

Research

Fabrication of Screen-Printing Pastes From TiO_2 Powders for Dye-Sensitised Solar Cells

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A preparation technique of TiO_2 screen-printing pastes from commercially-available powders has been disclosed in order to fabricate the nanocrystalline layers without cracking and peeling-off over 17 μm thickness for the photoactive electrodes of the dye-sensitised solar cells. A conversion efficiency of 8.7% was obtained by using a single-layer of a semi-transparent- TiO_2 film. A conversion efficiency of 9.2% was obtained by using double-layers composed of transparent and light-scattering TiO_2 films for a photon-trapping system. Copyright © 2007 John Wiley & Sons, Ltd.

KEY WORDS: titanium dioxide; nanocrystalline electrode; dye-sensitised solar cells

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INTRODUCTION

Dye-sensitised solar cells (DSCs) are currently attracting academic and commercial interest as regenerative low-cost alternatives to conventional solid state devices.^{1,2} So far, the best performing nanocrystalline- TiO_2 electrodes have been fabricated by hydrothermal autoclaving and screen-printing deposition.^{3–5} Screen-printing of TiO_2 is a widespread industrially-applied method because of the fast-printing technique and of the coating facility with fine controlling of the position and thickness. Other applied fields are gas sensors (humidity, O_2 , H_2 , NO_x , CH_x , CO , etc.), ion sensors, piezoelectric devices, microfiltration membranes, Gamma-radiation sensors, electroluminescent devices, electrochromic display, antireflection coatings on silicon solar cells, microwave applications, photocatalyst coatings and so on. The nontoxicity of titanium dioxide, which is used in paints, cosmetics and health care products, adds advantages to the fields.

The key point on the screen-printing is the quality and characteristics of TiO_2 paste. For the best-performing TiO_2 electrodes, the synthesis of TiO_2 paste involves hydrolysis of $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ in water at 250°C (70 atms) for 12 h, followed by conversion of the water to ethanol by three-times centrifugation. Finally, the ethanol is exchanged with α -terpineol by sonication and evaporation.³ Totally, it takes 3 days. Such a long-time procedure of TiO_2 pastes is economically unsuitable for industrial production and has to be reduced. Towards this goal, several reports were published in order to fabricate screen-printing paste from a commercially-available TiO_2 powder (P25, Degussa).^{6–9} Most of the pastes were based on water and alcohols, which induce TiO_2 aggregation and yielding poorly reproducible results in long-term experiments. On the other hand, α -terpineol-based

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pastes^{3–5} are very stable at long-term and give very reproducible results for several years. However, a reported paste made from P25 and α -terpineol did not give better DSCs than that of a water-based paste.⁹

In this study, we have developed a new procedure which takes only 4 h to produce TiO₂ pastes with α -terpineol from commercially-available powders, resulting in DSCs with *ca.* 9% conversion efficiencies. Moreover, the most important point of this work is to utilise the commercially-available TiO₂ particles for the high-efficiency DSCs, because the synthesis of the homemade TiO₂ particle demands the delicate techniques and consequently the different batch of TiO₂ particle might give different results. For the reproducible results, therefore, it is important to investigate a new fabrication method of TiO₂ paste from commercially-available particles. This report will be of great help for the people who are engaged with DSCs.

EXPERIMENTAL

Materials

Three kinds of commercially-available TiO₂ powders were used: P25 (av. 30 nm by Brunauer-Emmett-Teller (BET), 80% anatase ($d = 21$ nm) and 20% rutile ($d = 50$ nm), via TiCl₄-fumed gas synthesis, Degussa, Germany); ST21 (av. 25 nm by BET, 100% anatase, via sulfuric-acid synthesis, Ishihara Sangyo, Japan); ST41 (av. 160 nm by BET, 100% anatase, via sulfuric-acid synthesis, Ishihara Sangyo, Japan). Two kinds of pure powders of ethyl celluloses (5–15 mPas at 5% in toluene:ethanol/80:20 at 25 °C, #46 070, Fluka; 30–50 mPas at 5% in toluene:ethanol/80:20 at 25 °C, #46 080, Fluka) were dissolved beforehand in an ethanol solution (these powders of ethyl cellulose don't contain toluene and ethanol which were mixed with ethyl cellulose just to show the specification results of viscosity). Each concentration of the ethyl cellulose was 5 wt%: the total amount of ethyl celluloses was 10 wt% in ethanol.

4-*tert*-butylpyridine (Aldrich), acetonitrile (Fluka) and valeronitrile (Fluka) were purified by vacuum distillation. Guanidinium thiocyanate (Aldrich) and H₂PtCl₆ (Fluka) were used as received. H₂O was purified by distillation and filtration (Milli-Q). TiCl₄ (Fluka) was diluted with water to 2 M at 0 °C to make a stock solution, which was kept in a freezer and freshly diluted to 40 mM with water for each TiCl₄ treatment of the F-doped tin oxide (FTO) coated glass plates. Iodine (99.999%, Superpur[®], Merck) was used as received. The synthesis of *cis*-di(thiocyanato)-*N,N'*-bis(2,2'-bipyridyl-4-carboxylic acid-4'-tetrabutylammonium carboxylate) ruthenium (II) (**N-719**) and butylmethylimidazolium iodide (BMII) were reported in our previous paper.^{10,11} The chromatographic purification of N-719 was carried out three times on a column of Sephadex LH-20 using the following procedure.^{4,5}

Preparation of TiO₂ paste

The fabrication scheme for TiO₂ pastes was described in Figure 1. At each step, liquids were added drop by drop into an alumina mortar, which is more stable than a porcelain one. The diameter of the mortar was *ca.* 20 cm. The condition was in the ambient air at room temperature. The TiO₂ powders stuck on the inside of the mortar should be removed by a plastic spatula in order to grind large aggregates. The TiO₂ dispersions in the mortar were transferred with excess of ethanol (100 ml) to a tall beaker and stirred with a 4 cm long magnet tip at 300 rpm. The ultrasonic homogenisation was performed with using a Ti-horn-equipped sonicator (Vibra cell 72408, Bioblock scientific). Anhydrous terpineol (Fluka) and the mixture solution of two ethyl celluloses in ethanol were added, followed by stirring and sonication. The contents in dispersion were concentrated by evaporator at 35 °C with 120 mbar at first. The pressure was evacuated until 10 mbar. The pastes were finalised with a three-roller-mill grinder (EXAKT).

In this scheme (Figure 1), the coexistence of water and acetic acid was important. We tried another combination with nitric acid, hydrochloric acid, acetyl acetone, polyethylene glycol, triton X-100 and so on. Without water and/or acetic acid, however, the porous-TiO₂ layers over 10 μ m thickness were mechanically unstable and did not keep the structure after sintering due to the large cracks and peeling-up from substrate.

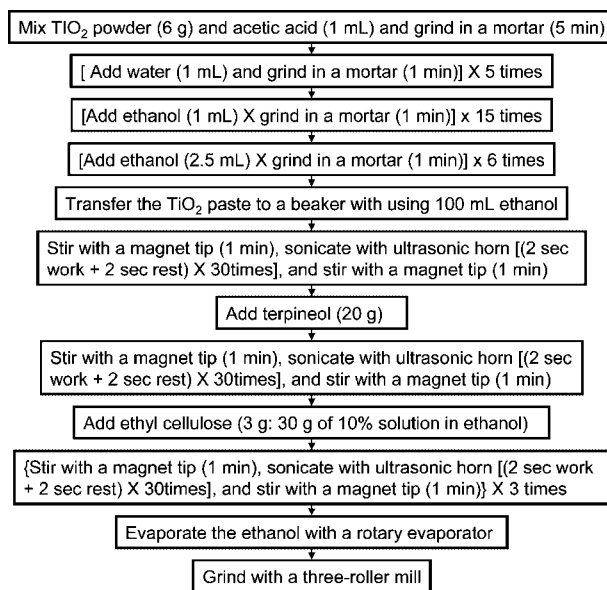
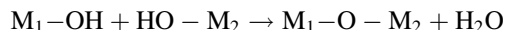


Figure 1. Fabrication scheme of screen-printing paste from a nanocrystalline-TiO₂ powder

We speculate the reason as below. In order to make a good connection between TiO₂ particles and between a TiO₂ particle and SnO₂ surface, hydroxides (–OH) have to be on the surface and make strong chemical bonding between each other by dehydration at sintering:



where, M₁ shows a titanium atom on a surface of a particle and M₂ shows a titanium atom of another particle or a tin atom on a plate of transparent conductive oxide (TCO) substrate (F-doped tin oxide (FTO) glass). The water added at first can make the surface covered by hydroxides. At the same time, each particle has to be isolated from each other and not to be aggregated. The aggregates in matrix can make large shrinkage of the film at the sintering, resulting in the peering-off from the TCO substrate. The acetic acid can be adsorbed on the surface of TiO₂ and prohibits each particle from the aggregation. At the same time, the proton (H⁺) of acid can also be adsorbed on the surface and shifts the Zeta potential to positive, resulting in repelling the particles from each other.

About the reproducibility, as long as the timing of adding, mixing and grinding the materials in the mortar is kept up, the result is quite reproducible (the data was not shown). However, by changing the timing, it can change. For example, if we add all of the ethanol in one time, it is very difficult to remove the aggregate. The paste can be a film peeled-off from the substrate or be a DSC electrode with a low photovoltaic efficiency.

Preparation of nanocrystalline-TiO₂ electrodes

To prepare the DSC working electrodes, the FTO glass used as current collector (Solar 4 mm thickness, 10 Ω/□, Nippon Sheet Glass, Japan) was first cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. After treatment in a UV-O₃ system (Model No. 256–220, Jelight Company, Inc.) for 18 min, the FTO glass plates were immersed into a 40 mm aqueous TiCl₄ aqueous solution at 70°C for 30 min and washed with water and ethanol. A layer of paste was coated on the FTO glass plates by screen-printing (90T, Estal Mono, Schweiz. Seidengazefabrik AG Thal), kept in a clean box for 3 min with ethanol so that the paste can relax to reduce the surface irregularity and then dried for 6 min at 125°C. The screen characteristics are as

follows: material, polyester; mesh count, 90T mesh/cm (or 230T mesh/inch); mesh opening, 60 μm ; thread diameter, 50 μm ; open surface, 29.8%; fabric thickness, 83 μm ; theoretical paste volume, 24.5 $\text{cm}^3 \text{m}^{-2}$; K/KS volume, 17.0 $\text{cm}^3 \text{m}^{-2}$; weight, 48 g m^{-2} . This screen-printing procedure (with coating, storing and drying) was repeated to change the thickness of the nanocrystalline-TiO₂ working electrode. For the single-layer electrode, the TiO₂ paste of ST21 was used, resulting in a light-scattering film. For the double-layer electrode, the paste of P25 for the transparent layer was coated by screen-printing and dried at 125°C, and then, the second layers of ST41 for the light-scattering layer were deposited by screen-printing to 4–5 μm thickness. The electrodes coated with the TiO₂ pastes were gradually heated under an airflow at 325°C for 5 min, at 375°C for 5 min, at 450°C for 15 min and 500°C for 15 min. After sintering, the surface area of the TiO₂ electrodes was measured precisely by a scanner with 600 dpi resolution in grey mode, followed by integration of the resulting image.⁴

DSC assembling

After the size measurement, the TiO₂ film was treated with 40 mM TiCl₄ solution as described above, rinsed with water and ethanol and sintered at 500°C for 30 min. At 80°C in the cooling, the TiO₂ electrode was immersed into a 0.5 mM N-719 dye solution in a mixture of acetonitrile and *tert*-butyl alcohol (volume ratio: 1:1) and kept at room temperature for 20–24 h to complete the sensitizer uptake.

To prepare the counter electrode, a hole was drilled in the FTO glass (LOF Industries, TEC 15 Ω/\square , 2.2 mm thickness) by sand blasting. The perforated sheet was washed with H₂O as well as with a 0.1 M HCl solution in ethanol and cleaned by ultrasound in an acetone bath for 10 min. After removing residual organic contaminants by heating in air for 15 min at 400°C, the Pt catalyst was deposited on the FTO glass by coating with a drop of H₂PtCl₆ solution (2 mg Pt in 1 ml ethanol) and repeating the heat treatment at 400°C for 15 min.

The dye-covered TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of 25 μm thickness made of the ionomer Surlyn 1702 (Dupont). The aperture of the Surlyn frame was 2 mm larger than that of the TiO₂ area and its width was 1 mm. A drop of the electrolyte, a solution 0.60 M BMII, 0.03 M I₂, 0.10 M guanidinium thiocyanate and 0.50 M 4-*tert*-butylpyridine in the mixture of acetonitrile and valeronitrile (volume ratio: 85:15) was put on the hole in the back of the counter electrode. The electrolyte was introduced into the cell via vacuum backfilling. The cell was placed in a small vacuum chamber to remove inside air. Exposing it again to ambient pressure causes the electrolyte to be driven into the cell. Finally, the hole was sealed using a hot-smelt ionomer film (Bynel 4702, 35 μm thickness, Du-Pont) and a cover glass (0.1 mm thickness).

Photovoltaic measurement of DSC

Light reflection losses were eliminated using a self-adhesive fluorinated polymer film (ARKTOP, ASAHI GLASS) that served at the same time as a 380 nm UV cut-off filter. Photovoltaic measurements employed an AM 1.5 solar simulator. The power of the simulated light was calibrated to be 100 mW cm^{-2} by using a reference Si photodiode equipped with an IR-cutoff filter (KG-3, Schott), which was calibrated at three solar-energy institutes (ISE (Germany), NREL (USA), SRI (Switzerland)).⁴ I-V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. The voltage step and delay time of photocurrent were 10 MV and 40 ms, respectively.

RESULTS AND DISCUSSION

Morphology of screen-printed TiO₂ films

Figure 2 shows SEM pictures of porous TiO₂ films. We can notice that the particles of P25 contained small particles (anatase, 20 nm) and large particles (rutile, 40 nm). Compared with the pictures of TiO₂ films made via

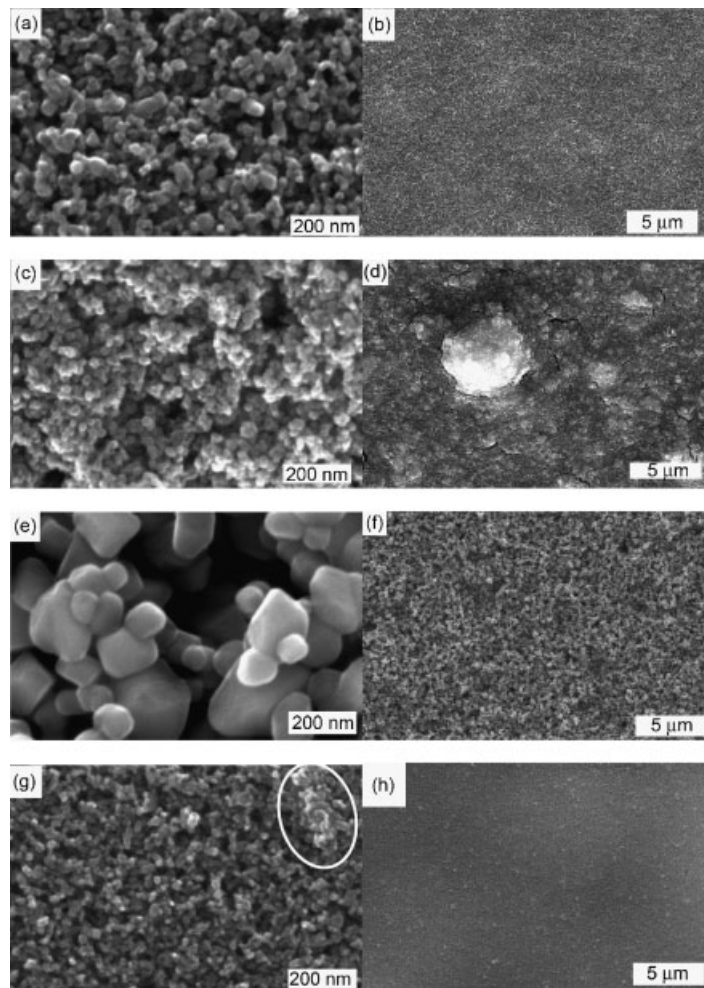


Figure 2. SEM photographs of porous TiO_2 films showing the surface morphology of P25 (a, b), ST21 (c, d), ST41 (e, f) and homemade TiO_2 ($d=20$ nm) (g, h) with two types of magnification: $120000\times$ (a, c, e, g) and $5000\times$ (b, d, f, h)

colloidal synthetic routes (Figure 2g and h), the P25 film contained no aggregates (Figure 2a), and was dispersed homogeneously over the large area (Figure 2b). On the other hand, ST21 showed the small aggregates (*ca.* 100 nm, Figure 2c) and the large aggregates (micron-meter order, Figure 2d). The large aggregates of ST21 were very difficult to be broken by this procedure and gave small cracks in the porous TiO_2 layer (Figure 2d). The difference of the morphologies between P25 and ST21 was due to the synthesis method: fumed- TiCl_4 and sulphuric-acid routes, respectively. ST41 contained 50–200 nm large particles (Figure 2e). The average was 160 nm from BET data (measured by Ishihara Sangyo). Although ST41 also was made by the sulphuric-acid synthesis, this layer was homogeneous over the large area (Figure 2f). Hence, the aggregations between ST41 particles did not affect the surface morphology on a large scale. For the comparison with homemade TiO_2 , we added the SEM pictures (Figure 2g and h). Although the aggregates about 200 nm existed (in a white circle of Figure 2g) and we can find small dots in Figure 2h from the aggregate, the surface was very smooth and uniform over the large area (Figure 2h).

Figure 3 shows cross sections of nanocrystalline- TiO_2 layers by surface-profiling method (Alphastep 550). Each layer was the single screen-printing using a 90T mesh. The layer of P25 and ST41 was relatively flat

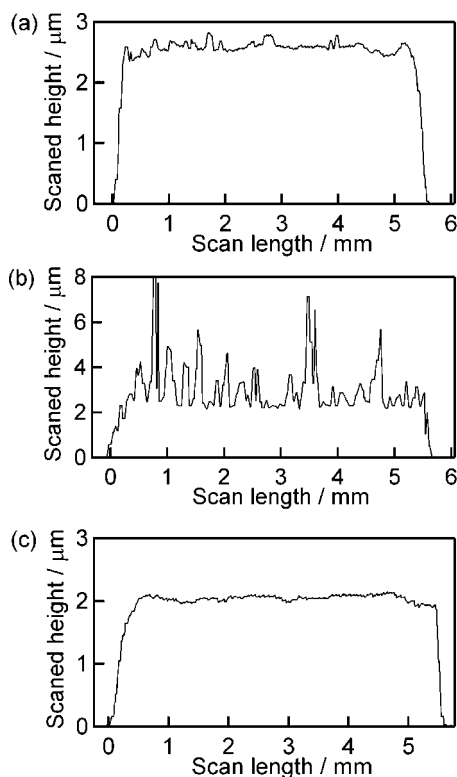


Figure 3. Cross sections of nanocrystalline-TiO₂ layers by surface-profiling method (Alfastep550): P25 (a), ST21 (b) and ST41 (c)

compared with that of ST21. This phenomenon reflected the morphology which was observed by SEM (Figure 2). The flatness of P25 and ST41 layers reflect the homogeneous dispersion of particles. On the other hand, the roughness of ST21 layer reflects the aggregations (Figure 2d).

Figure 4a shows the photograph of screen-printed layers with a background of garden plants. The P25 film was transparent and pale blue. We can see the clear image of the background. The ST21 film was semi-transparent and we can see slightly the images of background. The ST41 was opaque and completely white and we cannot see any images through the film. Figure 4b shows the transmittance spectra of screen-printed TiO₂ layers used in Figures 3 and 4a. The P25 layer transmitted 60% of incident light above 480 nm wavelength and diffused the shorter wavelength effectively. Therefore, the P25 layer was pale blue (Figure 4a). The transmittance of ST21 increased linearly from 378 to 820 nm wavelength, and the transmittance at 820 nm was half that of P25. ST41 blocked the incident light below 600 nm wavelength and let the incident light slightly through above that. For the comparison with homemade TiO₂, we added the data of transmission, which shows the higher transparency of the homemade TiO₂ layer than those of commercially-available TiO₂ powders. However, if 100%-anatase nanoparticles made by fumed-TiCl₄ synthesis is available, more highly-transparent TiO₂ layer can be fabricated.

It has been reported that particles over 100 nm can diffuse visible light effectively.^{12–14} Hence, ST41 (av. 160 nm) was able to diffuse visible light. This is the reason why the layer of ST41 was white and opaque (Figure 4). On the other hand, the particle sizes of P25 (av. 21 nm) and ST41 (av. 20 nm) were close. Hence, the optical difference between layers of P25 (transparent) and ST21 (hazy) (Figure 4) arises from the aggregates and the roughness, acting as light-scattering centres (Figures 2 and 3). The difference of morphologies was due to the synthetic variation: a liquid-phase synthesis for ST21 and a gas-fumed synthesis for P25.

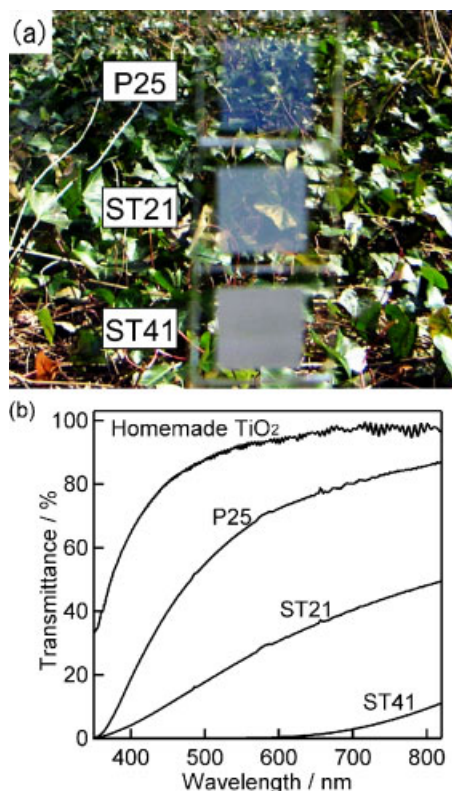


Figure 4. A picture (a) and transmittance spectra (b) of screen-printed nanocrystalline-TiO₂ layers. The transmittance measurements were performed with cover glass plates which were attached on the surface of TiO₂ layer, and the pores in nanocrystalline-TiO₂ layers were filled with butoxyacetonitrile to decrease the light-scattering effect. The optical back ground for (b) was obtained by using the same FTO/glass substrate, butoxyacetonitrile and the cover glass plate

DSC Photovoltaics related with thickness of nanocrystalline-TiO₂ electrodes

In order to fabricate DSCs, the TiO₂ pastes were coated by screen-printing on FTO/glass substrates and assembled to DSC. For the high-efficiency DSC, therefore, we applied P25 and ST41 to transparent and light-scattering layers in double-layer photon-trapping system as reported, respectively.^{3–5} Since the ST21 layer was semi-transparent, we cannot expect the optical merit for applying the ST21 layer to the double-layer photon-trapping system. Therefore, the ST21 layer was used in DSC electrodes as a single layer.

Figure 5 shows the relationships between the screen-printing times and the thickness of nanocrystalline-TiO₂ (P25 and ST21) layers, which were used for DSC electrodes (Figures 5 and 6). The ‘P25 + ST41’ and ‘ST21’ layers were double-layer and single-layer structures, respectively, as written in the previous paragraph. The thickness of ST41 was fixed at 5.7 μm, which was obtained by the interception of y-axis. The linear relationship between the coating time and the thickness was confirmed. The thicknesses of one screen-print coating of P25 and ST21 were obtained as 1.9 μm and 2.0 μm, respectively. Each paste gave a thick layer over 17 μm without cracking and peeling-up at the exterior; nanoscale cracks in the ST21 layer were observed by SEM (see Figure 2d).

Figure 6 shows the photovoltaic-characteristic variations of open-circuit photo voltage (a, V_{OC}), short-circuit photo current density (b, J_{SC}), fill factor (c, FF) and conversion efficiency (d, η). The V_{OC} and FF decreased linearly with increasing thickness, but the changing ratios were just 10% and 2%, respectively (Figure 6a and c). On the other hand, J_{SC} of P25-ST41 and ST21 increased by 30% and 50%, respectively (Figure 6b), which

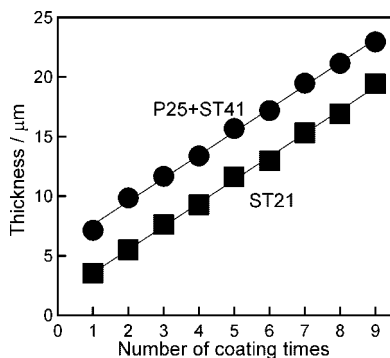


Figure 5. Relationship between number of coating times and thickness of screen-printed nanocrystalline-TiO₂ layers of P25 + ST41 and ST21. In P25 + ST41, the thickness of P25 was varied and that of ST41 was fixed at 5.7 μm by two-times screen printing for utilisation of photovoltaic measurements in Figures 6 and 7

projects the variation of η (Figure 6d). Resulting efficiencies of double-layer (P25-ST41) and single-layer (ST21) electrodes had peaks at 14 and 17 μm thickness of nanocrystalline layers (P25 and ST21), respectively (Figure 6d). Figure 7 shows photo I-V curves of best efficiency DSCs using P25-ST41 and ST21. The photovoltaic characteristics were $J_{SC} = 16.25 \text{ mA cm}^{-2}$, $V_{OC} = 779 \text{ mV}$, $FF = 0.730$, and $\eta = 9.24\%$ with P25-ST41 and $J_{SC} = 15.3 \text{ mA cm}^{-2}$, $V_{OC} = 778 \text{ mV}$, $FF = 0.733$, and $\eta = 8.75\%$ with ST21. These efficiencies are the best results published ever with using commercially-available TiO₂ powders.

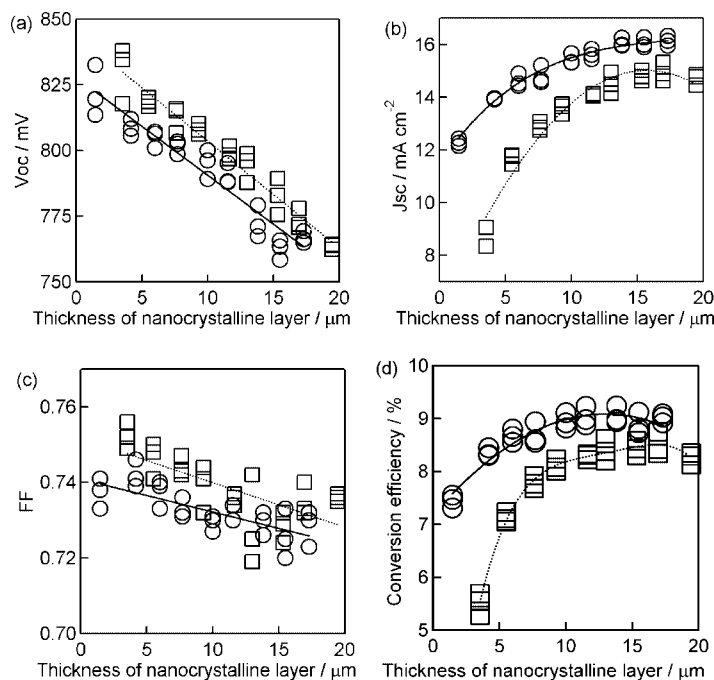


Figure 6. Photovoltaic-characteristics relationship with nanocrystalline (P25 and ST21)-layer thickness of P25 + ST41 (○) and ST21 (□) electrodes: V_{OC} (a), J_{SC} (b), FF (c) and conversion efficiency (η) (d). The thickness of ST41 was fixed at 5.7 μm for the light-scattering layer. The solid and dotted lines were fitted to the average data of P25 + ST41 and ST21, respectively

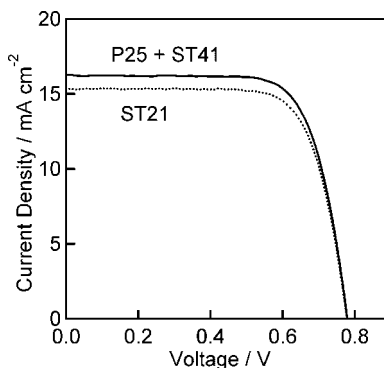


Figure 7. Photo I-V curves of best-efficiency dye-sensitized solar cells using nanocrystalline-TiO₂ electrodes fabricated from commercially-available nanocrystalline-TiO₂ powders (P25 + ST41, $\eta = 9.24\%$; ST21, $\eta = 8.75\%$) under 100 mW cm^{-2} AM 1.5 irradiation

CONCLUSION

In summary, this screen-printing technique enabled the fabrication of nanocrystalline layers over $17 \mu\text{m}$ thickness from commercially-available TiO₂ powders. The result of 9.2% efficiency was lower than that from our homemade double-layered electrode ($10\text{--}11\%$).^{4,5} However, this report shows the best efficiencies using commercially-available TiO₂ powders, which is very important for the world-wide market production of solar cells.

Since P25 and ST21 contained rutile particles and large aggregates, respectively, the efficiencies were lower than 10% . If we can get more transparent electrodes using 100% -anatase nanoparticles made by fumed-TiCl₄ synthesis, more highly efficient photovoltaic DSC can be fabricated.

We believe that this report can be of great help for the DSC researchers. The results of this study imply that using TiO₂ powders of a large commercial batch instead of TiO₂ particles of homemade small different batches result in a more reproducible cell efficiency. This methodological investigation can contribute not only to the research of DSC, but also to various applications of industrial and scientific works in several fields as suggested in the introduction.

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