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10% Efficiency Dye-sensitized Solar Cells Using P25 TiO_2 Nanocrystalline Electrode Prepared by a Bead-milling Method

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Dispersions of TiO_2 nanoparticles were prepared from titania powder (P25, Degussa) using a bead-mill method. The dispersion was controlled by the mixing time and was observed using dynamic laser-light scattering. TiO_2 screen-printing pastes were prepared from the TiO_2 dispersions for application as photoelectrodes in dye-sensitized solar cells (DSSCs). The coated nanocrystalline TiO_2 electrodes were evaluated using X-ray diffraction (XRD) and a haze meter. The shape and crystallinity of the TiO_2 nanoparticles were not changed, but the transparency was improved by the bead-milling process. However, aluminum contamination on the TiO_2 surface was found to increase with bead-milling time. A TiO_2 paste prepared from an optimized dispersion was used to fabricate a DSSC with 10% photoenergy-conversion efficiency.

Solar cells that convert the energy of sunlight directly into electricity have been developed as an alternative electricity generation technology to fossil fuels, of which utilization is becoming limited due to CO_2 emissions and the expected exhaustion of the resource. Therefore, the expansion and demand of solar cell systems as a renewable energy alternative is expected.

Solar cells are mainly developed using silicon, so that the cost of solar panels is rather high due to the high price of silicon. For cost effective solar cells, dye-sensitized solar cells (DSSCs) were proposed by Grätzel.[1] The best conversion efficiency of DSSCs is 11.1% reported by the SHARP group (Japan), as confirmed by the National Institute of Advanced Industrial Science (AIST) of Japan.[2]

Electrodes for DSSCs are produced from TiO_2 nanoparticles for increased dye absorption. The amount of dye adsorption corresponds to the specific surface area of the TiO_2 particles and the particle size; therefore, the dispersion conditions of the electrode coating paste is important for the resulting conversion efficiency. The dispersing condition of TiO_2 affects the transparency of the electrode.[3]

Although DSSC conversion efficiencies have been improved by changing the structure of nanocrystalline TiO_2 electrodes[4–7] and the crystallinity or purity of the TiO_2, which influence the conversion efficiency, a relationship between the dispersion condition of TiO_2 and the conversion efficiency of the cell has not yet been reported.

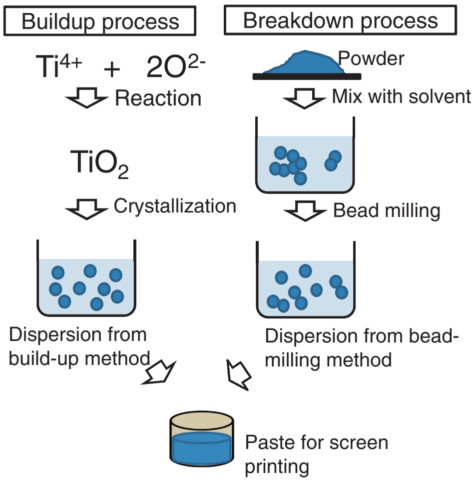

Figure 1. Conventional methods for the preparation of TiO_2 paste.

There are two methods for preparing TiO_2 dispersions; one is a buildup process including hydrothermal synthesis, and the other is a breakdown process using a stirred media mill (Figure 1). The buildup process has an advantage in that the size of the resultant particles is fine and that the particle distribution is uniform, although the production is expensive and mass production is also difficult. On the other hand, despite the broad particle distribution compared to the buildup method, the breakdown method is more suitable for mass production and for controlling the degree of dispersion, in addition to lower processing costs. In the breakdown process from TiO_2 nanopowder (P25, Degussa), 9.2% efficiency DSSCs have been fabricated by use of an alumina mortar;[3] however, bead-mill operation is most effective under wet conditions for future industrialization.[8,9]

In this study, dispersions of titania powder (P25, Degussa) were prepared using a bead mill. The TiO_2 nanoparticle diameter was changed during the dispersion process. The dispersions were then converted to screen-printing pastes, which were coated as nanocrystalline TiO_2 films for the photoelectrodes of DSSCs. It was confirmed that the particle dispersion in the paste could be regulated during the dispersion process, and the optimum particle size was obtained using the bead-milling method. DSSCs that exceed 10% conversion efficiency were

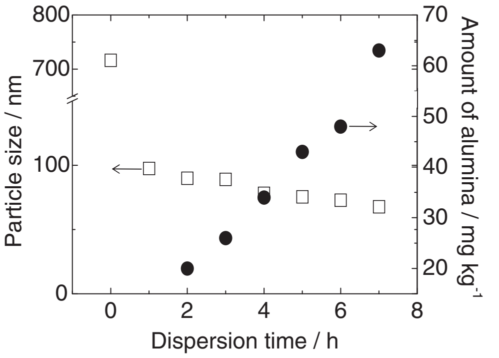

Figure 2. Change in particle size (□) and the amount of alumina (●) in the titania paste measured with dispersion time.

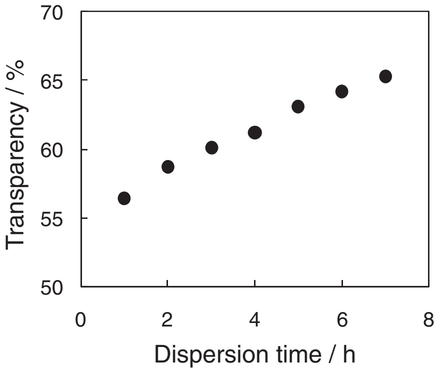

Figure 3. Relationship between transparency and dispersion time at 10 µm of coated layer.

fabricated using the screen-printing TiO_2 (P25) photoelectrode paste prepared from a TiO_2 dispersion with optimum conditions.

A bead mill (Ultra Apex mill UAM-2, Kotobuki Industries Co., Ltd.) was used as a milling system. The grinding vessel and agitator were made of zirconia toughened with alumina (ZTA). The vessel was 107 mm in diameter and 320 mm long, with a volume of 2000 cm^3. The top speed of the agitator was fixed at 8 $m\,s^{-1}$. The size of the milling beads used was 0.1 mm. The bead-filling ratio was set at 80 vol %. The sample for milling contained titania powder (Aeroxide TiO_2 P25, Degussa, Germany) and a small amount of dispersant. The dispersion samples were evaluated every 1 h up to a total milling time of 7 h. The dispersion progress was evaluated by measuring the particle size distribution using dynamic laser-light scattering (Zetasizer nano, Malvern instrument Ltd., U.K.). The crystallinity of the TiO_2 from the dispersed pastes was checked using X-ray diffraction (XRD; Mini Flex II, Rigaku, Japan), and the metal contamination was measured by inductively coupled plasma spectrometry (ICP, Optima 5300DV, Perkin-Elmer, U.S.A). The TiO_2 paste was coated onto glass plates and heated at 500 °C for 1 h in air. The transparency of the coated plates was measured using a haze meter (NH2000, Nippon Densyoku Industries Co., Ltd., Japan). According to the published paper,[3] the DSSCs were prepared.

Photovoltaic measurements were performed employing an AM 1.5 solar simulator. The power of the simulating light was calibrated to be 100 $mW\,cm^{-2}$ using a reference Si photodiode equipped with an IR-cutoff filter (Bunkou Keiki, Japan). Current–voltage (*I–V*) curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a digital source meter. The voltage step and delay time of the photocurrent were 10 mV and 40 ms, respectively.

It is necessary to disperse TiO_2 under optimum conditions to ensure a high conversion efficiency of the DSSC by maintaining the crystallinity of the TiO_2. Figure 2 shows the mean particle size of the 7-h milled dispersion measured by dynamic laser-light scattering and the amount of alumina in the paste measured by inductively coupled plasma mass spectrometry. The mean particle size decreased gradually with increased processing time. The amount of the alumina in the paste increases as dispersion time passes. It can be thought that the contamination from the milling beads may decrease the conversion efficiency.

XRD measurement confirmed that the TiO_2 peak remained unchanged after 7 h of milling. The crystallinity of the TiO_2 was unchanged by the bead-milling dispersion process employed in this study.

The pastes were coated on the FTO glass plates by screen printing and were then heated at 500 °C for 1 h. The transparency of the coated film increased with dispersion time (Figure 3) because the mean particle size of the TiO_2 is reduced during the dispersion process; therefore, the amount of light scattering by TiO_2 particles decreases. Furthermore, the specific surface area increases for well-dispersed TiO_2 particles, because the amount of contact between the particles decreases. Therefore, it is thought that TiO_2 particles with a large specific surface area could contribute to improvement of the conversion efficiency by increasing the amount of dye adsorption.

Figure 4 shows the photovoltaic–characteristic variations of open-circuit photovoltage (V_{oc}) (a), short-circuit photocurrent density (J_{sc}) (b), fill factor (*FF*) (c), and conversion efficiency (η) (d). The nanocrystalline TiO_2 layer thickness in single layer and double layers were 12 ± 1 and 15 ± 1 µm, respectively (double layers included scattering layer about 3 µm). The V_{oc} decreased linearly with dispersion time; however, the changing ratios in single layer and double layers were 6% and 3%, respectively. The V_{oc} falls along with dispersion time because the contact area of TiO_2 to electrolyte may increase.

The *FF* has a tendency to decrease as a whole though it varies in the initial part about the double layers, and the changing ratios in single layer and double layers were only 1% and 3%, respectively. The *FF* of double layers increases as dispersion time passes because the diffusion of electrolyte may increase. However, *FF* of single layer is constant because the current value is low and the influence of the power loss by IR drop of the voltage is small. Since changes in V_{oc} and *FF* are small, the conversion efficiency reflects variance of J_{sc} because variance of J_{sc} is larger than V_{oc} and *FF*.

As value for single layer, the conversion efficiency reached the highest at 3 h of dispersion time. As for double layer, on the other hand, the conversion efficiency reached the highest value at 6 h. When dispersion time becomes longer than 3 h, the single layer cannot convert incident light into energy well because the transmitted light increases due to the permeability of the coated layer. On the other hand, the conversion efficiency increases for double layer when dispersion time is longer than 3 h. Hence, the incident light in double layer can be effectively utilized in the effect of the scattering layer when the transparency of light-

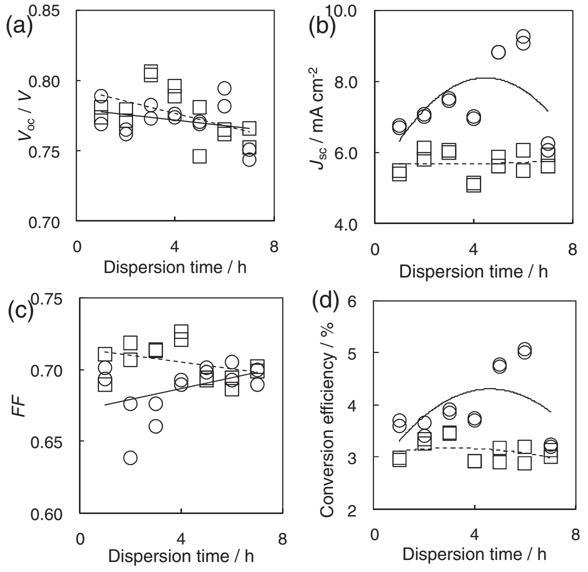

Figure 4. Photovoltaic–characteristics relationship with dispersion time. Single layer (□) and double layers (○): (a) V_{oc}, (b) J_{sc}, (c) *FF*, and (d) conversion efficiency. The solid and dotted lines were fitted to the average data of double layers and single layer, respectively. (a) and (d) are fitted by linear appoximation. (b) and (d) are fitted by polynomial approximation. Dye: N719 (Solaronix). Electrolyte: 0.60 M 1-butyl-3-methylimidazolium iodide (BMII), 0.03 M I_2, 0.10 M guanidinium thiocyanate, and 0.50 M 4-*tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (85:15 v/v).

absorbing layer is high. However, the conversion efficiency decreases when dispersion time is longer than 6 h, because of too much contamination in the TiO_2 dispersion (Figure 2).

After the optimization of TiO_2 condition as shown in Figure 4, the purification of dye and electrolyte was optimized. Figure 5 shows the optimum conversion efficiency obtained using TiO_2 paste prepared by 6 h bead-milling dispersion with the double-layered structure. The characteristic photovoltaic parameters of short-circuit density, open-circuit voltage, fill factor, and photovoltaic conversion efficiency are presented in Figure 5. TiO_2 paste prepared from nanocrystalline TiO_2 powder (P25) under optimum dispersion conditions resulted in a DSSC with a conversion efficiency over 10%. Furthermore, a higher conversion efficiency can be expected by optimization of the layer structure of the TiO_2 film and the dye.

In summary, the dispersivity of TiO_2 in the dispersion could be controlled by employing bead-mill processing. The mean particle size decreased with increasing dispersion time, and the transparency of the coated film prepared from the screen-printing TiO_2 paste also increased with dispersion time. Therefore, the TiO_2 aggregates were crushed to the optimum size for the production of DSSC photoelectrodes (providing conversion efficiency over 10%); however, the crystallinity of the TiO_2 was maintained, as confirmed by XRD.

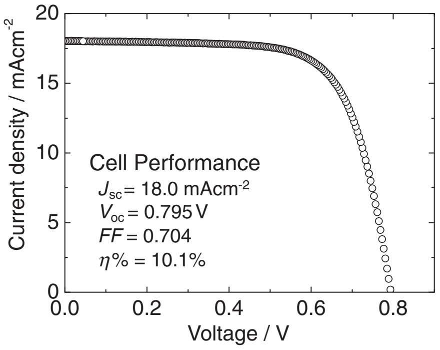

Figure 5. *I*–*V* curve for a DSSC fabricated using TiO_2 paste prepared under optimum dispersion conditions. The chromatographic purification of N719 was conducted three times on a column of Sephadex LH-20 as described in the literature.[10,11]

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