Low-temperature Fabrication of Nano-porous TiO_2 Layers for Dye-sensitized Solar Cells. Fabrication of Ion-diffusion Paths

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In dye-sensitized solar cells, it is required to build up both of ion paths and electron paths in TiO_2 layers for low-temperature fabrication process. In this report, ion paths are focused on. Semiconductive layers are composed of TiO_2 nanocrystals (P25) and needle-shape TiO_2 crystals (FTL 100). By adding 20% of the needles into P25, photocurrent increased from 5.3 to 7.7 mA/cm^2. Pore distributions, surface areas, Cole–Cole plot and currents passing through TiO_2 layers were measured. These results suggest that the increase in the photocurrent is associated with the formation of ion paths in TiO_2 layers.

Dye-sensitized solar cells (DSSC) have been paid great attentions as the next generation of solar cells. The photoenergy conversion efficiencies reached 10%.[1] Another interest on DSSCs is fabrication of plastic type DSSCs. Normally, temperatures more than 450 °C are required to make porous TiO_2 layers. There are two reasons for 450 °C baking. One is to make necking between TiO_2 nanocrystals which promotes electron diffusions in porous TiO_2 layers.[2] The other is to make effective ion paths in porous TiO_2 layers. TiO_2 pastes usually contain polymers which are removed by heating. This makes ion paths through which I^- and I_3^- can diffuse effectively. Plastic substrates such as poly(ethylenetelephthalate) (PET) can not withstand the heat more than 150 °C. Therefore, low-temperature heat treatment is required. There are a lot of reports on low-temperature processes targeting TiO_2 necking. It has been reported that energy conversion efficiencies for DSSCs baked at lower temperatures were not as good as those baked at higher temperatures.[2–5] Minoura and his co-workers treated TiO_2 layers with steam in an autoclave at 100 °C and obtained a crack-free porous thick TiO_2 films.[6] They have reported 6.23% efficiency at 100 mW/cm^2 light intensity. Miyasaka and his co-workers have reported electrophoretically deposited TiO_2 layers. After TiO_2 films were post-heated at 80 °C under titanium alkoxide vapor, they have reported 4.1% energy conversion efficiency under 100 mW/cm^2 light intensity.[7] They have also reported binder free processes to fabricate TiO_2 layers.[8] Lindstrom and his co-workers have reported the method to form mechanically stable, electrically conducting porous films by compressing TiO_2 layers. They reported 5.2% at 0.1 sun light intensity.[9–11] We have reported low accelerated EB exposures to promote TiO_2 necking.[12] However, as far as I know, there is no report on low-temperature processes focusing on ion path fabrication in TiO_2 layers. In order to fabricate ion paths in TiO_2 layers, 50 to 100% of polymers against TiO_2 particles are commonly added to the paste for 450 °C baking process, during which process, polymers are burned out. In case of low-temperature process, TiO_2 pastes must not contain a lot of polymers because these polymers are not removed by the low-temperature baking. It has been reported that photoenergy conversion efficiencies for DSSCs fabricated at low-temperature are lower at 100 mW/cm^2 exposure than at 24 mW/cm^2 exposure.[8] Low photoenergy conversion efficiencies and the nonlinearity of J_{SC} should be actually associated with low diffusion coefficients of electrons in porous TiO_2 layers.[2] Our purpose is to examine the possibility of whether or not ion diffusion in nanoporous TiO_2 layers may influence the photocurrents. In order to fabricate ion paths in TiO_2 layers simply, we added needle-shape TiO_2 crystals in TiO_2 layers. The idea is explained in Figure 1. The bottom line is to fabricate both of main streams and branches for ion diffusions without the aid of polymers.

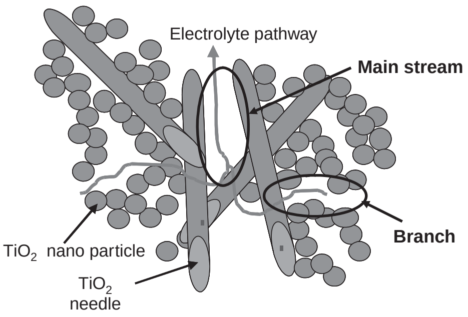

Figure 1. Nanoporous TiO_2 layers with main stream and branch.

P25 (Nippon Aerosil Corp.) and needle-shape TiO_2 crystal (Rutile, diameter:around 0.1 µm, length: about 1 µm, Ishihara Techno Corp.) were mixed in water–methanol solvents (1:1 (w/w)). The mixture was well dispersed in a mortar. The paste was spread on SnO_2/F layered glasses (30 ohm/square, Nippon Sheet Glass Co., Ltd). The substrates were baked at 150 °C to fabricate 5-micron-thick TiO_2 layers. The substrates were immersed in *cis*-di(thicyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) (Kojima Kagaku) solution in ethanol (0.1%). Aqueous H_2PtCl_6 solution was spin-coated on SnO_2/F layered glass substrates and were heated at 450 °C to deposit Pt on the substrates. They were employed as the counter electrodes. A plastic sheet (HIMILAN, Mitsui-Dupont Co., Ltd, 50 micron) was inserted between the TiO_2 electrode and the counter electrode as spacers. Electrolyte (E-1) consisting of 40 mM of I_2, 500 mM of LiI and *t*-butylpyridine (*t*-BuPy) in acetonitrile was injected in the cell at room temperature. The cell area was 1 cm^2. Photoelectrochemical measurements were performed using a solar simulator (YSS-50A, Yamashita Denso Co., Ltd., AM 1.5, 100 mW/cm^2).

Table 1 summarizes the results. Short circuit current (J_{SC}) increased from 5.3 mA/cm^2 to 6.3 and 7.7 mA/cm^2 when 10%

Table 1. Photovoltaic performances and surface areas

Abbreviation	Particle:Needle[a] (w/w)	V_{OC} /V	J_{SC} /mA/cm^2	ff	η /%	Surface area /m^2/g
T-0	100:0	0.71	5.3	0.61	2.3	64
T-10	90:10	0.76	6.3	0.58	2.8	48
T-20	80:20	0.70	7.7	0.55	2.9	51
T-30	70:30	0.72	6.3	0.48	2.2	43

[a] P25:FTL100

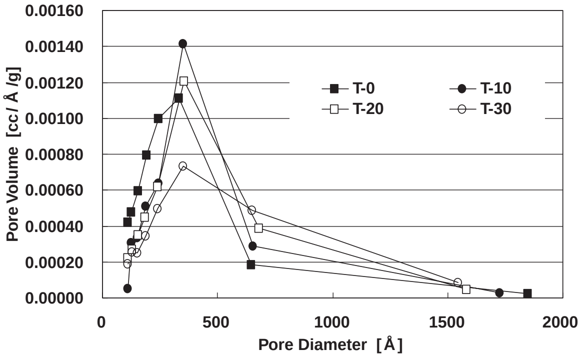

Figure 2. Pore size distribution.

and 20% of needle-shape crystals (FTL100) were added. However, when 30% of FTL100 was added, J_{SC} decreased to 6.3 mA/cm^2. Open-circuit voltage (V_{OC}) varied in the range between 0.71 and 0.76 V. Efficiency had a maximum value at 20% addition of needle-shape crystals. The surface area tends to decrease from T-0 to T-30 within a small experimental error. It is reasonable to explain that the decrease in J_{SC} for T-30 was caused by the decrease in the surface areas of TiO_2 layers. Pore of T-0 film was distributed in the range from 20 to 60 nm. When 30% of needle shape crystal was added (T-30), large size pore increased and the pore size distribution was broadened to 20–100 nm. These results suggest that both of nanopores and large pores were fabricated by the addition of needle-shape crystals.

In order to examine whether or not ion diffusion in porous TiO_2 was improved, currents through porous TiO_2 layers were measured as shown in Figure 3. The difference of the cell A from DSSC is that Pt sheet is fabricated under the TiO_2 layers (TiO_2/Pt electrode). When the positive potential is applied on the TiO_2/Pt electrode against the counter Pt electrode (Figure 3), I^- species diffuse through the ion paths in TiO_2 layers to reach the Pt sheet and give electrons to the Pt sheet of TiO_2/Pt electrodes to form I_3^-. I_3^- species diffuse out from the Pt sheet of TiO_2/Pt electrodes through ion paths in TiO_2 layers. This ion movement is the same as that of DSSC cells. Most of the electrochemical reactions occur only on the Pt sheet of TiO_2/Pt, not on TiO_2 surfaces, because TiO_2 is n-type semiconductor. If these ion diffusions were disturbed in porous TiO_2 layers, photocurrents should decrease.

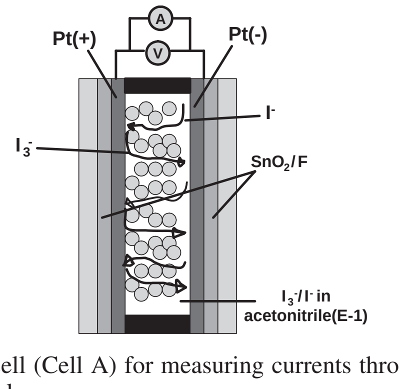

Figure 3. Cell (Cell A) for measuring currents through porous TiO_2 relatively.

When positive potential was applied on TiO_2(T-0)/Pt electrodes, then current was 23.6 mA/cm^2 at 1.0 V. In case of TiO_2(T-20)/Pt, the current became 36.4 mA/cm^2 at 1.0 V. The results suggested that current through TiO_2 layers increased when needle-shape TiO_2 was added.

In Cole–Cole plot, a semicircle assigned to electron charge-transfer resistances within TiO_2 layers (at around 1 kHz) were 10–12 ohms for all DSCs.[13–15] This suggests that charge-transfer resistances within TiO_2 layers did not change when FTL100 was added at least up to 30%. From these results, we concluded that the increases in the J_{SC} were brought about by fabrication of ion paths in TiO_2 layers when needle-shape crystals were added in the TiO_2 layers. We also expect that this would be more effective for increasing J_{SC} of DSSCs using high-viscosity electrolytes such as ionic liquids.

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