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Fabrication of Dye-Sensitized Solar Cells with Hydrothermally-Synthesized TiO₂ Nanopowder Films

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Abstract. TiO₂ nanopowders were synthesized hydrothermally from TiCl₄ aqueous solution. Particle diameters could be varied in the range 5–65 nm by controlling the synthesis time and temperature. Dye-sensitized solar cells were fabricated using the powders and their power generation efficiencies were evaluated.

Introduction

Since their introduction by Grätzel [1], dye-sensitized solar cells (DSCs) fabricated using TiO₂ have attracted much attention as alternatives to Si-based solar cells because they can be fabricated without the need for large-scale plants.

Adsorption of a greater quantity of the sensitizing dye on the electrodes is expected to increase the conversion efficiency of DSCs. Therefore, there is a demand for porous electrodes that have larger surface area. Hydrothermal synthesis methods of TiO₂ nanoparticles from Ti aqueous solutions were reported. In most cases, the pH of the precursor solutions were adjusted by adding alkali metals, alkali earth metals, ammonia, or acids [2, 3]. The aim of this study is the synthesis of TiO₂ nanoparticles by rapid hydrothermal synthesis without adjustment pH of precursor solution. Moreover, nanoparticles generally agglomerate because of surface charges before they can be formed into electrodes. The synthesized nanoparticles were used as porous electrodes in DSCs without dry process, which has never been reported.

Experimental

TiCl₄ (Nacalai) was dropped on ice made from distilled water. The ice was thawed by the heat of dissolution. Finally, more distilled water was added to the solution to adjust the concentration to 0.1 mol dm⁻³ TiCl₄. The solution was colorless and transparent for more than 30 h at room temperature. A volume (100 cm³) of this solution was introduced into an autoclave reactor comprising a polytetrafluoroethylene inner vessel and a stainless-steel outer vessel weighing 225 and 3330 g and with thicknesses of 7.2 and 10.8 mm, respectively. The reactor was heated in an electric oven (Yamato, DR-22) for 1–12 h at 50–170 °C. After heating, the reactor was cooled under running water for 10 min, and then kept in a freezer for 1 h. By this process, orange translucent-white opaque suspensions were obtained. HNO₃ (Nacalai) were added to the suspensions for precipitation. Subsequently, the precipitates were separated by centrifugation and washed in distilled water to afford white pastes (Fig.1). The particle size distributions of these pastes were measured by the dynamic light scattering method (Otsuka denshi, FPAR-1000). The pastes were dried at 50 °C in a vacuum drier for 24 h. The obtained white blocks were milled and identified using an X-ray diffractometer (Shimadzu, XRD-6100).



Fig.1 Photograph of TiO₂ paste synthesized hydrothermally at 170 °C for 3 h.

The pastes (30 mg in the dry state) were dispersed in 30 cm³ of ethanol. Fluorine-doped tin oxide (FTO)-coated glasses (AGC Fabritech, A110U80) were attached to conductive wires and sealed with plastic tapes such that only a 1-cm square of their surface was exposed. Next, this assembly was connected to the anode, and a carbon plate was connected to the cathode of a high-voltage power supply (Anatech, Model-3860). The entire setup was immersed into the dispersion liquid. The FTO-coated glasses were laid on the bottom of a vessel and the carbon plate was placed above the glasses. A 30-V potential was applied across the electrodes for 10 min. The pastes were deposited on the FTO-coated glasses by electrophoresis. The glasses were subsequently dried at room temperature and normal pressure for 1 h and then sintered in an electric oven at 450 °C for 30 min. After cooling down to room temperature, they were dipped in 0.3 mmol dm⁻³ ruthenium organic complex (N₃, Kisco) in ethanol and left for 3 d to be dyed. The dye was strongly chemisorbed onto the TiO₂ surface. Thus, N₃-dyed TiO₂ nanoparticle porous thin films were obtained.

A dye-sensitized solar cell was assembled using a 10-mm² black opaque paper punched with a hole of diameter 6 mm (douser), the TiO₂ thin film (anode), a 10-mm² cellophane film punched with a hole of diameter 6 mm (spacer), and a 10 mm × 20 mm × 0.2 mm Pt plate (cathode) (Fig. 2). A few drops of 0.3 mol dm⁻³ LiI (Wako) and 0.03 mol dm⁻³ I₂ (Nacalai Tesque) solution (solvent: acetonitrile (Nacalai Tesque) with 3-methyl-2-oxazolidinone (Wako), 1:1 vol.%), which acted as an electrolyte, were added through the hole in the cellophane film. The cell was evaluated using a homemade system consisting of a Xe lamp (Ushio, SX-UI501XQ), a filter (Edmund Optics, 54517), an electrometer (Advantest, R8240), and a potentiostat (Hokuto Denko, HA301), which acted as the light source, IR-cut filter, generated potential and current logger, and electronic resistance, respectively. The data from the electrometer and the potentiostat were recorded using a homemade program on a personal computer via an A/D converter (Adtek System Science, aPCI-A57).

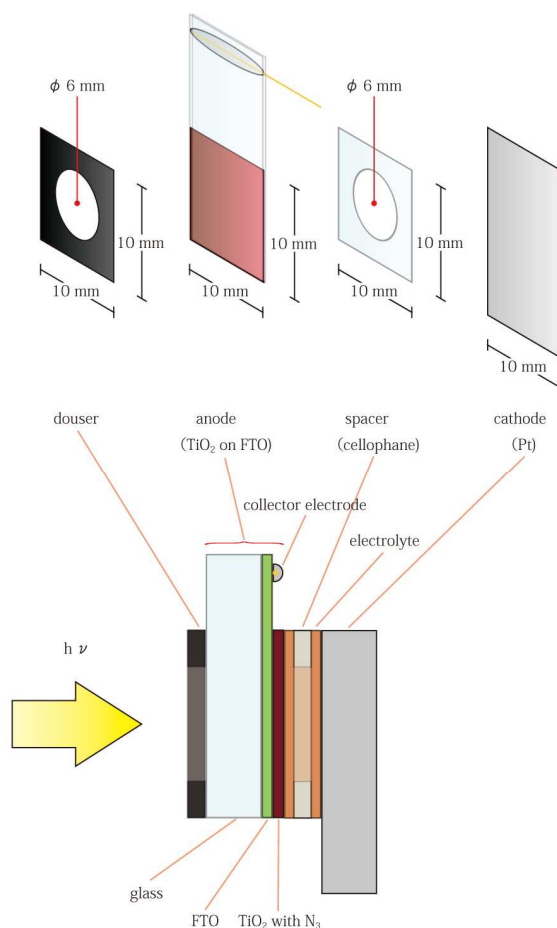


Fig.2 Illustrations of (top) individual parts of dye-sensitized solar cell and (bottom) side view of assembled cell.

Results and discussion

First, the hydrothermal synthesis was carried out at various temperatures (T) of 50, 75, 100, 125, 150, and 170 °C for 6 h. Fig.4 shows the XRD peaks of the powders. The peaks were found to be caused by a mixture of anatase-, brookite-, and rutile-type TiO₂. At a low temperature, the powders consisted of anatase- and rutile-type TiO₂. As the synthesis temperature increased, the heights of the peaks belonging to the rutile- and brookite-type TiO₂ decreased and increased, respectively. As the temperature increased, the peaks also became sharper. It is supported that the particle size increased with temperature (Fig. 3), where d represents the diameter of the particles. It is reported that DSCs that are fabricated using anatase-type TiO₂ can generate higher power than those based on rutile- or brookite-type TiO₂ [4, 5]. Therefore, the synthesis temperature was selected as 170 °C.

Next, the hydrothermal syntheses were carried out for various times (t) such as 1, 1.5, 2, 3, 6, and 12 h at 170 °C. Fig.6 shows the XRD peaks of the powders. Mainly, peaks belonging to anatase-type TiO_2 were found, and small peaks belonging to rutile- and brookite-type TiO_2 were also found. The alteration in the ratio when the synthesis time was varied was not determined. As shown by fig.5, the particle size d grew linearly with $\log(t)$. After 6 h, the particle size growth stopped. At that time, the yield was 92.5%. It is considered that the growth stoppage was ascribable to the drain of the precursor.

TiO_2 powders hydrothermally synthesized at 170 °C for 1, 2, and 6 h and ST-21 were suspended in water (Fig.7 left) and ethanol (Fig.7 right). The suspensions in water become more clouded with the increase in particle diameter ((a) < (b) < (c)). It was supported that the TiO_2 powders were sufficiently suspended, and therefore, they could not scatter light, considering that they were significantly smaller than the wavelength

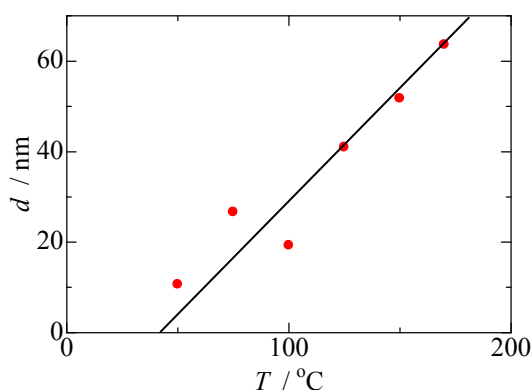


Fig.3 Diameters of synthesized TiO_2 nanoparticles for various temperatures. Synthesis time is 6 h.

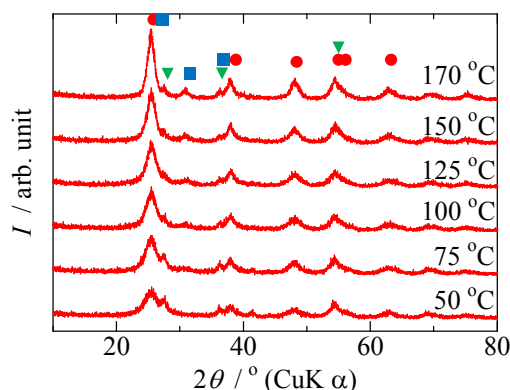


Fig.4 X-ray diffraction peaks of synthesized TiO_2 nanoparticles at various temperatures. Synthesis time is 6 h. Circles, squares, and triangles indicate the peaks of anatase-, brookite-, and rutile-type TiO_2 , respectively.

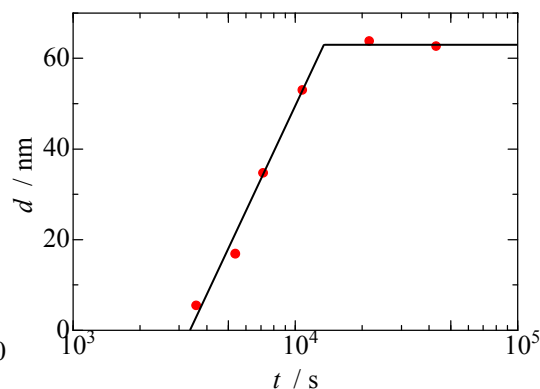


Fig.5 Diameters of synthesized TiO_2 nanoparticles for various times. Synthesis temperature is 170 °C.

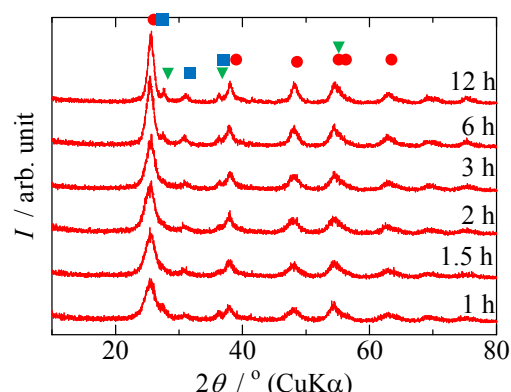


Fig.6 X-ray diffraction peaks of synthesized TiO_2 nanoparticles for various times. Synthesis temperature is 170 °C. Circles, squares, and triangles indicate the peaks of anatase-, brookite-, and rutile-type TiO_2 , respectively.

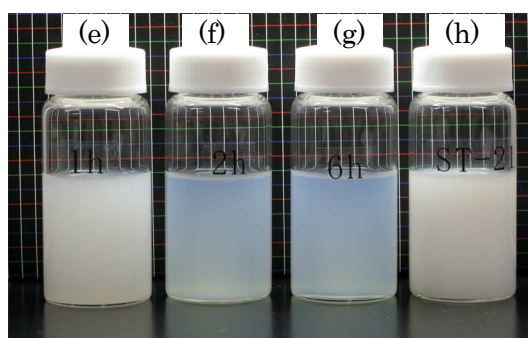
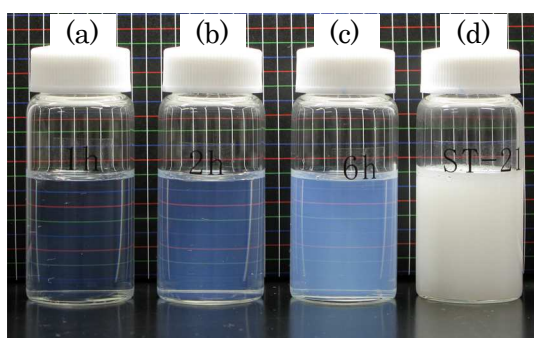


Fig.7 Photographs of TiO_2 suspensions in (left) water and (right) ethanol. In each photograph, starting from the left, TiO_2 powders synthesized at 170 °C for 1, 2, and 6 h as well as ST-21 were separately suspended.

of visible light. However, in ethanol, the solution in (e) was clouded, and those in (f) and (g) had almost the same amount of transparency. It possibly depended on the amount of water in the paste. The solution in (e) contained 30% water, and those in (f) and (g) contained 20% water. The difference in the amount of water influenced the surface charges on the TiO_2 particles. Although ST-21 had a particle diameter of 20 nm, it could not be suspended ((d), (h)).

In TiO_2 /ethanol suspensions, TiO_2 powders were deposited by the electrophoresis method on FTO-coated glasses (Fig. 8). Translucent films ((A) and (B)) were deposited in the suspension in (e) and (f), respectively. A transparent film was deposited in the suspension in (g). The parameters related to the power generation efficiency of DSCs are listed in Table 1. In this table, E_{OC} , J_{SC} , W_{Max} , E_{Max} , and J_{Max} represent the open-circuit potential, short-circuit current, maximum power, potential at W_{Max} , and current at W_{Max} , respectively. It was found that (C) generated power with the highest efficiency, although (A), which consisted of the smallest particles, could generate the highest amount of power. The porous film of (C) was transparent. In contrast, the films of (A) and (B) were cloudy. From the SEM images, the latter were observed to have cracks. The formation of local circuits because of these cracks is considered to cause the reduction in generated power. The decorrelation between the generation efficiencies and particle size were considered to cause to the decorrelation between the roughness and particle size by the cracks.

As a next step, the conditions for depositing transparent films should be determined. Then, the film thickness should be increased to ensure that it adsorbs a larger amount of dye.

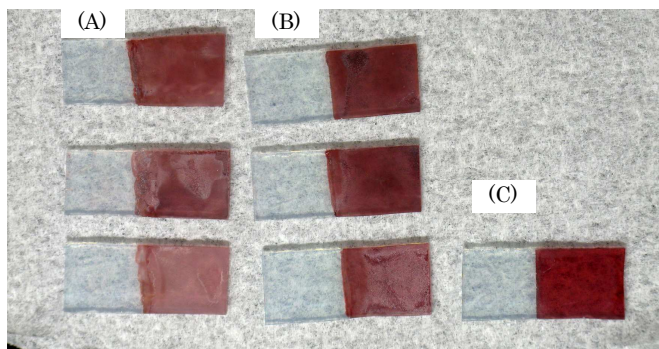


Fig.8 Photographs of TiO_2 porous electrodes.

(A), (B), and (C) were deposited by electrophoresis in (e), (f), and (g), respectively.

Table 1 Parameters related to power generation efficiency of dye-sensitized solar cells

Particle size [nm]	E_{OC} [mV]	J_{SC} [mA cm^{-2}]	Fill factor	Generation efficiency [%]	W_{Max} [mW cm^{-2}]	E_{Max} [mV]	J_{Max} [mA cm^{-2}]
5.4	667	2.24	0.67	1.00	1.00	515	1.96
34.6	705	1.08	0.72	0.552	0.552	564	0.979
63.7	625	4.39	0.60	1.64	1.64	444	3.70

Summary

TiO_2 nanopowders were hydrothermally synthesized from a TiCl_4 aqueous solution. Their particles were 5–65 nm in diameter for controlled synthesis time and temperature. They were effectively obtained by precipitation, the addition of acid, and subsequent centrifugation. They were dispersed in a dispersion medium once again. Porous electrodes of dye-sensitized solar cells were fabricated by the electrophoresis deposition method. The cells were evaluated for their power generation efficiencies. The transparent porous electrode having a 63.7-nm diameter exhibited the highest power generation efficiency.

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