatase structure with particles diameter 7-15 nm) were about 19, 10, and 80 m²/g, respectively. The BET surface area of the commercial TiO2, P-25 (Fig. 5 (d), anatase 70 % and rutile 30 % structure with particles diameter 30-50 nm), JRC-01 (Fig. 5 (e), anatase structure with particles diameter 15-30 nm), JRC-03 (Fig. 5 (f), rutile structure with particles diameter 20-50 nm) were about 56, 71, and 48 m²/g, respectively.

3.2 Photocatalytic activity results

The I3− concentration at 60 min of the irradiation period of the nanorods/nanoparticles TiO2 were about 2.32 x 10⁻⁷ M (Fig. 6), which is higher than that of other synthesized powders (nanorods TiO2, nanofibers TiO2, mesoporous TiO2) and also that of 3 commercially available titania nanomaterials, P-25, JRC-01, and JRC-03 which exhibit I3− concentration about 1.50 x 10⁻⁸ M, 0.66 x 10⁻⁸ M, and 0.25 x 10⁻⁸ M, respectively. The introduction of mesopore into titania photocatalyst substantially improved the photocatalytic performance [15].

3.3 Dye-sensitized solar cell results

Fig. 7 shows comparison between photocurrent–voltage characteristics of the cell using the mesoporous anatase TiO2 nanopowders (thickness = 10.0 μm) and P-25 (thickness = 13.8 μm). The solar energy conversion efficiency of the cell using the mesoporous anatase TiO2 nanopowders was about 6.30 % with Jsc of 13.28 mA/cm², 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/cm², 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 10⁻¹⁸ mol/cm² for the mesoporous anatase TiO2 nanopowders and 5.68 x 10⁻¹⁸ mol/cm² for P-25), owing to larger surface area of the mesoporous anatase TiO2 nanopowders (Table 1). Fig. 8 (a, c) depict the nitrogen adsorption-desorption isotherms and pore size distributions of the mesoporous anatase TiO2 nanopowders calcined at 450 °C 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 N2 was observed and located in the P/P0 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/P0 position of the pore size distribution is related to the pore dimension. The pore size distribution obtained by BJH approach (Fig. 8 (c)) is noticeably narrow, confirming good quality of the sample. In comparison, the isotherm of the P-25 after calcined at 450 °C for 2 h is also shown in Fig. 8 (b). It can be seen that the isotherm elucidates the typical IUPAC type II pattern, revealing the absence of mesopore structure in the commercial nanoparticles P-25. The BET surface area of the mesoporous anatase TiO2 nanopowders and P-25 were around 101 and 54 m²/g, respectively. Second, electron transport of anatase structure faster than rutile structure [16]. The crystalline structure of the mesoporous anatase TiO2 nanopowders calcined at 450 °C for 2 h was anatase, while P-25 calcined at 450 °C for 2 h was a mixture of anatase and rutile (Fig. 9).
Fig. 1 (a) X-ray diffraction pattern of the as-synthesized mesoporous anatase TiO₂ nanopowders. (b) Nitrogen adsorption isotherm pattern of the as-synthesized mesoporous anatase TiO₂ nanopowders, and the pore size distribution of the sample with pore diameter about 4-5 nm (inset).

Fig. 2 (a) SEM, (b) TEM, (c) SAED, and (d) HRTEM images of the as-synthesized mesoporous anatase TiO₂ nanopowders.
Fig. 3 SEM, TEM, SAED, and BET surface area results of the prepared and commercial TiO$_2$. (a) nanorods TiO$_2$ prepared by hydrothermal at 170 °C for 72 h as ref. 6. (b) nanofibers TiO$_2$ prepared by hydrothermal at 150 °C for 72 h as ref. 3-4. (c) mesoporous TiO$_2$ prepared by sol-gel at 80 °C for 7 days as ref. 8-10. (d-f) the commercial TiO$_2$ (P-25, JRC-01, and JRC-03)
Fig. 4 (a) Photocatalytic activity (I$_3$ concentration) of the mesoporous anatase TiO$_2$ nanopowders (prepared by this study, hydrothermal method), the nanorods TiO$_2$ (prepared as ref. 6), the nanofibers TiO$_2$ (prepared as ref. 3-4), the mesoporous TiO$_2$ (prepared as ref. 8-10, sol-gel method) and commercial TiO$_2$ (P-25, JRC-01, and JRC-03). (b) The comparison between photocurrent-voltage characteristic of a typical dye sensitized solar cells fabricated by the mesoporous anatase TiO$_2$ nanopowders and P-25.

Fig. 8 (a) Nitrogen adsorption isotherm pattern of the mesoporous anatase TiO$_2$ nanopowders calcined at 450 °C for 2 h, BET surface are 134 m$^2$/g), P-25 (450 °C for 2 h, BET surface are 54 m$^2$/g), and the pore size distribution of the mesoporous anatase TiO$_2$ nanopowders with pore diameter about 6-10 nm (inset). (b) X-ray diffraction patterns of the mesoporous anatase TiO$_2$ nanopowders calcined at 450 °C for 2 h and P-25 calcined at 450 °C for 2 h.

Table 1 BET surface area and amount of adsorbed dye of the mesoporous anatase TiO$_2$ nanopowders (prepared by this study) calcined at 450 °C for 2 h and P-25 calcined at 450 °C for 2 h.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area (m$^2$/g)</th>
<th>Amount of adsorbed dye (mol/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoporous TiO$_2$</td>
<td>101</td>
<td>10.21 x 10$^{-8}$</td>
</tr>
<tr>
<td>P-25</td>
<td>54</td>
<td>5.68 x 10$^{-8}$</td>
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</tbody>
</table>

4. CONCLUSION

In summary, high surface area (about 180 m$^2$/g) anatase TiO$_2$ with mesoporous structure (pore diameter about 3-4 nm) were synthesized by hydrothermal method at 130 °C for 12 h. Mesoporous anatase TiO$_2$ nanopowders (prepared by this study) showed higher photocatalytic activity than the nanorods TiO$_2$, nanofibers TiO$_2$, mesoporous TiO$_2$ (prepared by sol-gel method), and commercial TiO$_2$ (P-25, JRC-01, and JRC-03). The $\eta$ of the cell using mesoporous anatase TiO$_2$ nanopowders (prepared by this study) was about 6.30 %, while $\eta$ of the cell using P-25 reached 5.82 %. This synthesis method providing a simple route to fabricate mesoporous anatase TiO$_2$ nanopowders with mild condition.
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6. REFERENCES


