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Nano-porous TiO_2 Thin Film for Dye-sensitized Solar Cell

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The dye-sensitized solar cell is a new type of photovoltaic device that is expected as low cost, low environmental loading and high efficiency solar cell. In dye-sensitized solar cells, the oxide semiconductor of porous thin film plays an important role, because it is conjunction with a large amount of the sensitizing dye which absorbs the wide wavelength range of the solar light and discharge the electrons to semiconductor. In this study, the thin films of nano-porous titanium dioxide (TiO_2) semiconductor were prepared on conducting F:SnO_2/glass substrate by sol-gel method and occasionally by paste-squeegee method. The film thickness, dye adsorption amount and scratch hardness (as a measure of adhesive strength) were examined, and the performance of photovoltaic device (energy conversion efficiency etc.) was further evaluated as a dye-sensitized solar cell consisted of TiO_2 -coated electrode.

The increase of film thickness up to ca. 5 μ m resulted in the increase of dye-absorbed amount. In addition, the energy conversion efficiency increased with dye absorbed amount, but saturated at about 2%. As a result of the photovoltaic experiment, the performance of dye-sensitized solar cell depends on the film thickness of TiO_2 and the adsorption amount of dye.

Key words: dye-sensitized solar cell, thin film, titanium dioxide, sol-gel method

1. INTRODUCTION

Solar cell is photovoltaic device working by self-supporting energy. For the development of durable human society, the environment-friendly solar cell is desired to come into wide use in the world. However, at the present stage, the solar cells based on the p-n junction of silicon are very high in cost because it has some disadvantages of requiring high-purity raw materials, expensive manufacture facilities and so on. Therefore, we have to develop the lower cost solar cells in the technical demand for realizing the solar cell society.

Recently, the dye-sensitized solar cell (DSC) is expected as low cost, low environmental loading and high efficiency solar cell[1]. In this new type photovoltaic device (Fig.1), the dye absorbs the wide wavelength range of solar light, and the semiconductor thin film acts as a charge separate function. As compared with the silicon solar cell in which the p-n junction shoulders both light absorption and charge separation, the manufacture process of dye-sensitized solar cell is relatively easy and do not always need the vacuum-system facility. The manufacture cost is therefore expected to become lower.

In the dye-sensitized solar cell, one of technical problems is the preparation of porous TiO_2 thin films with high photo-activity. As thin film preparation method of oxide semiconductor for practical application, electrodeposition[2] and sputter deposition[3], sol-gel processing, etc. are well-known. The sol-gel method is the low-temperature synthesis method under the atmospheric pressure, and therefore, it lowers the manufacture cost in practical applications. And, the porosity of TiO_2 film can be controlled by the addition of organic polymer[4]. There is seldom the research of DSC using TiO_2 thin films prepared by the sol-gel method[5, 6].

In this study, nano-porous TiO_2 thin films were prepared on conducting F:SnO_2/glass substrate by sol-gel method and occasionally by paste-squeegee method. The film thickness, dye adsorption amount and scratch hardness (as a measure of adhesive strength) were examined, and the performance of photovoltaic device was further evaluated as a dye-sensitized solar cell with TiO_2 -coated electrode.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of TiO_2 thin films

TiO_2 thin films were prepared by sol-gel method according to the flow chart shown in Fig.2. Tetra-iso-propoxide (TIP: $Ti(OC_3H_7)_4$, NACALAI TESQUE INC.) and diethanolamine (DEA: $NH(CH_2CH_2OH)_2$, Wako Pure Chemical Industry Ltd.) was mixed with ethanol, then water mixed ethanol was added. To control hydrolysis rate, mixed water was added drop by drop using a burette under stirring at 0oC. The precursor solution was then stirred at room temperature. Two kinds of additives, polyethylene glycol M.W 2000 (PEG: $H(OCH_2CH_2)_nOH$, NACALAI TESQUE INC.) and TiO_2 powder (P25, Degussa AG) were added to the precursor solution to control the film property.

TiO_2 thin films were prepared by dip-coating method using the precursor solution, and F:SnO_2-coated glass plate well rinsed was used as substrate. The TiO_2 thin

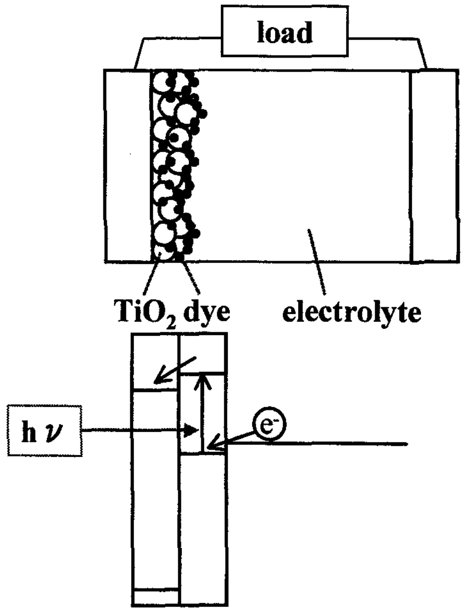

Fig.1 The scheme of dye-sensitized solar cell. The dye absorbs the wide wavelength range of solar light and injects electron to the conduction band of TiO_2. Then, the excited dye is reduced by redox mediator in the electrolyte.

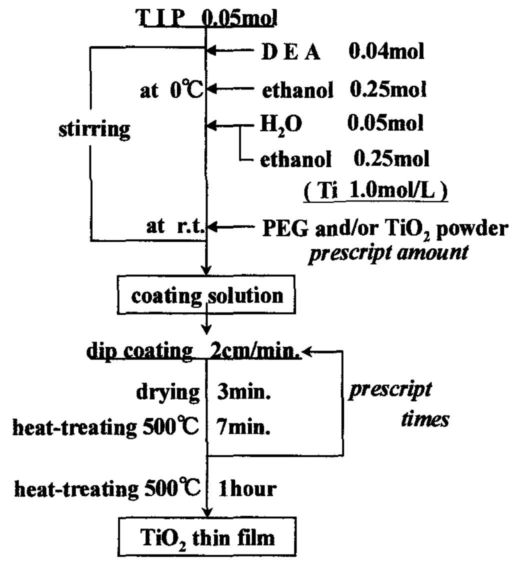

Fig.2 Flow chart for preparation of TiO_2 thin film by sol-gel method.

film was coated to have effective surface area 1cm^2 at dip-coating rate 2cm/min. The obtained thin film was dried for 3 minutes, then heat-treated at 500oC for 7 minutes. This coating process was repeated the prescribed times, and finally, the film was sintered at 500oC for 1hour.

Dye (Ru(4,4'-dicarboxy-2,2'-bipyridine)$_2$(NCS)$_2$, Kojima Chemicals Co., Ltd.) was adsorbed onto the surface of the TiO_2 thin film by immersing the film in the 0.3mM dye-ethanol solution. For making the dye-sensitized solar cell, a Pt-passivated ITO glass was placed on the dye-adsorbed TiO_2 film, and the inter-electrode space was filled with an electrolyte. The electrolyte composition is 0.5M KI and 0.03M I_2 in 80:20- ethylene carbonate / acetonitrile solvent.

In comparison, TiO_2 thin films were prepared by the conventional paste-squeegee method[7] and utilized in a dye-sensitized solar cell as electrode.

2.2 Characterization of TiO_2 thin film

The adhesive strength of the obtained TiO_2 thin film was measured by scratch test using a pencil with different hardness (order 6B(softest), 5B 4B, 3B, 2B, B, HB, H, 2H-8H, 9H(hardest)).

The thickness and morphology of thin films were determined by observing the cross section and the surface of samples using scanning electron microscopy S4100 (HITACHI Co., Ltd.). The surface area and pore size distribution of thin films were characterized with AUTOSURB-1 (QUANTA CHROME Co., Ltd.) using N_2 gas as adsorbent by the BET 3-points adsorption method and BJH adsorption method, respectively.

The adsorption amount of dye was evaluated from the concentration of dye in 0.1M KOH desorbed solution using the absorption spectroscopy V-580 (JASCO Co., Ltd.).

2.3 Photovoltaic performance of dye-sensitized solar cell

Photovoltaic performance of the cell under irradiation (AM1.5, 0.1W/cm^2) was recorded using a solar simulator ModuleX (Ushio Optical Co., Ltd.). Short-circuit current (Isc), open-circuit voltage (Voc), fill factor (FF) and total energy conversion efficiency (h) of solar cells were calculated from I-V curve obtained by sweeping voltage in 50 points at room temperature.

3. RESULT AND DISCUSSION

3.1 Scratch hardness of TiO_2 thin films

The scratch hardness of TiO_2 thin films was evaluated as a measure of adhesive strength. In the case of TiO_2 thin films prepared by paste-squeegee method, all the film samples were broken in the pencil hardness range from HB to H. On the other hand, the TiO_2 thin films prepared by sol-gel method shows the excellent scratch hardness for which the thin film is not broken even using the hardest 9H pencil.

The excellent property results in making handling easy and improving the productivity of thin films. Therefore, the sol-gel processing is a powerful way for the practical production of thin films.

3.2 Effect of dip-coating repeat number

Figure 3 shows the dependence of dip-coating number for the thin film characterization and photovoltaic performance of the dye-sensitized solar cells, for TiO_2 thin films prepared from sol-gel method. As is seen in the figure, the thickness of TiO_2 thin films (d) and the adsorption amount of dye (Cda) increased proportionally with the repeat number of dip-coating. The conversion efficiency (h) increased with the repeat number of dip-coating, and the value was saturated around 1%. The short-circuit current (Isc) showed a similar tendency to conversion efficiency (h). On the other hand, the open-circuit voltage (Voc) and fill factor (FF) were decreased gradually with increasing the repeat number of dip-

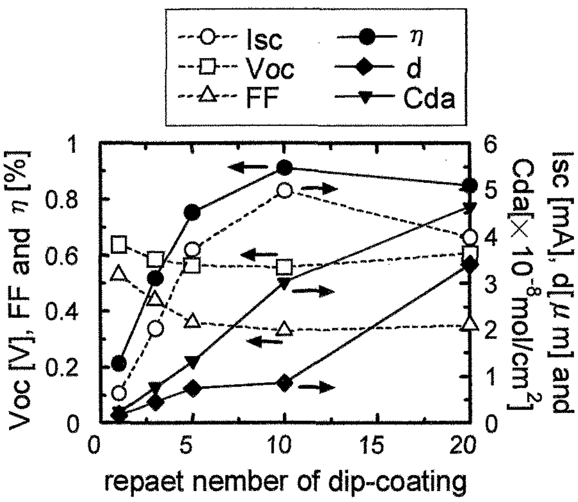

Fig.3 The dependence of dip-coating number for the thin film characterization and photovoltaic performance of the dye-sensitized solar cells, for TiO_2 thin films prepared from sol-gel method. Open-circuit voltage (Voc) [V], fill factor (FF) and total energy conversion efficiency (h) [%] are shown by the left axis. Short-circuit current (Isc) [mA], thickness of TiO_2 film (d) [μ m] and the adsorption amount of dye (Cda) [$\times 10^{-8}$mol/cm^2] are shown by the right axis.

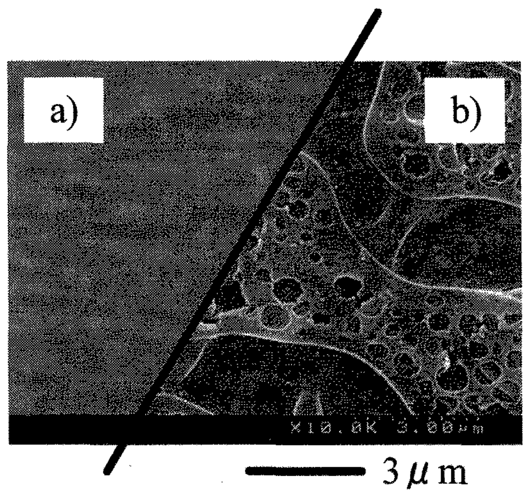

Fig.4 Surface morphology of TiO_2 thin films (heated at 500℃) prepared from (a) no PEG-added, and (b) PEG-added sol solutions.

coating, and they remained unchanged when the dip-coating was repeated more than 10 times.

These results indicate that the conversion efficiency depends on the repeat number of dip-coating, which is related closely with the thickness of thin film and further adsorption amount of dye. However, the sleight decrease of conversion efficiency (h) for thick film is estimated to be due to cutting off the incident light and preventing diffusion of electrolyte into the thin film.

3.3 Effect of additives

PEG: Figure 4 shows the surface morphology of TiO_2 thin films prepared from no PEG-added and PEG-added sol solutions. The TiO_2 thin film

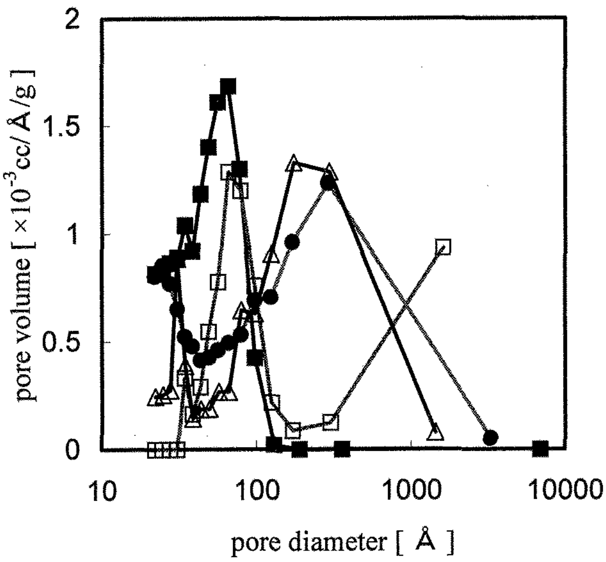

Fig.5 Pore size distribution of TiO_2 thin films prepared from non-additive sol (■), PEG added sol (□), PEG and TiO_2 powder added sol (△), and paste-squeegee method (●).

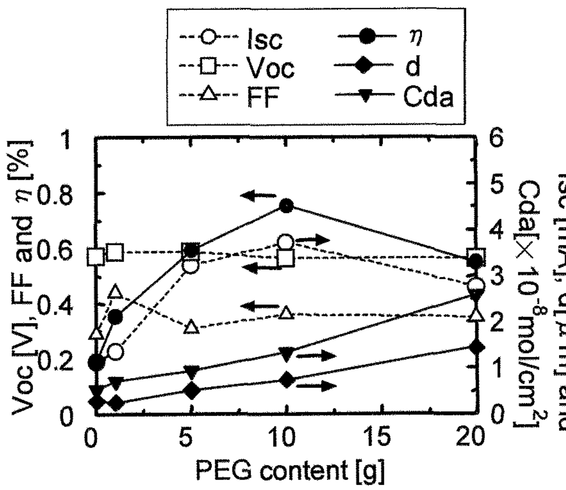

Fig.6 The dependence of the PEG content for the thin film characterization and photovoltaic performance of the dye-sensitized solar cells, for TiO_2 thin films prepared from sol-gel method. Open-circuit voltage (Voc) [V], fill factor (FF) and total energy conversion efficiency (h) [%] are shown by the left axis. Short-circuit current (Isc) [mA], thickness of TiO_2 film (d) [μ m] and the adsorption amount of dye (Cda) [$\times 10^{-8}$ mol/cm^2] are shown by the right axis.

without PEG-additive is flat and dense. In contrast, the TiO_2 thin film with PEG additive is not flat and has a three-dimensional island structure containing many sub-micrometers sized pores. This phenomenon of pore formation seems to arise from the thermal decomposition of special TiO_2 precursor modified by the addition of PEG into sol solution.

The surface area was, however, constant at approximately 34m^2/g, regardless of addition of PEG or not. According to the pore size distribution (Fig.5), only the sub-micrometer sized pore increases. Therefore, this indicates that the addition of PEG does not gives only a few change for the surface area of thin films but affects the morphology of thin film.

Figure 6 shows the PEG content dependence of the thin film characterization and photovoltaic performance for TiO_2 thin films prepared from sol-gel method. With the amount of PEG addition, both h and Isc increased and then saturated in the similar way to the case of multiple dip-coating. Voc and FF did not depend on the amount of PEG addition, and the observed values were nearly constant. Both d and Cda increased linearly with PEG content. The addition of PEG also affects the increase of film thickness.

TiO_2 powder: In the case of TiO_2 thin films prepared from sol solution without any additive, the conversion efficiency (h) of solar cell was 0.19%. In the case of TiO_2 thin films prepared from the sol solution dispersed with TiO_2 powder (10wt% of the sol), however, the conversion efficiency (h) of solar cell was found to be 1.05%. The h value became higher. The surface area of 42m^2/g and film thickness of 2.62 μm were also larger. On the other hand, the film prepared from the sol solution containing both TiO_2 powder and PEG showed the larger thickness of 3.55 μm and the h value of 1.03%. In this case, the h value seems to reach a certain degree of limit.

As can be seen in Fig.5, the pore size distribution of the film prepared by TiO_2 powder-added sol-gel method is very similar pattern to that of the film prepared by the paste-squeegee method. Therefore, a variety of surface morphology of thin film would be well controlled by additives using the modified sol-gel method.

3.4 Effect of film thickness

As mentioned previously, it is suggested that the photovoltaic performance of dye-sensitized solar cell is related to the thickness of TiO_2 thin film. Consequently, the plots of the film thickness against the adsorption amount of dye and conversion efficiency are shown in Fig.7.

In Fig.7a, the adsorption amount of dye increases linearly with the increase of the film thickness, except the case of TiO_2 powder additive. This tendency of linearly increase doesn't depend on the preparation method of thin film. Next, in Fig.7b, the conversion efficiency (h) increases with the increase of the film thickness and then is limited up to 2%, independent of the preparation method of thin film.

4. CONCLUSION

As the electrode of the dye-sensitized solar cell, the nano-porous TiO_2 thin films were prepared by the sol-gel method. The scratch hardness of TiO_2 thin film was much strong and the film had excellent productivity for the practical process. By using the sol-gel method, film thickness and surface morphology of thin film could be controlled by changing dip-coating times, kind and amount of the additives. The cell performance per thickness did not change when the film thickness was within 5 μm. The cell performance depended on the absorbed amount of dye which is conjunction with the TiO_2 film, and the increase of film thickness is expected to increase the absorbed amount of dye. In the present study, however, the maximum efficiency was almost 2%.

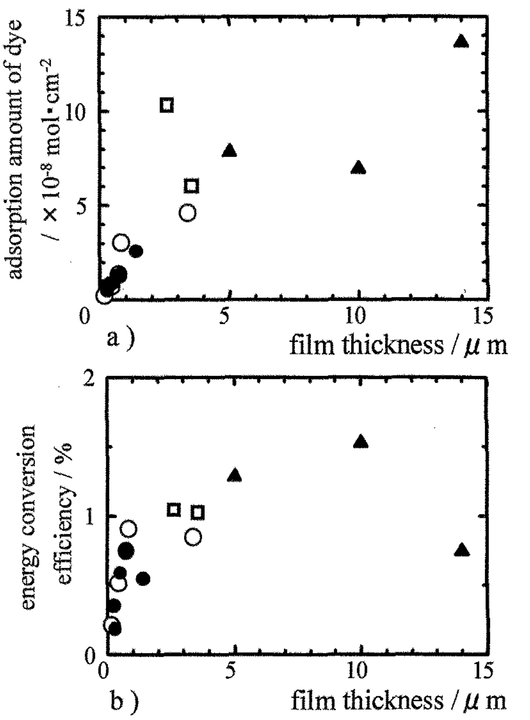

Fig. 7 Plots of the thin film thickness vs. (a) adsorption amount of dye (b) energy conversion efficiency. Symbols show changing dip-coating times (○), PEG amount (●), TiO_2 powder additives (□), and prepared by paste-squeegee method (▲).

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