

Preparation of spray-coated TiO₂ electrodes and I-V characteristics for Dye-sensitized Solar Cells

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Abstract

Fabrication and characterization of dye-sensitized TiO₂ solar cells(DSSC) consisting of spray-coated TiO₂ electrode, an electrolyte containing I-/I³⁻ redox couple, and a Pt-coated counter electrode was carried out, using mainly FE-SEM and solar simulator. Also, effect of rapid thermal annealing(RTA) temperature on I-V curves of DSSCs consisting of approximately 10m thickness and 5x5mm² active area. No significant difference in the apparent size of TiO₂ clusters was observed with increasing RTA temperature. Also, an open circuit voltage(V_{oc}) of approximately 0.70V and a short-circuit photocurrent(J_{sc}) of 8 to 12mA/cm² were observed in the TiO₂solar cell. With increasing RTA temperature upto 550oC, photocurrent density of dye-sensitized solar cells was enhanced, leading to enhancing the efficiency of dye-sensitized solar cells having Pt-electroplated counter electrode.

Keywords: sprayed-coating, TiO₂, electrode, DSSC,

1. INTRODUCTION

The dye sensitized solar cell(DSSC) consisting of dy electrode, an electrolyte containing I-/I³⁻ redox couple, and Pt coated counter electrode is a promising alternative to the inorganic solar cell[1]. Due to low cost, permanence, environmental compatibility and relatively simple fabrication process, great interest in DSSC has grown continuously[2]. In spite of the cost-efficiency of DSSC, the improvement of efficiency and long term stability is needed in terms of practical application.

TiO₂ electrode is used as a cathode for DSC. TiO₂ materials have anatase and rutile crystalline phases, which are well known to be formed as a meta-stable phase at temperatures lower than ~ 400 °C and as a thermodynamically stable phase at higher temperatures, respectively. Also, TiO₂ polycrystal transforms anatase to rutile phase easily by high temperature treatment with inevitable growth of the particles size [3]. Mainly, anatase phase TiO₂ materials, i.e. P25(comercialized powder) was mainly

used for DSC, since good particle size distribution, high purity, good moisture stability, etc. Simultaneously, other attempts into developing Titanium oxides for DSSC have been carried out, using hydrate (TiO (OH)₂ , TiO (OH)₂), also, TiO₂ sol-gel.

Many studies on fabricating TiO₂ electrodes for dye sensitized solar cells have been carried out until now. Screen printing, tape casting (Dr Blade method) and spin coating are mainly used. However, spray coating has not much used for dye sensitized solar cells in conjunction with rapid thermal annealing so far. Especially, diluted TiO₂ sol can not be used for fabricating TiO₂coating layer, also, it is difficult to make an enlarge in the active area of TiO₂ electrode, using screen printing and tape casting. Here, spray coating is very useful for applying especially very dilute sol of TiO₂ to prepare enlarged TiO₂ electrode.

In these respects, it can be very meaningful investigation for understanding characteristics of spray coated TiO₂electrode for DSSC. Therefore, we

investigated spray coating, its characteristics of TiO₂ electrode, and dye-sensitized solar cell. Photoelectric property of DSSC having TiO₂ electrode and Pt electrode was measured, using solar simulator and Keithley 2400 I-V source meter. Microstructural study of TiO₂ electrode and counter electrode were carried out, using FE-SEM (field emission scanning electron microscope), AFM (atomic force microscope). Also, we suggested possibility of using spray coating method for fabricating TiO₂ electrode used in DSSC. e-modified wide band semiconducting TiO₂

2. EXPERIMENTAL PROCEDURE

2.1 TiO₂ ELECTRODE PREPARATION

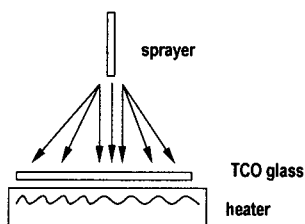


Fig.1 Schematic diagram of spray-coating

Fig.1 shows a schematic diagram of spray-coating for dye-sensitized solar cell. In order to fabricate TiO₂ electrode, nano-crystalline TiO₂ (P25, Degussa) powders were used. First, slurry of TiO₂ (10w%) powder and alcohol, done with ball milling for 24 hr was prepared, second, spray coating was conducted on SnO₂:F glass (FTO, 8 ohm/sq, 80% transmittance in the visible, 5mm5mm in active area of TiO₂), third, TiO₂-coated FTO glass was thermally treated as a function of temperature.

Table 1. Fabrication condition of spray coating for TiO₂ electrodes at 25°C

Nozzle Dia.	Distance btwn spray and sample	Coating time	Substrate temperature
0.3mm	200mm	<1min	Room temperature

In order to sensitize TiO₂ films, TiO₂ electrodes were immersed in a solution of 0.02mg/cc red dye

(RuL₂(NCS)₂[L=2,2'-bipyridine-4,4'-dicarboxylic acid] in ethanol for 24h at room temperature. The cleaning process was followed with pure ethanol.

2.2 COUNTER ELECTRODE

Pt counter electrodes were deposited from Pt targets on FTO glass by using a DC-magnetron sputtering system with a base pressure of 3×10⁻⁶ torr and a deposition pressure 3×10⁻³ torr. The input power was 100W. The thickness of Pt is ~300nm.

2.3 CELL CONSTRUCTION

In order to assemble solar cell having 5x5 mm² active area, the structure of solar cell were design as shown in Fig.2.

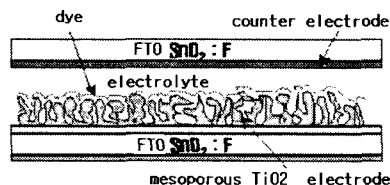


Fig. 2. Schematic diagram of dye sensitized solar cell.

The Pt electrode and the dye-adsorbed TiO₂ electrode were sandwiched, using clamps and the redox electrolyte containing I⁻/I₃⁻ redox couple was introduced into the solar cell by capillary effect through spacer (50µm thick). The spacer was loaded with clamps. Ag paste was put on the side edge of two electrodes. Therefore, solar cell having an active of approximately 0.25cm² was fabricated.

2.4 CHARACTERIZATION

Photoelectric property of DSSC having TiO₂ electrode and Pt electrode was measured, using solar simulator and Keithley 2400 I-V source meter in order to measure short-circuit photocurrent (J_{sc}), open-circuit voltage (V_{oc}), fill-factor (FF) and cell efficiency. Microstructural investigation of mesoscopic TiO₂ electrode and counter electrode were carried out, using FE-SEM (field emission scanning electron

microscope) and sheet resistance was measured with 4-point probe. α -step (Tencor Alpha-step 200 profilometer) was employed for measuring thickness of TiO₂ electrode.

3. RESULTS AND DISCUSSION

3.1 SURFACE THICKNESS & ROUGHNESS

The thickness of spray-coated TiO₂ electrode was measured by α -step. In the case of as-prepared TiO₂ electrode, its thickness is approximately 10m under the above spray coating condition.

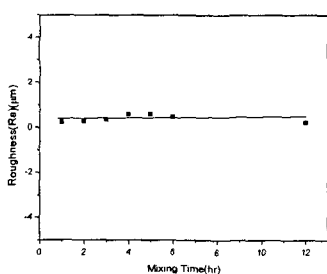


Fig. 2 Surface roughness of spray coated TiO₂ electrode ($R_a = 0.1 \mu\text{m}$) heat-treated by rapid thermal annealing at 550°C

Fig.2 shows surface roughness of spray coated TiO₂ electrode measured by α -step. In general, it is considered that the roughness of spray-coated layer is more rougher than that in the case of tape casting. In this reason, spray coating has not applied to fabricate TiO₂ electrode. From our observation, Surface roughness of spray coated TiO₂ electrode is approximately $R_a < 0.1 \mu\text{m}$. This means that such roughness does not significantly affect on breaking-down between TiO₂ electrode and Pt counter electrode, since the spacers between TiO₂ electrode and Pt counter electrode is used to be approximately 20~50m

3.2 MICROSTRUCTURE OF TiO₂ ELECTRODE

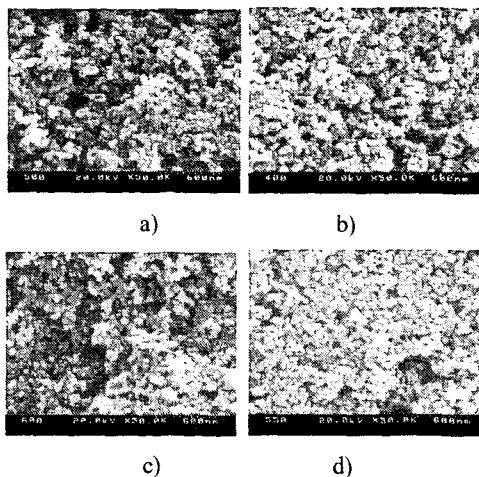


Fig.3 SEM micrographs of nanocrystalline TiO₂ deposited by spray coating.

Fig.3 shows FE-SEM micrographs of TiO₂ electrode deposited by spraying coating, following rapid thermal annealing as a function of temperature. There is no significant change in the microstructure of spray-deposited TiO₂ electrodes with increasing RTA temperature. This means that TiO₂ powders(P25) is narrow particle size distribution of 25nm.

The particle size of TiO₂ particles experienced with rapid thermal annealing was approximately 60nm. In this case, majority of TiO₂ particles were agglomerates (~60nm) consisting of several TiO₂ particles, forming grain boundary between TiO₂ particles. Although it is difficult to distinguish the increase in number of necking between TiO₂ particles, we may consider the increase in number of necking between TiO₂ particles with increasing RTA temperature, without any significant change in apparent microstructure of TiO₂ electrodes. Such increase in number of the necking allows electron generated during exposed sunlight to enhance its transfer. We expect enhanced photocurrent of dye-sensitized solar cells.

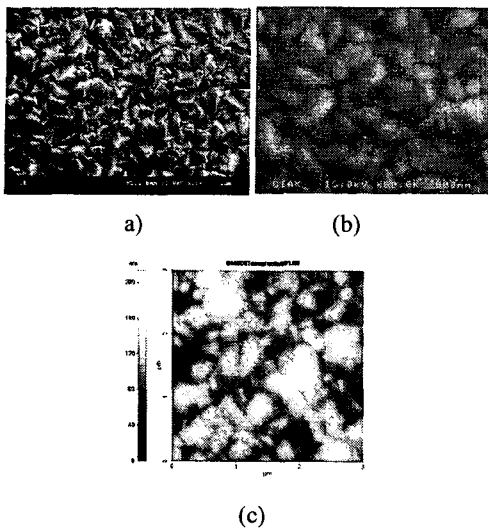


Fig. 4. FE-SEM and AFM images of FTO glass (a) and Pt films prepared by sputtering methods.

Fig. 4 shows FE-SEM and AFM micrographs of FTO glass (a) and Pt films(b) prepared by sputtering methods. Fig.4a shows FE-SEM photograph of FTO glass consisting of triangular facets. Fig.4b shows full Pt coverage with small Pt cluster on the surface of FTO glass. The sheet resistance of Pt sputtered film on FTO glass is approximately 4~5 ohm/sq, smaller than that in the case of FTO glass itself. Fig.4c shows more precise image of Pt sputtered film. From this observation, we expect the large surface area of Pt sputtered film plays a key role in occurring good catalytic reaction.

3.3 I-V CHARACTERISTICS OF DSSCS

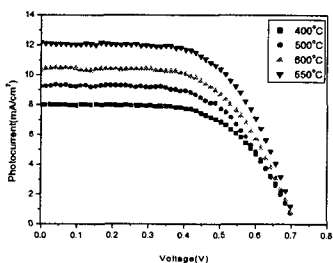


Fig. 5 Photocurrent-voltage curves of DSSCs in variation of RTA temperature

Fig.5 shows photocurrent-voltage curves in variation of RTA temperature. Solar cell was exposed to simulated sunlight with AM1.5 spectral distribution. Light intensity was 100mW/cm² and the active area was approximately 0.25cm². With increasing RTA temperature, photocurrent density of dye-sensitized solar cells was enhanced.

4. CONCLUSION

Fabrication and characterization of dye-sensitized TiO₂ solar cells(DSSC) consisting of TiO₂ electrode, an electrolyte containing I⁻/I₃⁻ redox couple, and a Pt-coated counter electrode was carried out. TiO₂ electrodes for DSSC were prepared by spray-coating. Also, effect of substrate temperature on I-V curves of solar cell consisting of approximately 10m thickness and 5x5mm² active area, The heat treatment was carried out at 550oC for 1min, using rapid thermal annealing(RTA) furnace. Solar cells having 5x5 mm² active area were assembled for measuring I-V characteristics. There was no significant difference in the apparent diameter of TiO₂particles, but the increase in number of vertical cracks occurred with increasing substrate temperature. Also, an open circuit voltage(Voc) of approximately 0.70V and a short-circuit photocurrent(Jsc) of 8 to 12mA/cm² were observed in the TiO₂ solar cell. With increasing RTA temperature, photocurrent density of dye-sensitized solar cells was enhanced, leading to enhancing the efficiency of dye-sensitized solar cells having Pt-electroplated counter electrode.

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