

# The Impact of PDDA in CNT Counter Electrode on the Conversion Efficiency of DSSC

Yoshiki Kurokawa, Dang Trang Nguyen, and Kozo Taguchi

**Abstract**—Dye-Sensitized Solar Cell (DSSC) is one of the equipment to convert sunlight into electricity. DSSC consists of anode electrode, titanium oxide ( $\text{TiO}_2$ ) thin film, sensitizer dye, electrolyte and cathode electrode (CE). In general, platinum (Pt) is usually used for CE. This paper studied the fabrication of CE using carbon nanotube (CNT) and CNT mixed with Poly (diallyl dimethylammonium chloride) (PDDA) (CNT/PDDA) as the substitution for Pt electrode. For the fabrication process, Electrophoresis Deposition (EPD) method was employed. CNT electrode was dried at room temperature at 25 °C or annealed at 400 °C for 1 hour, and CNT/PDDA CE was dried at room temperature at 25 °C. The thickness of CE we fabricated was around 15 $\mu\text{m}$ . We adapted MK2 dye which was an organic dye for DSSC. Experimental results showed that the conversion efficiency of the DSSC in the case of CNT/PDDA CE (4.12%) was higher than that of the case of dried CNT electrode (2.78%) and annealed CNT electrode (3.49%) under the 1 sun illumination (100mW/cm<sup>2</sup>). From this experiment results, PDDA has improved CE ability. In addition, CNT/PDDA CE do not need annealing process, so enabling flexible DSSC.

**Index Terms**—Dye sensitized-solar cell, carbon nanotube, poly (diallyl dimethylammonium chloride), organic dye mk2, no annealing, flexible.

## I. INTRODUCTION

Your goal is to simulate the usual appearance of papers in the. We are requesting that you follow these guidelines as closely as possible. Dye Sensitized-Solar Cell (DSSC) is a device that converts sunlight into electricity. This solar cell was firstly developed by Gratzel in 1991 who is a professor of the University of Swiss Federal Institution of Technology in Lausanne (EPFL). [1] In 2013, his team announced the highest conversion efficiency of 15 %. [2] The general structure composes of an anode electrode (dye-sensitized  $\text{TiO}_2$  electrode on conductive glass), electrolyte-containing redox, and a catalyst counter electrode (CE). DSSC has attracted attention due to low production cost, simple structure and possibility for high conversion efficiency. [3], [4] Under the illumination of solar light, sensitizer dye absorbs visible light, then dye molecules are excited then electrons are produced. The electrons pass thought anode electrode, external circuit and CE. The function of CE is to transfer electrons from the external circuit back to the redox electrolyte [5], [6]. Oxidation-reduction reaction (ORR) is repeated between CE and electrolyte solution. ORR also happens between electrolyte and sensitizer dye. Sensitizer dye is deoxidized and gets back to the original state. DSSC

repeats these processes and creates electrical current (Fig. 1).

Usually, platinum (Pt) is used for CE of DSSC because it catalyzes ORR with high efficiency than other metals and has superior electro catalytic activity [7], [8]. Nevertheless, Pt electrode has some drawbacks such as high costs, short-time durability and rare metal [9], [10]. Therefore, we should find substitution for Pt-based CE. One promising substitution is Carbon nanotube (CNT), which has advantages of large surface area, high electrical conductivity, low cost and chemical stability [9], [11]-[13]. However, using CNT for CE causes low conversion efficiency and early degradation compared with Pt.

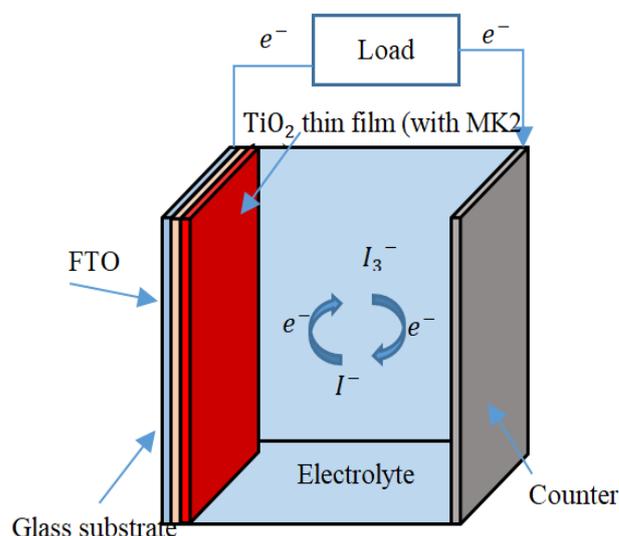


Fig. 1. DSSC configuration.

In this paper, we proposed a high catalysis CE for DSSC as a substitution for Pt. There are some methods to laminate carbon materials including Electrophoresis Deposition method (EPD), spin coating [9] or doctor-blading [14], [15]. EPD method is coating method by charging particles and has some advantages (short fabrication time, controllable thin film thickness and simple setting). It has been proved that Poly (diallyl dimethylammonium chloride) (PDDA) has ability of withdrawing electrons from CNT. [16] By using this method, we fabricated and tested CNT electrode and CNT mixed with PDDA (CNT/PDDA) electrode.

## II. EXPERIMENT METHOD

### A. Preparing $\text{TiO}_2$ Thin Film

As  $\text{TiO}_2$  thin film fabricated by EPD method, we used 0.2g of P25  $\text{TiO}_2$  powder (JAPAN AEROSIL), 40mL of ethanol (Wako) and 0.2g of Polyethylene glycol (PEG, Wako, average molecular 1500) to make  $\text{TiO}_2$  solution for EPD. They were mixed at the speed of 700rpm for 24 hours

with magnetic stirrer. The anode (Aluminum plate, 20×20×1mm) and counter electrode (FTO (fluorine doped SnO<sub>2</sub> coated glass substrate 20×20×1.8 mm) were placed in parallel into the TiO<sub>2</sub> solution, leaving 10 mm between anode and counter electrode with a silicon strip, and EPD current was set at 0.12 mA from a current source (ADVANTEST R6144). In process of EPD to fabricate four layers TiO<sub>2</sub> thin film, we executed 25 seconds EPD four times and drying process three times at 60°C for 1 minute each time in a dry oven (Iuchi, DO-450). Fig. 2 shows the flow for fabrication of multilayer thin film. After completing deposition, TiO<sub>2</sub> thin film was annealed at 400°C for 1 hour with an electric furnace (ASONE SMF-1).

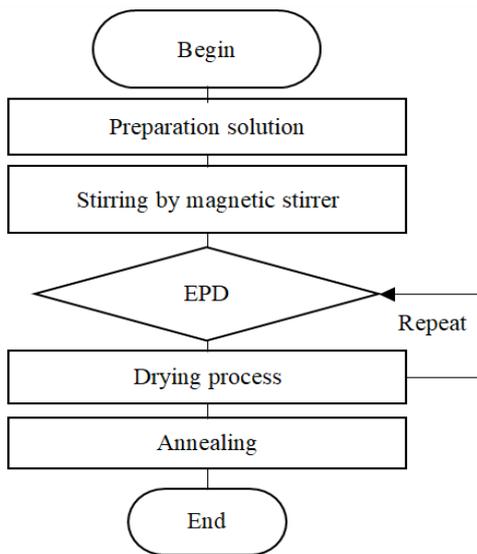


Fig. 2. Fabricating multilayer flow.

### B. Carbon Nanotube CE

By using EPD method, we fabricated three types of CE. Firstly, we prepared pure CNT electrode. To execute EPD process, we used CNT dispersion liquid (KJ, X7006L, MWCNT). For the EPD to prepare CNT electrode, the anode (FTO substrate 40×20×1.8mm) and counter electrode (Aluminum plate 40×20×1mm) were placed parallel in CNT dispersion, with 9 mm between anode and counter with silicon strip. The EPD voltage was set at 3V from a direct current stabilized power source equipment (AD-8723D, AND) and EPD time was set to be 80 seconds. After deposition, fabricated electrode was annealed at 400 °C for 1 hour or dried at room temperature of 25 °C for 24 hours. Thickness of the fabricated CNT electrodes was measured.

### C. Preparing PDDA on CNT CE

Secondly, PDDA solution was dropped on CNT electrode. We dropped two types with different PDDA concentration (20wt % or 1wt %) on dried CNT electrode or immediately after EPD process (Fig. 3). After dropping, they were dried at room temperature of 25 °C for 24 hours.

### D. Preparing CNT Mixed with PDDA CE

Finally, we made CNT and PDDA mixed solution (CNT/PDDA) to conduct EPD. To make CNT/PDDA solution, we used CNT dispersion solution (KJ, X7006L), PDDA solution (sigma Aldrich, 20wt %) and deionized

water (Monotaro). We mixed 20wt % of PDDA solution with suitable amount of deionized water to obtain 1wt % PDDA solution. After that, CNT and 1wt % PDDA solution were mixed in proportion of 10:1. Then we obtained CNT/PDDA solution. To execute EPD process, voltage was set 3V and EPD time was 90 seconds. After the EPD process, CNT/PDDA CE was dried at room temperature of 25 °C for 24 hours.

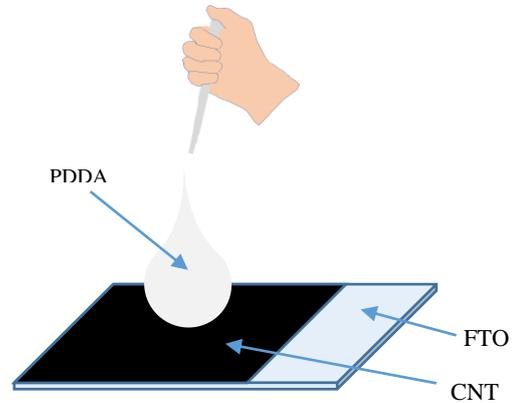


Fig. 3. Demonstration of dropping PDDA solution on CNT electrode.

### E. Electrolyte Blending and Soaking Sensitizer Dye

The electrolyte was consisted of 0.6 M of 1,2-dimethyl-3-propylimidazolium iodide (Wako), 0.1M of Lil (sigma Aldrich), 0.2 M of I<sub>2</sub> (sigma Aldrich), 0.5 M of 4-tert-butylpyridine (sigma Aldrich) and 10mL of acetonitrile (Wako).

The prepared TiO<sub>2</sub> thin film was soaked in sensitizer dye solution at 25 °C for 3 hours. The sensitizer dye solution was consisted of 10mg of organic dye (2-Cyano-3-[5''-(9-ethyl-9H-carbazol-3-yl)-3',3'',3''',4-tetra-n-hexyl-[2,2',5',2'',5'',2''']-quarterthiophen-5-yl] acrylic acid) (MK2, sigma Aldrich) and 108mL of toluene (Wako). In general, as a sensitizer dye, ruthenium is usually used. Ruthenium dye absorbed long wavelength light, so it realizes high conversion efficiency. However, high cost material and environmental hazards are problems of ruthenium dye. So, in order to improve these problems, researchers try to find natural dye for DSSC. Therefore, we used organic dye (MK2 dye). After the thin film absorbed the dye, its surface was rinsed by toluene and deionized water continuously to remove any dye that had not adsorbed on the surface of thin film. Then thin film was dried at 80 °C in dry oven for 5 mins.

### F. Making DSSC and Measurements

We assembled DSSC using two electrodes (dye soaked TiO<sub>2</sub> thin film and fabricated CE) and electrolyte as shown in Fig. 4. Masking tape was cut 25 mm<sup>2</sup> square and it was stuck on TiO<sub>2</sub> thin film with MK2 dye. We dropped electrolyte on this active area and sealed by CE.

The thickness of TiO<sub>2</sub> thin film and CE were measured by a step gauge (BRUKER DektakXT), and surface of TiO<sub>2</sub> thin film was observed by a metallurgical microscope (OLYMPUS BX60M). Absorption spectrum of dye adsorbed TiO<sub>2</sub> thin film was measured by a spectrophotometer (SHIMADZU, UV-3600). The open-circuit voltage *V*<sub>oc</sub> (V), short-circuit current density *J*<sub>sc</sub>

(mA/cm<sup>2</sup>), fill factor FF (%) and conversion efficiency (%) of DSSC was measured with solar simulator (OAI, TriSOL) by simulating the Sunlight (AM1.5, 100mW/cm<sup>2</sup>).

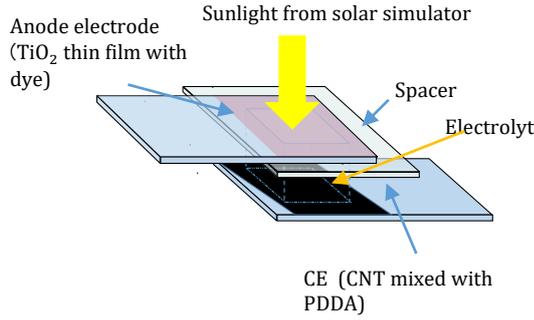


Fig. 4. Assembling DSSC.

### III. RESULT AND DISCUSSION

#### A. Evaluation of TiO<sub>2</sub> Thin Film by Metallurgical Microscope

Fig. 5 shows the surface image of TiO<sub>2</sub> thin film. Thin film with single layer has many crevices (Fig. 5 (a)) in contrast, thin film with four layers (Fig. 5 (b)) has no cracks. The occasion of cracks is due to the volatilization of ethanol. [17] In order to reduce crevices on the thin film, EPD process was executed four times and drying process was executed three times at high temperature. Cracks on the surface of film reduce the amount of sensitized dye adsorbed and cause low conversion efficiency.

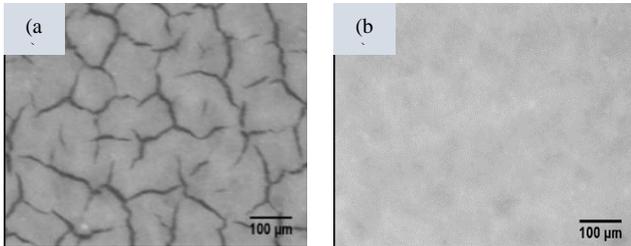


Fig. 5. Surface of TiO<sub>2</sub> thin film (a) single layer, (b) four layers.

#### B. Absorption Spectra

Fig. 6 shows absorption spectra of absorbed dye in TiO<sub>2</sub> thin film. To compare, two types thin film were measured (single layer and four layers). TiO<sub>2</sub> thin film with four layers adsorbed much dye than the case of single layer. The maximum adsorption wavelength of MK2 dye is 480 nm. From Fig. 6, absorption of the visible range of about 400-600 nm was better with four layers. From surface image of TiO<sub>2</sub> thin film and absorption spectra, multilayer TiO<sub>2</sub> thin film has essential role in DSSC anode electrode.

Sample	Jsc(mA/cm <sup>2</sup> )	Voc (V)	FF (%)	Eff (%)
Dropping PDDA (20wt%)	6.21	0.22	27.21	0.38
Dropping PDDA (1wt%)	4.24	0.24	30.82	0.32
Dropping PDDA after EPD	5.14	0.28	25.74	0.38

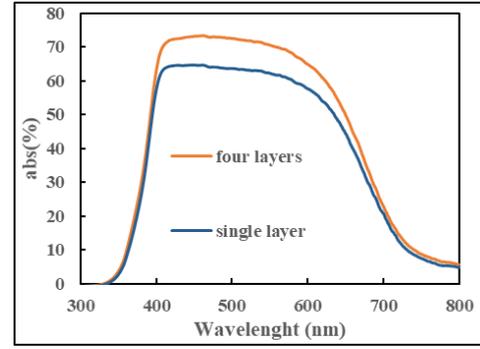


Fig. 6. Absorption spectra of absorbed dye in TiO<sub>2</sub> thin film.

#### C. Solar Cell Measurement

##### 1) Pure CNT CE

Table I shows measurement results when we used two patterns (dried and annealed) pure CNT CE. It shows that, short-circuit current density of dried CNT and annealed CNT have different values, which were 10.31 and 12.70 mA/cm<sup>2</sup> respectively. The conversion efficiency of these two patterns were 2.78% and 3.49% respectively. Compared with dried CNT, annealed CNT achieved better performance. Annealing process for CE is important because it removed dispersion solution and stuck CNT with FTO substrate. To further improve the efficiency, we tried to fabricate CNT CE using PDDA solution.

TABLE I: MEASUREMENT DATA OF THE DSSC USING DRIED CNT AND ANNEALED CNT

Sample	Jsc(mA/cm <sup>2</sup> )	Voc (V)	FF (%)	Eff (%)
Dried CNT	10.31	0.67	40.62	2.78
Annealed CNT	12.70	0.65	41.95	3.49

##### 2) CNT CE dropped PDDA solution

Table II shows measurement results when we used CNT CE dropped PDDA solution after EPD process. We measured three patterns of counter electrode (dropped 20wt%, 1wt% PDDA, and dropped PDDA after EPD), but these conditions had almost same results. All parameters were lower compared with annealed CNT electrode. This is because CNT cannot contact electrolyte because of the presence of PDDA layer on the CNT, as shown in Fig. 7, Fig.8 (a) shows the picture of a CNT CE with PDDA solution dropped on its surface, compared with a pure CNT electrode in Fig. 8 (b).

TABLE II: RESULT OF THE DSSC MEASUREMENT WITH DROPPING PDDA ON CE SURFACE

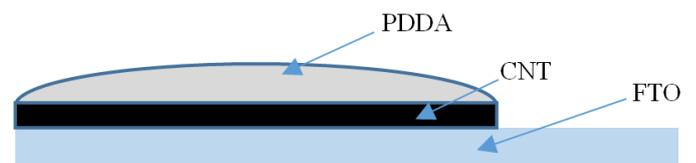


Fig. 7. Image of CNT CE dropped PDDA solution.

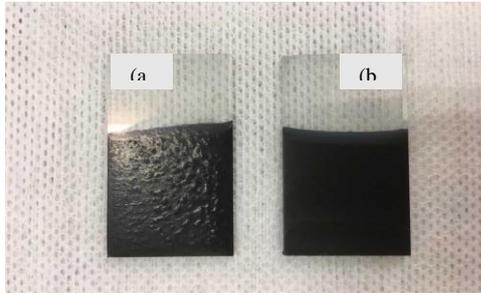


Fig. 8. Picture of CNT CE with (a) dropped PDDA solution, and (b) pure CNT electrode.

### 3) CNT/PDDA solution

TABLE III: RESULT OF DSSC MEASUREMENT WITH DRIED OR ANNEALED CNT AND CNT/PDDA ELECTRODE

Sample	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF (%)	Eff (%)
Dried CNT	10.31	0.67	40.62	2.78
Annealed CNT	12.70	0.65	41.95	3.49
CNT/PDDA	12.82	0.70	45.64	4.12

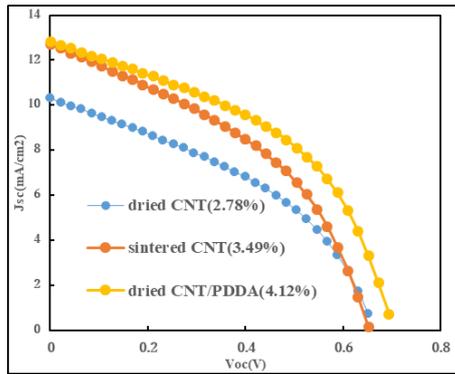


Fig. 9.  $J_{sc}$ - $V_{oc}$  curve dried CNT CE (blue), annealed CNT CE (orange), dried CNT/PDDA CE (yellow).

Table III shows results when we used pure CNT electrode (dried or annealed) and CNT electrode mixed with PDDA solution. In case of this proportion CNT: PDDA (1wt %)=10:1, the best energy conversion efficiency was achieved (4.12%). Therefore, it is obvious that PDDA helped improve the efficiency significantly.

Fig. 9 shows the photocurrent density-voltage curve for DSSC based on different CEs (dried CNT, sintered CNT and dried CNT/PDDA) measured under the illumination of 1 sun.  $J_{sc}$  of sintered CE and dried CNT/PDDA CE increased remarkably compared with dried CNT CE. Compared with dried CNT CE and dried CNT/PDDA CE, FF value of dried CNT/PDDA CE was improved.

## IV. CONCLUSION

In this paper, we fabricated CNT CE and CNT/PDDA CE using EPD method for DSSC. A little PDDA solution improved quality of CE. Experiment result shows that the conversion efficiency could be improved up to about 50 % (2.78% to 4.12%) by PDDA solution. Besides, our proposed method does not need annealing process, therefore contributing to the more flexible DSSC.

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