

Low Temperature Fabrication of Titanium Dioxide Porous Electrode and Flexible Dye-sensitized Solar Cell Treated with Titanium Butoxide

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Dye-sensitized nanocrystalline solar cell, presented by Grätzel in 1991, is widely researched recently, because of its low cost and high efficiency properties. In this study, we describe the low temperature sintering and the fabrication on the flexible substrate of TiO₂ electrode. The solar-to-electrical energy conversion efficiency of the cells sintered at 150°C was 0.51%, it is lower than that of the cells sintered at 450°C. By the titanium butoxide treatment of the substrate surface, amorphous TiO₂ layer was formed on the top of substrates, and open circuit voltage and fill factor were increased by this treatment. It is explained by the decrease of back electron transfer at the interface between the transparent electrode and electrolyte. The titanium butoxide treatment was also effective to strengthen the adhesion force of TiO₂ electrode to the substrates. The solar-to-electrical energy conversion efficiency of the cells fabricated on flexible substrate was 0.31%.

Key words: dye, titanium dioxide, solar cell, flexible

1. INTRODUCTION

Photoelectrochemical solar cells based on dye-sensitized porous semiconductor electrode are regarded as a low cost, recyclable, high efficiency solar cell. In 1991, Grätzel reported on dye-sensitized nanocrystalline solar cell (DSSC). It is composed from Ru dye sensitized nanocrystalline porous TiO₂ electrode and I⁻/I₃⁻ redox mediator[1]. Solar-to-electrical energy conversion efficiency was reported as 10–11% under the AM 1.5 light source[2]. The most popular constitution of DSSC is shown in Figure 1. Ru dye is adsorbed onto the nanocrystalline TiO₂ electrode surface. By the adsorption of incident light, Ru dye is excited and injects electron into the conduction band of TiO₂. The oxidized Ru dye is reduced by I⁻. The maximum photovoltage is limited to the difference between the quasi-Fermi level for electrons in the TiO₂ and the redox potential of I⁻/I₃⁻ redox mediator[3].

Most researches were forced on maximizing the cell performances. Usually, these high performance cells are sintered at 450°C for the formation of the necking between the TiO₂ particles[1][2]. And for the improvement of the dispersion of TiO₂ nanoparticles and the porosity of TiO₂ electrode, poly ethylene glycol and some surfactants are also added into the TiO₂ colloidal dispersion[1][2]. The high temperature annealing is required to burn out these materials.

On the other hand, the low temperature sintering technique of TiO₂ electrode is necessary to fabricate the cells on the organic substrate[4][5]. The cells, fabricated on the organic substrate, are applied to the low power applications, such as pocket calculators (5 μW), watches (2 μW) and photoelectrochromic windows. The use of organic substrates increases the flexibility, and such cells

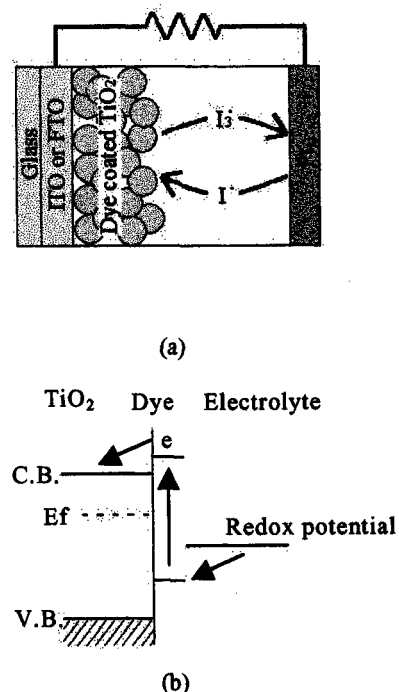


Figure 1. (a) Schematic model of the dye-sensitized nanocrystalline solar cell (b) Energy level diagram based on TiO₂/Ru dye/I⁻ system

are light and thinner than the cells fabricated on the glass substrate. However, there are many problems on the cells sintered at low temperature. The first is that it is inhibited the formation of the necking between the TiO₂ particles[5] and the crystallization of amorphous TiO₂[6].

The second is that the organic compounds can not to be used in the TiO₂ colloidal dispersion. Therefore, the photocurrent of the cells sintered at low temperature is decreased obviously. The third is that the adhesion force of the TiO₂ electrode to the substrates is weaker than those of the cells sintered at high temperature. To increase the adhesion force and to decrease the charge recombination at the interface between the electrolyte and optically transparent electrode, the surface of substrates is covered by TiO₂ layer by using titanium butoxide treatment[7]. However, this treatment has not been applied to the cells sintered at low temperature. Finally, the fourth is that the ideality factor of the cells is worse than those of the cells sintered at high temperature. The ideality factor is reported as 3.2 for the cells sintered at low temperature[5] and the value is usually reported between 1 and 2 for the cells sintered at high temperature[7][8][9][10]. The reasons of the poor ideality factor are recombination at the surface state and the interface between the particles[5][9][10].

In this study, we report on the cell performances of the DSSC sintered at 150°C onto the flexible substrates. We discuss about the change of the TiO₂ electrode and the cell performance by changing the sintering temperature. For improving the cell performances, we carried out the titanium butoxide treatment of the substrates. And we fabricate the cells on the flexible substrate.

2. EXPERIMENTAL SECTION

All chemical reagents, I₂ (Wako), LiI (Wako), *Cis*-Dithiocyanate-N,N'-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II) dihydrate ([Ru L₂(NCS)₂]·H₂O, Kojima Chemical Reagents Inc.), *tert*-butylpyridine (TBP, Aldrich), acetonitrile (Wako) and 3-methyl-2-oxazolidinone (NMO, Aldrich) were used as received.

Three types of transparent electrode were used as substrate. ITO (Sn doped In₂O₃) coated glass plate (10 Ω/sq), ITO coated PET film (50 Ω/sq, Fujimori Kougyou Co Ltd.) and FTO (F doped SnO₂) coated glass plate (10 Ω/sq, Asahi Glass Co.) were washed by acetone and 2-propanol. After the washing, 10 mM titanium butoxide (Aldrich) in 2-propanol was spread on the substrates. To control the thickness and to mask conducting substrates, the substrates were covered each edge with kapton tape (53 μm, 3M). Then, the TiO₂ colloidal dispersion, contained 3 g of anatase type TiO₂ nanoparticles (20 nm size, Ishihara Sangyo Kaisha Ltd.), 0 - 1.0 ml acetylacetone (Wako), and 4 - 7 ml of pH 3 acetic acid aqueous solution, was spread on the substrates. After removing the kapton tapes, TiO₂ was sintered at 100 - 450°C for 30 min in air.

The sintered TiO₂ electrodes were soaked into 3 × 10⁻⁴ M RuL₂(NCS)₂ in dehydrated ethanol at room temperature for 12 - 20 hours. After the sensitization, TiO₂ electrodes were kept in dehydrated ethanol.

The Ru dye coated TiO₂ electrode and the Pt counter electrode were clamped together, and a small quantity of redox electrolyte solution was introduced between the electrodes by capillary force. The redox electrolyte was contained 300 mM of LiI, 30 mM of I₂ and 0.2 M of TBP in the mixture of acetonitrile and NMO (50:50wt%).

Photocurrent-voltage curves are measured under the illumination of AM 1.5 solar simulator. The device area is 1 cm² for all samples.

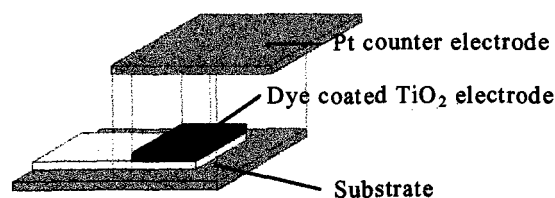


Figure 2. Cell structure of DSSC

3. RESULTS AND DISCUSSION

The observed photocurrent density J_{ph} is given by

$$J_{ph} = J_{inj} - J_r \quad (1)$$

where J_{inj} is the electron injection current and J_r is the surface recombination current. J_r is given by

$$J_r = qk_{et}c_{ox}^m(n^{u\alpha} - n_0^{u\alpha}) \quad (2)$$

where q is the electron charge, k_{et} is the rate constant for back electron transfer, c_{ox} is the concentration of oxidized half of the redox couple, n_0 is the electron population of semiconductor in the dark, and n is the electron population in the light. The order of the rate of reaction is expressed as the exponents m and u , and α is the electron-transfer coefficient. At open circuit voltage V_{oc} ($V = V_{oc}$, $J_{ph} = 0$), V_{oc} is given by

$$V_{oc} = \frac{kT}{qu\alpha} \ln \left(\frac{AI_0}{n_0^{u\alpha} k_{et} c_{ox}^m} \right) \quad (3)$$

where k is the Boltzmann constant, T is the temperature, A is the ratio of absorbed photon flux to I_0 and I_0 is the incident photon flux[7]. The $1/u\alpha$ is corresponds to the ideality factor for inorganic diode.

Nanocrystalline TiO₂ electrodes are sintered at different temperature and analyzed. From the results of X-ray diffraction, TiO₂ electrodes were pure anatase type under 450°C. It is confirmed from the optical absorbance. Figure 3 shows optical absorbance spectrum of the TiO₂ electrode sintered at 150°C, it is measured by photoacoustic spectroscopy. For the TiO₂ powder, optical bandgap E_g is according to the expression,

$$(Phv)^2 = B(hv - E_g) \quad (4)$$

where B is a constant, $h\nu$ is the photon energy and P is the photoacoustic intensity[11][12]. The value of E_g is calculated as 3.21 - 3.24 eV for all samples, it is conformed with the previously reports[11]. The SEM image of the TiO₂ electrode sintered at 150°C is shown in Figure 4. The TiO₂ particles of the cells sintered at 150°C were aggregated, because the surfactants can not be added to the TiO₂ colloidal dispersion.

Figure 5 and Table 1 show the performances of the cells sintered at various temperatures. Fill factor FF and solar-to-electrical energy conversion efficiency η is given by the equation 5 and 6.

$$FF = \frac{W_{max}}{V_{oc} \times J_{sc}} \quad (5)$$

$$\eta = \frac{W_{max}}{L} \times 100 \quad (6)$$

Where W_{max} is the max power of the cell. There are no changes for V_{oc} , because the physical and chemical

properties of the TiO₂ electrode are not changed by annealing. On the other hand, J_{sc} are increased by sintering at high temperature. We consider that the reasons were the improvement of surface state and the formation of the necking between the particles. Therefore, the back electron transfer and the charge recombination were decreased and the cell performance was improved.

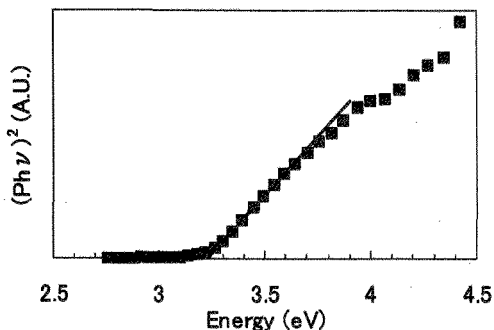


Figure 3. Optical absorbance spectrum of the TiO₂ electrode sintered at 150°C

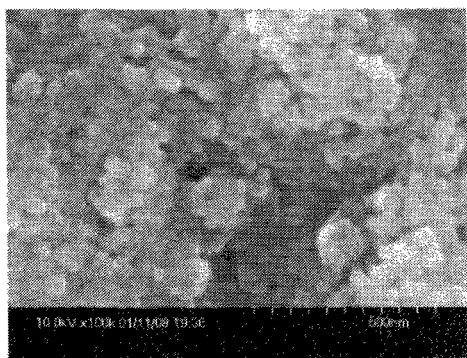


Figure 4. SEM image of TiO₂ electrode sintered at 150°C

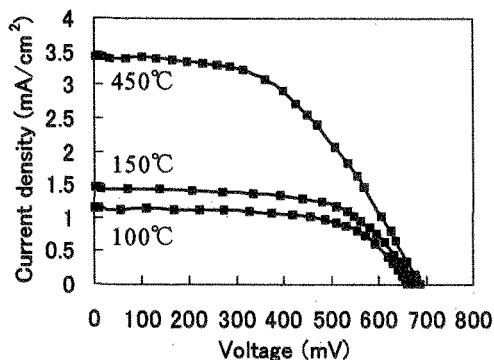


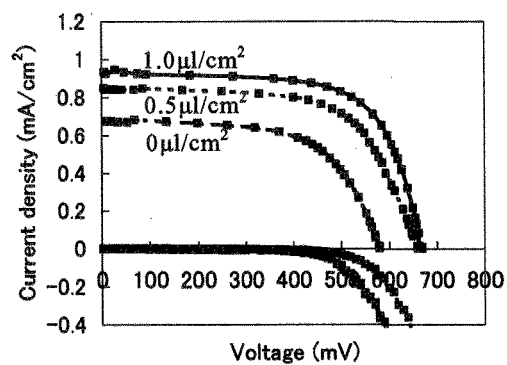
Figure 5. Photocurrent-voltage curves of DSSC sintered at various temperatures on ITO glass substrate

Table 1. Cell properties of DSSC sintered at various temperatures on ITO glass substrate

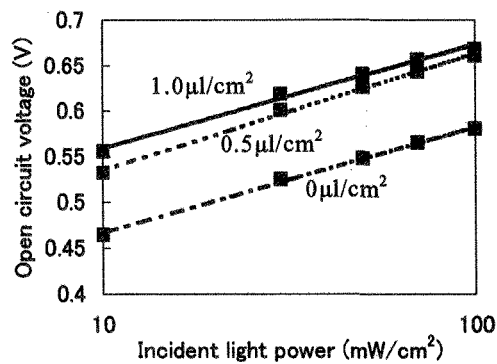
Sintering Temp.	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	η (%)
100°C	662.5	1.15	0.48	0.46
150°C	675.0	1.45	0.59	0.51
450°C	687.4	3.43	1.17	0.57

There are two ways of back electron transfer. One is from the TiO₂ to the electrolyte; the other is from the transparent electrode to the electrolyte. To improve the k_{et}, pyridine derivatives[7] or acetic acid are added into the redox electrolyte. These component are covered the surface of the TiO₂ particles, and the back electron transfer is decreased. Usually, the recombination at the interface between the transparent electrode and the electrolyte is ignored, because the surface area of the TiO₂ electrode is 1,000 times larger than that of the transparent electrode surface[1]. However, the electron transfer is not smooth in the TiO₂ electrode sintered at low temperature. Therefore, the recombination at the interface between the transparent electrode and the electrolyte cannot be ignored.

J-V curves and V_{oc}-lnL plots, where L is the incident light intensity, of the cells sintered at 150°C are shown in



(a)



(b)

Figure 6. (a) Photocurrent-voltage and dark current-voltage curves of DSSC sintered at 150°C on ITO glass substrate (b) Open circuit voltage-ln (incident light power) plots

Table 2. Cell properties of DSSC sintered at 150°C on ITO glass substrate

Ti(OBu) ₄ treatment	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	η (%)
0 μl/cm ²	580.6	0.67	62.0	0.24
0.1 μl/cm ²	614.2	1.00	62.4	0.38
0.3 μl/cm ²	595.1	0.68	62.9	0.26
0.5 μl/cm ²	660.7	0.85	63.8	0.36
1.0 μl/cm ²	669.0	0.94	67.0	0.42

Figure 6. For the improvement of the recombination at the transparent electrode surface and the adhesion force of the TiO₂ electrodes, the titanium butoxide treatment was carried out. Thin amorphous TiO₂ layer was formed on the substrates by spread titanium butoxide solution, contains 10⁻² M titanium butoxide in 2-propanol. By increasing the treatment amount, V_{oc} and FF were improved. On the other hand, 1/α is not changed; these values are 1.9 - 2.2 for all samples. From these results, we consider that the back electron transfer at the interface of ITO and electrolyte was improved by the titanium butoxide treatment.

Since the adhesion force of the TiO₂ electrodes to the flexible substrates was weaker than that of the glass substrate, the TiO₂ electrode was exfoliated. And the thicker TiO₂ film was also easily exfoliated. We consider that the titanium butoxide treatment was effective to strengthen the adhesion force of the TiO₂ electrodes to the ITO coated PET film. The J-V curve and V_{oc}-lnL plot of DSSC on the ITO coated PET film is shown in Figure 7. The titanium butoxide amount was 0.5 μl/cm². V_{oc} was 700 mV and J_{sc} was 0.72 mA/cm², they were closed to the values of the cells on the glass plate samples. FF was slightly decreased, because the resistivity of the PET film substrates is higher than the value of the glass plate substrates.

By the titanium butoxide treatment, the amorphous TiO₂ layer was formed on the top of substrates. The back

Table 3. Cell properties of DSSC sintered at 150°C on ITO coated PET film

V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	η (%)	1/α
702.4	0.72	61.6	0.31	1.80

electron reaction at the interface of the transparent electrode and the electrolyte was decreased by the treatment of the titanium butoxide. However, we consider that the amorphous TiO₂ layer inhibited the electron transfer from the TiO₂ to the transparent electrode. The crystallization of the amorphous layer is necessary to the increase of conversion efficiency.

4. CONCLUSION

In this study, the low temperature sintering of TiO₂ nanoparticles were successfully carried out. By the titanium butoxide treatment, V_{oc} and FF were increased, however, the 1/α was not changed. The treatment improved the recombination at the substrate/electrolyte interface, and it is effective to strengthen the adhesion force of the TiO₂ electrodes. The solar-to-electrical energy conversion efficiency of the flexible DSSC was 0.31%.

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REFERENCES

- [1] B. O'Regan and M. Grätzel, *Nature*, **353**, 737 (1991)
- [2] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, **115**, 6382 (1993)
- [3] F. Pichot and B. A. Gregg, *J. Phys. Chem. B*, **103**, 6 (2000)
- [4] F. Pichot, S. Ferrere, R. J. Pitts and B. A. Gregg, *J. Electrochem. Soc.*, **146**, 4324 (1999)
- [5] F. Pichot, R. Pitts and B. A. Gregg, *Langmuir*, **16**, 5626 (2000)
- [6] N. -K. Park, G. Schlichthörl, J. van de Lagemaat, H. M. Cheong, A. Mascarenhas and A. J. Frank, *J. Phys. Chem. B*, **103**, 3308 (1999)
- [7] S. Y. Huang, G. Schlichthörl, A. J. Nozik, M. Grätzel and A. J. Frank, *J. Phys. Chem. B*, **101**, 2576 (1997)
- [8] Y. Liu, A. Hagfeldt, X. -R. Xiao and S. -E. Lindquist, *Sol. Ener. Mater. Sol. Cells*, **55**, 267 (1998)
- [9] Th. Dittrich, P. Beer, F. Koch, J. Weidmann and I. Lauer, *Appl. Phys. Lett.*, **73**, 1901 (1998)
- [10] Fei Cao, Gerko Oskam, Gerald J. Meyer and Peter C. Searson, *J. Phys. Chem.*, **100**, 17021 (1996)
- [11] T. Toyoda, T. Hayakawa, K. Abe, T. Shigenari and Q. Shen, *Journal of Luminescence*, **87-89**, 1237 (2000)
- [12] P. Madhu Kumar, S. Bandrinayanan and Murali Sastry, *Thin Solid Films*, **358**, 122 (2000)

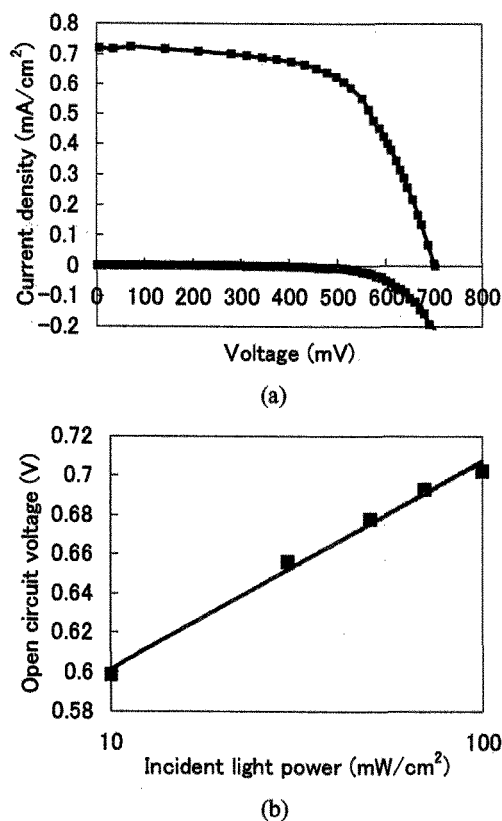


Figure 7. (a) Photocurrent-voltage and dark current-voltage curves of DSSC sintered at 150°C on ITO coated PET film (b) Open circuit voltage-ln (incident light power) plots