Experimental Investigation of Carbon Nanotubes Counter Electrodes for Dye-Sensitized Solar Cells

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***Abstract*—Carbon nanotubes (CNT) counter electrodes for dye-sensitized solar cells (DSSCs) were prepared by electrophoretic deposition (EPD). It was shown to be a convenient method to fabricate uniform coatings of CNT with desired thickness by changing voltage, electrophoresis time and inter electrode distance. Currently, CNT counter electrodes are lower conversion efficiency than that of Pt counter electrodes, and it needs to improve conversion efficiency as much as possible. We found that when we fabricated CNT counter electrodes at 500℃, both conversion efficiency and surface area obtained the best result. In this study, we examined that when we controlled film thickness by using EPD, how it would affect the conversion efficiency. We fixed DC voltage at 15V and controlled film thickness from 5μm to 20μm. After that, we sintered it at 500℃ and measured the conversion efficiency. As experimental results, we achieved the highest efficiency at 10μm and 2.4 % .**

***Index Terms*—Dye-Sensitized Solar Cells (DSSCs), Carbon Nanotubes (CNT), Electrophoretic Deposition (EPD), conversion efficiency, film thickness, surface area rate**

I. Introduction

Currently, researches about solar power generation are studied actively. There is a silicon shortage all over the world so currently dye-sensitized solar cells (DSSCs) have attracted much attention for their practical application as an alternative to p–n junction solar cells [1]-[12]. Above all, the study of DSSCs fabricated only organic materials without using silicon is active. Also, Pt used in a counter electrodes of DSSCs is a rare metal and has become more expensive than gold. But Pt demand of the world is rapidly increasing in such automotive catalyst. Production of Pt has remained at 150 tons per year and we worry about that the balance of supply and demand is lost. The development of counter electrodes material replaced Pt has been required in order to stabilize of the beneficiaries for balance and reduce costs. CNT is high conductivity, light, large surface area and flexibility. Using CNT which is an organic material instead of Pt, it has become possible to create low cost solar cells. CNT has many problems such as a low conversion efficiency and degradation early as compared with Pt. In this work, we aimed at fabricating processes of counter electrode.

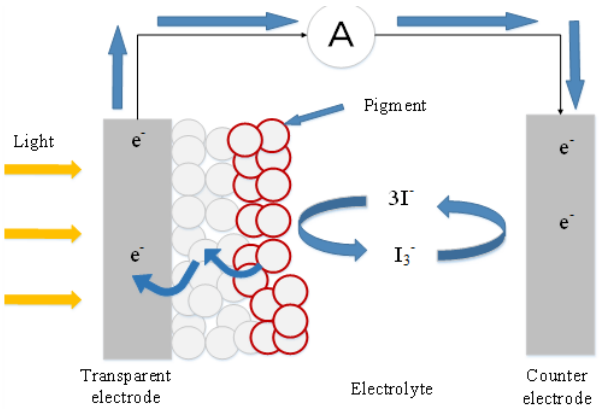


Figure 1. DSSCs structure.

II. DSSCs

Generally, DSSCs consist of transparent electrode, TiO_2, pigment, electrolyte and counter electrode as shown in Fig. 1. Transparence conductive film is formed on the transparent electrode and porous TiO_2 is formed on that. Porous TiO_2 consists of TiO_2 particle around 15nm. Pigment (MK-II) is absorbed on the TiO_2 surface. MK-II has functional groups such as carboxyl groups, hexyl groups. TiO_2 and pigment are bonded each other through chemical bond by dehydrogenation reaction the carboxyl groups [13], [14]. MK-II has advantages such as less limitation of resources than the ruthenium complex, having high molar absorptivity by π-π transition, structures are various and improvement easily. The hexyl groups have efforts reducing aggregate formation by π-π stacking between molecules. In this way, we can improve electronic infusion efficiency from the MK-II to TiO_2. Fig. 2 shows structural formula of the MK-II. Counter electrode is formed catalyst activating oxidation-reduction and DSSCs are formed oxidation-reduction property electrolyte between electrodes. As an operation principal, when the light shines the pigment from the outside, the pigment absorbed the light and electron is exited. The electron is injected into the conductor of TiO_2 in picosecond order and flow the electric circuit. The pigment oxidized receives electron from electrolyte and

Manuscript received August 11, 2012; revised October 17, 2015.

doi: 10.18178/ijpmbs.4.4.227-231

returns ground state pigment. While, the electrolyte transferred electron to the pigment and oxidized electrolyte diffused toward counter electrode, then receives electron from counter electrode and returns reduction state electrolyte. The electron flowing the circuit reaches counter electrode and oxidized counter electrode is reduced and returns original state. This is how electrons circulate and generate electricity by exposing the light.

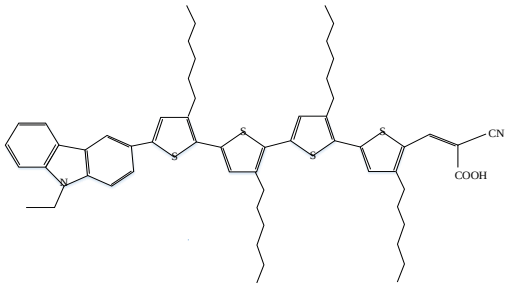


Figure 2. MK-II structural formula.

III. Electrophoretic Deposition (EPD)

When a pair of electrodes put in the solution and DC current flows, electrophoretic deposition is the phenomenon particles charged in the solution move to the opposite electrode. Fig. 3 shows view of EPD. When particles charged positively, particles move to cathode. In contrast, when particles charged negatively, particles move to anode.

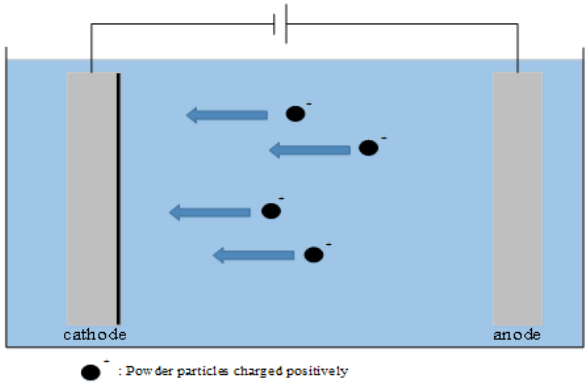


Figure 3. Over view of EPD.

EPD can divide, analysis and collect the molecule charged particles. Molecular weight and shape are difference. As advantages of EPD are (1) manufacturing processes are quick and easy to control film thickness, in other words, EPD can control the film thickness by changing various parameters (applied voltage, applied time, concentration of the dispersion) (2) EPD can form on large area and not level substrate, (3) EPD uses simple device and is cheap.

IV. Experimental

Instead of Pt, we used CNT for DSSC. In order to use EPD, we used CNT dispersion (meijo nano carbon). At present several methods have been employed for the fabrication of CNT counter electrodes such as chemical vapor deposition [15]-[17], screen-printing [18], drop coating [19], [20], spin coating, and spray coating [21]. The solvent of CNT dispersion was Isopropyl alcohol and concentration was 1wt%. As first step of fabricating CNT counter electrode, we used ultrasonic process for CNT dispersion. Because, usually CNT was aggregation state, we could not obtain characteristic as nano structure substance when we use as is. As next step, we used EPD. The aluminum (2cm×4cm) was used as substrates (cathode), connected to the negative potential, and counter electrode was FTO (anode) with same area. Two electrodes were kept parallel at 9mm apart in the suspension. Applying a constant DC voltage of 15 V for different times carried out EPD. In this work, the CNT electrode with different deposition times at 0.5, 1, 1.5, and 2 min. After that, we sintered them at 300 ℃, 350 ℃, 400 ℃, 500 ℃ and 550 ℃. We measured surface area of CNT counter electrodes by using atomic force microscope (AFM). We changed sintering temperature of them because we expected that contacting suspension surface area of CNT changed if we changed sintering temperature.

As TiO2 substrate fabricating, we mixed 20 ml of ethanol (Wako junnyaku) with for 0.1g of TiO_2 and agitated for an hour with magnetic stirrer (700rpm, 25 ℃). Applying a constant DC current of 0.12A for 1.5min carried out EPD. We used aluminum (2cm×2cm) as substrats (anode), connected to the positive potential, and counter electrode was FTO (cathode) with same area. After that, it was dried for 5min at room temperature and sintered at 450 ℃ for 1.5h.

In process of absorbing pigment, we mixed 10mg of MK-II dye (sigma-aldrich) and 108mg of toluene (Wako junyaku) at 25 ℃ until all dyes were dissolved. TiO_2 substrate were immersed into MK-II dye solution and kept for 3h at 25 ℃. After that, the dye-treated electrodes were rinsed with pure water and dried for 5min at 80 ℃.

In process of electrolyte fabricating, we mixed 1.597g of 1.2-dimethyl-3-propylimidazolium iodide (Wako junyaku), 0.134g of LiI (sigma-aldrich), 0.508g of I_2 (sigma-aldrich), 0.676g of 4-tert-butylpyridine (sigma-aldrich) and 10mg of acetonitrile.

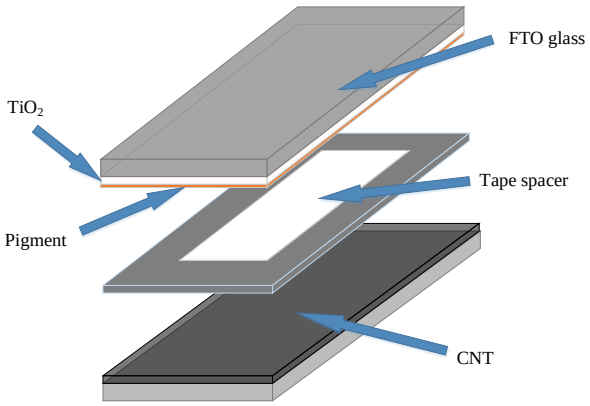


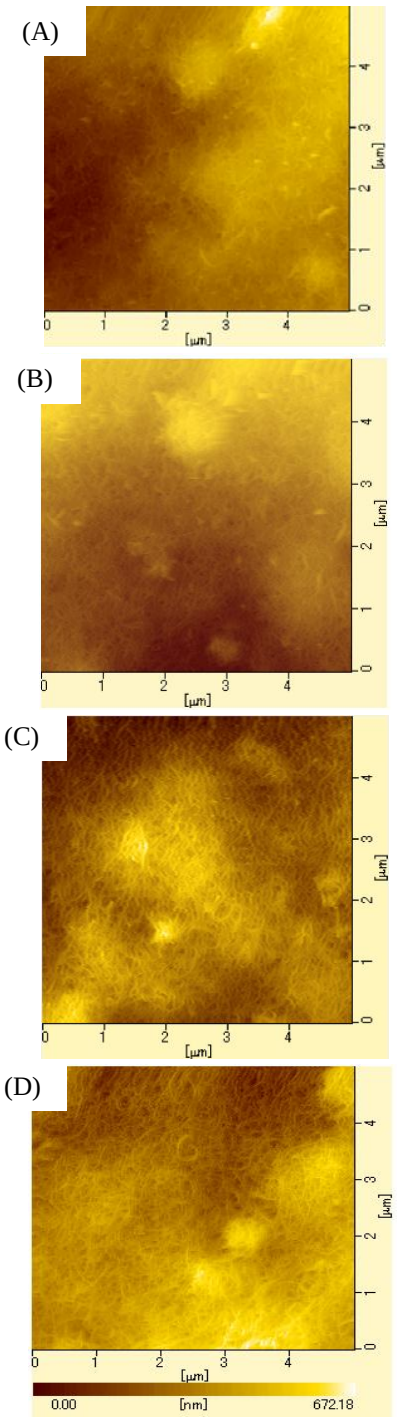
Figure 4. DSSC.

We fabricated DSSCs by using made TiO_2 substrate, electrolyte and CNT counter electrode. We made space between TiO_2 substrate and CNT counter electrode by

using mending tape and injected electrolyte. Fig. 4 shows DSSC.

The thickness of the prepared CNT electrodes was measured by using a surface profiler (Dektak). The conversion efficiency was measured by using solar simulator (Optical Associates Inc) at 1sun (AM 1.5G, 100 mW cm-2), which was calibrated with a reference Si reference solar cell.

Conversion efficiency is the highest when it is sintered at 500 ℃ and it is 2.50%. Based on this, we measured conversion efficiency when we used various film thickness CNT counter electrode at 500 ℃.



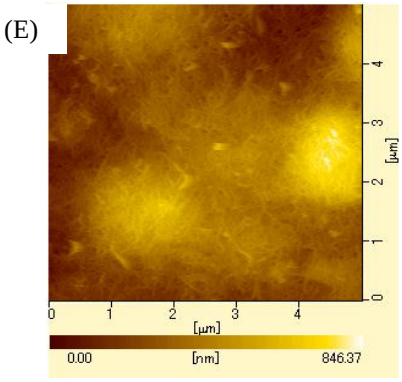


Figure 5. AFM image of the CNT counter electrode at (A) 300 ℃, (B) 350 ℃, (C) 400 ℃, (D) 500 ℃, (E) 550 ℃.

Then, when we measure surface area of CNT counter electrode, we used the CNT counter electrode fabricated by EPD applied a constant DC voltage of 15V and 1 min. After that, we changed the sintering temperature and measured surface area of CNT counter electrode. Fig. 5 shows surface images. This measurement conditions are that measurement area is 5μm × 5μm and resolving is 5nm. From these results of Table I and Fig. 5, the surface rate gradually increased from 300 ℃, but it decreased from 550 ℃. As these results, when we fabricated CNT counter electrode at 500 ℃, the highest surface rate is at 500 ℃. We expected that CNT counter electrode fabricated at 500 ℃ is the best for DSSC.

TABLE I. SINTERING TEMPERATURE AND SURFACE ARE RATE

Sintering temperature (℃)	Surface area rate
300	2.09
350	2.32
400	2.50
500	2.78
550	2.39

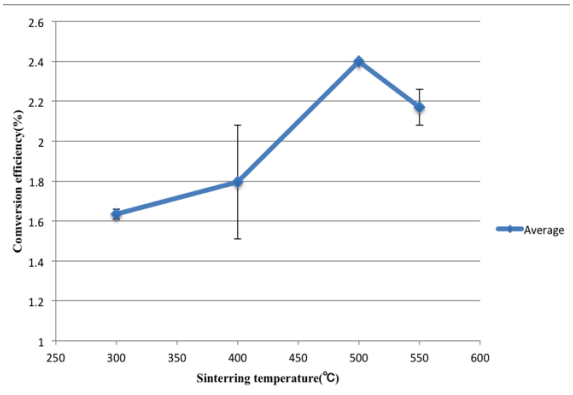


Figure 6. Sintering temperature and conversion efficiency.

Fig. 6 measured sintering temperature and conversion efficiency. It is said that fabricating at 500 ℃ can get the highest conversion efficiency when CNT counter electrode fabricated by EPD applied a constant DC voltage. Then, we fabricated CNT counter electrodes by EPD applied a constant DC voltage of 15V and changed EPD time from 0.5min to 2min and sintered 500 ℃. We

measured the conversion efficiencies and we worked the difference by the film thickness. As a result of measurement, Table II and Fig. 7, the conversion efficiency gradually increased from 5μm and it decreased from 10μm. Because increased impedance of counter electrode when increased film thickness, we considered that electric current hard to flow. Due to the aforementioned reasons, surface rate, sintering temperature and film thickness is important to conversion efficiency for DSSC.

TABLE II. FILM THICKNESS AND CONVERSION EFFICIENCY

Film thickness (μm)	Conversion efficiency (%)
5.0	1.88
9.2	2.40
17	1.25
22	0.77

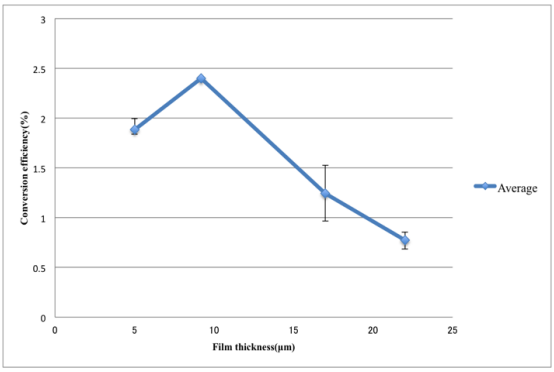


Figure 7. Relation of film thickness and conversion efficiency.

V. CONCLUSION

CNT counter electrode has been successfully fabricated by EPD and used for DSSC. Because CNT counter electrode consists of nanostructure substance with large surface area. When we fabricated CNT counter electrode at 500 ℃, the surface area rate reached maximally 2.78, and by the controlling of film thickness of CNT counter electrode, conversion efficiency of the DSSCs reached maximally 2.4%. Film thickness, sintering temperature and surface area rate are important for conversion efficiency of DSSCs. We expect that EPD method is a promising fabrication technique for a low cost production, fabrication easily production, flexible and conductive counter electrode for DSSCs

ACKNOWLEDGEMENT

The authors wish to thank to Minemoto laboratory in Ritsumeikan university. We got to use Solar simulator (OAI, TriSOL) and Step gauge (BRUKER DektakXT) for simulating DSSC performance.

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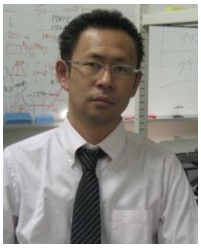

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