Fabrication of a plastic dye-sensitized solar cell by using the high concentration TiO_2 sol through a sol-gel process

Mitusnobo IWASAKI, Chang-wan LEE,^{*} Tae-hyun KIM^{**} and Won-Kyu PARK^{*}

Department of Applied Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

^{*}Department of Material Engineering, Graduate School of Paichai University, 439-6, Doma-2 dong, Seo-gu, Daejeon, Korea

^{**}DO Co., Ltd., 555-1, Yongsan-dong, Yuseong-gu, Daejeon 305-500, Korea

TiO_2 water/ethanol sol capable of interparticle connection was prepared through a sol-gel process and used to the fabrication of organic binder-free TiO_2 paste for photo-electrode layer formation of all plastic dye-sensitized solar cells. The average particle size in TiO_2 water/ethanol sol was in the range of 27 nm–80 nm and the crystal phase confirmed by XRD was anatase, brookite and rutile. The viscosity of the binder sol showed the strong dependence on the water/alcohol ratio in solution. The organic binder-free TiO_2 paste including P-25 powder as the main photoelectrode was prepared by using the TiO_2 water/ethanol sol as an inorganic binder and coated on an ITO-PEN (ITO coated on Polyethylene Naphthalate) conductive electrode by a squeeze method. And the processing parameters of TiO_2 paste fabrication on the energy conversion efficiency, η , were investigated. The maximum energy conversion efficiency of an assembled plastic dye-sensitized solar cell in this work was found to be 2.58%.

Key-words : High concentration TiO_2 sol, Inter-particle connection, Organic binder-free paste, Plastic dye-sensitized solar cell

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1. Introduction

Since the Gratzel's group has presented about dye-sensitized solar cell (DSSC),^{1,2)} there has been a tremendous number of studies and patents for industrialization. At present, power efficiency of DSSC exceeding 11% has been achieved by high-temperature sintering of a nanocrystalline TiO_2 paste on a conductive glass.³⁾ DSSC comparing to the Si solar cells has a feature to be manufactured by an environmentally benign low cost manufacture processes in the ambient atmosphere. It enables a dramatic cost reduction, in particular, by realizing roll-to-roll printing process for electrode fabrication using flexible substrate. Further, lightweight flexible DSSC is highly useful not only for attachment on round surfaces but also for applications to ubiquitous powers.⁴⁾ For these purpose, various methods have been invented previously to fabricate plastic DSSC, including mechanical compression,⁵⁾ microwave sintering⁶⁾ and low-temperature coating of TiO_2 particles.⁷⁾ Meanwhile, electrophoresis deposition of TiO_2 followed by chemical necking treatments was preponderantly reported by Miyasaka's group.^{8)–10)} Especially, this group has published low temperature binder-free coating of mesoscopic titania paste.^{4),11),12)} Another work about binder-free coating was done by Showa-denko Company.¹³⁾ Two groups similarly used an aqueous colloidal TiO_2 sol as an interparticle connection agent, which contains brookite-type TiO_2 nanocrystals (size; 27–80 nm) at 20 mass% in a mixture of 25% aqueous hydrochloric acid (pH 2) and 75% ethanol. However, no detail procedure data to prepare such a colloidal TiO_2 sol as an interparticle binder has been presented in their papers and patents.^{4),8)–13)}

While, an aqueous colloidal Al_2O_3 sol derived from sol-gel method was firstly developed by Yoldas in 1975, which was

used to fabricate the transparent alumina ceramics.^{14),15)} Another oxide sol such as TiO_2 and ZrO_2 also has been studied.^{16),17)} About an aqueous colloidal TiO_2 sol, Matsoukas's group has reported in detail¹⁸⁾ and Park's group also has presented the reaction conditions in their works.¹⁹⁾ However, the concentration of TiO_2 in their reports was limited to 10 mass% in solution.

In this report, we developed a sol-gel route to prepare a high concentration TiO_2 colloidal sol used as an inorganic binder for a plastic dye-sensitized solar cell over 10 mass% in water/ethanol solution. This process gives the one-step process different from N.G. Park's work⁷⁾ and has a different features from Miyasaka's one⁴⁾ in a point of using titanium alkoxide as a starting material and nitric acid as a peptization catalyst. This sol was used as interparticle connection agent to fabricate TiO_2 paste for the low temperature formation of plastic dye-sensitized solar cell photoelectrode and its properties such as viscosity and crystal phases according to reaction conditions were investigated. Finally, we assembled all plastic dye-sensitized solar cells by using this paste and investigated its photovoltaic properties depending on the processing parameters of TiO_2 paste fabrication.

2. Experimental procedure

2.1 High concentration TiO_2 sol

Titanium ethoxide was used as a starting material for preparation of TiO_2 sol. The final solid concentration of each sol was adjusted to 14.7 mass% as shown in **Table 1**. Each sample was named as Sol-1, Sol-2 and Sol-3 according to the water/ethanol ratio in mass. Herein, the ethanol in the solution includes the one extracted from the hydrolysis of titanium ethoxide. At first, a quantity (25 ml) of titanium ethoxide (Aldrich Chemical Co.) was drop-wise poured into 23.5–35 mL of the distilled water and/or ethanol in a round flask under vigorous stirring at 50°C. (See Table 1) After the hydrolysis, a quantity (2.0 ml) of concentrated nitric

[†] To whom correspondence should be addressed.
m-iwa@apch.kindai.ac.jp

Table 1. Solution Composition of 14.7 mass% TiO₂ Sol

Sample name	Ti(C ₂ H ₅ OH) ₄ / mL	H ₂ O / mL	Additional C ₂ H ₅ OH / mL	H ₂ O/C ₂ H ₅ OH / g
Sol-1	25	35	0	59/41
Sol-2	25	28.5	9	47/53
Sol-3	25	23.5	16	37/63

Table 2. Paste Composition using Sol-1 (14.7 mass% TiO₂ sol) as Inorganic Binder

Sample Name	Sol-1 / mL	P-25 / g	Coarse TiO ₂ / g	1-PrOH / mL	CH ₃ CN / mL
Paste-1	10	3.0 (not washed)	0.6	25	1.25
Paste-2	10	4.5 (not washed)	0.6	25	1.25
Paste-3	10	6.0 (not washed)	0.6	25	1.25
Paste-4	10	4.5 (washed)	0.6	25	1.25
Paste-5	10	4.5 (washed)	0.6	18	1.25

acid (Deoksan Chemical Inc. Korea, 60 mass%) was added to the milky precipitated sol. Refluxing time to obtain the semi-transparent viscous sol took 48 hours under this condition. The viscosity of the TiO₂ sol and the average particle size in the sol was measured by the viscometer (Brookfield, Programmable Viscometer DV-II+, 61spindle, 100RPM, USA) and the particle size analyzer (Brookhaven Instruments Co. 90Plus, USA), respectively. X-ray diffraction meter (Shimadzu Model; XD-D1, Japan) was used for the confirmation of the crystal phase in these sols.

2.2 Preparation of organic binder-free TiO₂ photo-electrode paste

The composition of paste consisted of 1-propanol, TiO₂ water/ethanol sol, fine P-25 powder (Daegussa; the average particle size; 17 nm), and coarse TiO₂ powder (Nanochemical Co., Korea; the average particle size; 300 nm), which were used as the main solvent, an inorganic binder, the main photoelectrode, and the light scattering agent, respectively. In order to investigate the effects of TiO₂ paste's processing parameters on the energy conversion efficiency (η), five kinds of paste were prepared as shown in Table 2. The procedure of Paste-2 fabrication as a typical example was as follow. For the preparation of organic binder-free TiO₂ photoelectrode paste, the above water/ethanol colloidal TiO₂ Sol-1 (10 mL) was added to the mixture of fine P-25 powder (4.5 g) and coarse TiO₂ powder (0.6 g) dispersing in the mixture of 1-propanol (18 mL) and acetonitrile (1.25 mL). Each paste was designated as Paste 1 to 5. Subsequently, the paste was ball-milled for 2 hours.

2.3 Measurement of photocurrent voltage of the open cells

Squeeze coating of the organic binder-free TiO₂ paste on an ITO-PEN (thickness; 200 μ m, sheet resistance; < 13 Ω /sq., Peccell Tech., Japan) sheet followed by drying at 120°C for 15 minutes gave a mesoporous TiO₂ layer tightly attached to the ITO-PEN surface. The TiO₂-loaded ITO-PEN sheet showed high anti-exfoliation of TiO₂ against bending. Interparticle connection of TiO₂ is assumed to proceed by

Fig. 1. Viscosity change of TiO₂ Sol-1 against aging time.

dehydration of hydrogen-bonded network of TiO₂ nanoparticles with surfaces covered with hydroxyl groups.⁴⁾ The TiO₂-coated ITO-PEN was dye-sensitized by R-535-bis-TBA dye (SOLANIX). The photoelectrode was combined with a platinum-coated PEN (thickness; 188 μ m, sheet resistance; 5 Ω /sq., Peccell Tech., Japan) counter electrode by insertion of an organic electrolyte comprising 0.1 M LiI (ACROS ORGANICS, USA), 0.5 M 4-tert-butyl pyridine (TBP, Aldrich, USA), 0.05 M I₂ (SHOWA, Japan), 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMP II, SOLANIX) in the methoxy acetonitrile (10 ml) to construct an open cell with 0.25 cm² irradiation area. Photocurrent (I)-voltage (V) characteristics were measured under 1.0 sun irradiation with solar simulator (KEITHLEY Model 2400 Source meter, USA) at room temperature.

3. Results and discussions

Figure 1 demonstrates the change in viscosity of TiO₂ Sol-1 (14.7 mass%) prepared by the peptization of titanium ethoxide using HNO₃. Just after being prepared, the viscosity of the sol showed the high value of 80 $\times 10^{-3}$ Pa·s (cP). But it decreased as the aging time elapsed. After 13 days, the value converged to 7 $\times 10^{-3}$ Pa·s (cP). This tendency resulted from that the stabilization of the sol occurred by the nitric acid.

The dependence of the average particle size and the viscosity of 14.7 mass% TiO₂ sol on the weight ratio of water/alcohol in solution are shown in Fig. 2. As shown in the figures, both of the average particle size and the viscosity increased as an increase of ethanol in the solution. The average particle size changed from 27 nm at water/ethanol = 59/41 (g/g) of Sol-1 to 80 nm at water/ethanol = 37/63 (g/g) of Sol-3. The multiplicity was about 4 times. This tendency had a good agreement to the previous study.¹⁸⁾ There, they reported that such larger particle growth would lead to the presence of ethanol, which decreased the dielectric constant of the solution and inhibited the peptization and resulted in both larger colloids and longer peptization treatment.¹⁹⁾

Meanwhile, comparing to the particle size, the viscosity showed the abrupt increase of 40 times from 7 $\times 10^{-3}$ Pa·s (cP) at water/ethanol = 59/41 (g/g) of Sol-1 to 270 $\times 10^{-3}$ Pa·s (cP) at water/ethanol = 37/63 (g/g) of Sol-3. This phenomenon would be explained as follows. The thickness of the electrical double layer on the colloidal particles is expressed by the following Eq. (1).²⁰⁾

Fig. 2. Dependence of the average particle size and the viscosity change of 14.7 mass% TiO₂ sol on the ratio of water/alcohol in solvent.

Fig. 3. Modified schematic diagram about the formation of secondary particles in the reference.²¹⁾

$$1/\kappa = \frac{(\epsilon_0 \epsilon R T)^{1/2}}{2 F^2 C Z} \quad (1)$$

where F is the Faraday constant, C and Z are the concentration and valence of the counter ions, ϵ_0 and ϵ are the dielectric constants in vacuum and solvent, and R and T are the gas constant and absolute temperature. Thus, the dielectric constant of the solvent determined the thickness of electrical double layer on the primary particles.

Meanwhile, the dielectric constant value of water and ethanol is 78.5 and 24.3, respectively.²¹⁾ This means that the thickness of electrical double layer for water has higher value than that of ethanol. According to Suzuki et al.,²¹⁾ the agglomeration behavior of primary fine particles formed by the hydrolysis of alkoxide in the solution was strongly affected by the electrical double layer. A relatively thin electrical double layer resulted in the coarse flock of the secondary particles to form a branched network structure in the sol as shown in the modified Fig. 3. This would lead to the increase of viscosity of Sol-3 which contained more quantity of ethanol than any other sol at the same TiO₂ concentration in the water/ethanol mixture solution. On the other hand, if the solvents with high dielectric constant such as water were used, primary colloidal particles had thick electrical double layers to suppress the agglomeration of the primary colloidal particles. Therefore, the viscosity of the sol such as Sol-1 and Sol-2, which contained lower quantity of ethanol comparing to Sol-3, would decrease.

Figure 4 shows the X-ray diffraction patterns of dried sample of each sol. As shown in figure, anatase, rutile and brookite phase were observed in the samples using Sol-1 and

Fig. 4. XRD patterns of dried sample of each sol.

Fig. 5. I - V characteristics for photocurrent of a plastic dye-sensitized open cell under 1.0 sun irradiation. Herein, fine P-25 powder/coarse TiO₂ powder weight ratio was 3.0/0.6 (g/g) for Paste-1, 4.5/0.6 (g/g) for Paste-2, and 6.0/0.6 (g/g) for Paste-3, respectively. P-25 powder was not washed. (Measured open cell area was 0.25×10^{-4} m². I_p : incident energy, J_{sc} : short circuit current density, V_{oc} : open-circuit voltage)

Sol-2, while there was no rutile in the sample using Sol-3 with the more quantity of ethanol in the solution. As aforementioned, ethanol decreased the dielectric constant of the mixture solution in the sols resulting in the re-aggregation¹⁸⁾ and hindrance of recrystallization.¹⁹⁾ Also, there are some reports that the organic ligand of titanium complex has a great effect on the formation of various TiO₂ crystal phase.²²⁾ Therefore, the ethanol would hinder the re-crystallization and formation of the rutile phase at the re-aggregation stage in the sample using Sol-3.

Next, the processing parameters of TiO₂ paste fabrication on the photo conversion efficiency were investigated.

At first, Fig. 5 demonstrates the I - V characteristics for photocurrent of plastic dye-sensitized solar cell depending on various fine P-25 powder/coarse TiO₂ powder ratios of Paste 1-3 as described in Table 2. The area of open cell was 0.25×10^{-4} m² and the artificial 1.0 sun was irradiated.

Fig. 6. Dependence of I - V characteristics of a plastic dye-sensitized open cell on the preliminary treatment of P-25 powder. Herein, P-25 powder of Paste-2 was not washed, while washed for Paste-4. For both of Paste-2 and Paste-4, P-25 powder/coarse powder weight ratio was 4.5/0.6(g/g). (Measurement was carried out under 1.0 sun irradiation, and the area of the open cell was $0.25 \times 10^{-4} \text{ m}^2$. I_p ; incident energy, J_{SC} ; short-circuit current density, V_{OC} ; open-circuit voltage)

Here, fine P-25/coarse powder weight ratio was 3.0/0.6(g/g) for Paste-1, 4.5/0.6(g/g) for Paste-2, and 6.0/0.6(g/g) for Paste-3, respectively, wherein Sol-1 was used as an inter-particle connection agent. From the results, the energy conversion efficiency, η , increased from 1.59% of Paste-1 to 2.18% of Paste-3 as an increase in P-25 powder which had a function as the main photoelectrode in this solar cell.

Figure 6 shows the dependence of I - V characteristic on the preliminary treatment of P-25 powder with/without being washed by ethanol. Herein, P-25 powder used in Paste-2 was not washed, while it was washed for Paste-4. By washing, the energy conversion efficiency, η , increased from 1.78% to 2.14% by 36 percentage increment irrespective of the same P-25/coarse powder ratio. This increment wouldn't depend only on the preliminary treatment, but also on the morphology of the dried film as shown in the following Fig. 7.

Figure 7 demonstrates the optical photographs of the surface morphology of dried TiO₂ film for photoelectrode of DSSC. Herein, fine P-25 powder/coarse TiO₂ powder weight ratio for Paste-2 and Paste-4 was fixed at 4.5/0.6(g/g). Especially, for (b) Paste-4, P-25 powder was washed one time by ethanol and dried before coating and cell assembly. And the ratio was 6.0/0.6(g/g) for Paste-3.

Comparing the surface morphology of both Paste-2 and Paste-3 film to that of Paste-4 film, it's clear that more homogeneous and denser film was obtained for overall area of Paste-4 film by the preliminary ethanol washing treatment. While, both of Paste-2 and Paste-3 film showed the rough surface and severe cracks on the surface of thick area. Washing by ethanol caused ethyl group's replacement of OH group on the surface of P-25 powder and it enhanced the adhesion to ITO-coated PEN substrate.⁴⁾ Also, it may have the effect that lessens the capillary force due to the evaporation of water in solvent during drying. This explained the

Fig. 7. Optical photographs of the surface of TiO₂ film for photoelectrode of DSSC. Herein, P-25 powder/coarse powder weight ratio was 4.5/0.6(g/g) for (a) and (b). And for (c) and (d), the ratio was 6.0/0.6(g/g). P-25 powder was washed for (b) before coating and assembly.

Fig. 8. Dependence of I - V characteristics of a plastic dye-sensitized open cell on the amount of 1-propanol as the main solvent. The quantity of 1-propanol used in the paste preparation was 25 mL for Paste-4 and 18 mL for Paste-5, respectively. Herein, P-25 powder/coarse powder weight ratio was fixed at 4.5/0.6(g/g) for both of Paste-4 and Paste-5. (Measurement was carried out under 1.0 sun irradiation, and the area of the open cell was $0.25 \times 10^{-4} \text{ m}^2$.)

reason why the energy conversion efficiency ($\eta = 2.14\%$) of Paste-4 film showed higher value than that of Paste-2 ($\eta = 1.78\%$). Especially, as shown in Fig. 7(d), thick area of the Paste-3 film, which contained the more fine P-25 powder than Paste-2, showed the coarser surface morphology and severe cracks. This difference of the surface morphology resulted in that the energy conversion efficiency ($\eta = 2.14\%$) of Paste-4 film showed the similar value to that of Paste-3 film ($\eta = 2.18\%$) even though Paste-4 contained the fine P-25 powder much less than Paste-3.

Figure 8 shows the dependence of I - V characteristics on the amount of 1-propanol as the main solvent in each paste. The quantity of 1-propanol used in the fabrication of paste

was 25 ml for Paste-4 and 18 ml for Paste-5, respectively. Herein, fine P-25 powder/coarse powder weight ratio for both of Paste-4 and Paste-5 was fixed at 4.5/0.6(g/g). As afore-mentioned in table 2, each paste consisted of 1-propanol, TiO₂ water/ethanol sol, fine P-25 powder, and coarse TiO₂ powder, which were used as the main solvent, an inorganic binder, the main photoelectrode, and the light scattering agent, respectively. From the figure, the energy conversion coefficient, η , of Paste-5 was found to be 2.58% comparing with 2.14% of Paste-4, that is, the η value difference between each paste showed about 19 percentage increments. It probably results from that the portion of P-25 powder in Paste-5 might be relatively larger than that of Paste-4, but further consideration is necessary and the detailed research is currently underway. However, the photo-current conversion efficiency of 2.58% obtained in this work could be comparable to the value of 3.0% reported by Miyasaka's group⁴⁾ using 20 nm size similar to 17 nm size of fine TiO₂ powders used in this work, even though they reported the maximum value of 6.4% by controlling the processing parameters such as the size change of fine TiO₂ particles and the electrolyte composition.

4. Conclusions

TiO₂ water/ethanol sol capable of being used as an inorganic binder was successfully prepared through sol-gel process and applied to the fabrication of organic binder-free TiO₂ paste for photo-electrode layer formation of all plastic dye-sensitized solar cells. The viscosity of the inorganic binder sol decreased as the aging time elapsed and showed the strong dependence on the water/alcohol ratio in solvent, that is, the viscosity increased as the quantity of ethanol in the solution increased. The energy conversion efficiency, η , of an assembled plastic dye-sensitized solar cell had the different dependence on the processing parameters of TiO₂ paste. The energy conversion efficiency increased as an increase in P-25 powder which has a function as the main photoelectrode. And it also increased by the preliminary washing treatment even at the same fine P-25 powder/coarse powder ratio. In this work, the maximum energy conversion efficiency was found to be 2.58%.

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