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The dye-sensitized solar cell devices using PEDOT:PSS films as counter electrodes have the lower production cost and more simple fabrication process than devices using Pt counter electrode. To enhance the power conversion efficiency of devices, we fabricated DSSC devices using thermal treated poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) as counter electrodes. The power conversion efficiency of DSSC device using a counter electrode based PEDOT:PSS film treated at 45°C for 720 min achieved a value of 3.22%.

Keywords: Counter electrode; dye-sensitized solar cells; thermal treated PEDOT:PSS

I. INTRODUCTION

Dye-sensitized solar cells (DSSCs) using dye molecules, nanocrystalline metal oxides and organic liquid electrolytes have attractive features of high power conversion efficiency. Recently, the power conversion efficiencies of DSSCs using Ruthenium complex dyes, liquid electrolytes, and Pt counter electrode have reached 10.4% (100 mW/cm^2, AM1.5) by Grätzel group [1]. Enormous efforts were

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made to improve the power conversion efficiency through the optimization of DSSC structures and modification of material chemical structures [2,3]. These researches are divided into three parts. The first describes studies of working electrodes such as a nanoporous titanium oxide layer with different thickness [4] or counter electrode such as a platinum layer or organic materials. Yanagida et al. reported that the power conversion efficiencies of the DSSC devices using no thermal treated PEDOT:PSS and TsO^- doped PEDOT (PEDOT:TsO) as a counter electrode were 2.10% and 4.60% under AM 1.5 illumination, respectively [5,6]. The second study is on the chemical structure of dye and its optical property. And the third part is a study of the electrolytes. The research on the chemical structure, morphology, optical, and electrical properties of the electrolytes are some of the major ones dealing with the design of high power conversion efficiency dye-sensitized solar cells. In the viewpoint of the cost in order to commercialize the DSSCs, the development of the counter electrode with alternative materials is required to reduce production cost of DSSC cells. There are expected several organic materials (porous carbon, doped PEDOT derivatives, etc.) to reduce the production cost of cells and to simplify complicated fabrication process. When carbon or PEDOT:PSS counter electrode compared with Pt counter electrode, the power conversion efficiency of DSSC devices has relatively a low value due to the poor catalytic activity for I_3^- reduction per unit area and lower conductivity [7]. However, the application with the counter electrode of the organic materials such as PEDOT:PSS could be reduced the production cost, and the PEDOT:PSS counter electrode could be fabricated more simple and low temperature process than vacuum or thermal deposition. Therefore, PEDOT:PSS seems to be more suitable candidate for counter electrode instead of Pt.

In 1998, an electronically conducting polymer, poly(3,4-ethylenedioxythiophene) (PEDOT) developed by Jonas group has many attractive properties such as high conductivity, transparency, remarkable stabilities [8–11]. PEDOT is such a low band gap semiconducting polymer, after doping, doped PEDOT has high electrical conductivity, excellent chemical and environmental stability. These advantages have attracted considerable attention in organic electronic devices because of its high transmittance in the visible range and its good dc-conductivity [12]. However, doped PEDOT derivatives such as PEDOT:PSS still needs to improve its transport properties. The studies for improving the electrical properties of PEDOT:PSS have been undergone in many research groups. One is to synthesize new PEDOT derivatives by attaching a substituted side-chain into the main backbone [13,14]. The other manner of improving electrical properties,

adding organic solvents such as *N,N*-dimethylformamide (DMF) into the PEDOT:PSS solution has also been attempted. Although the electrical properties of the PEDOT:PSS films from organic mixtures are enhanced, the electrical conductivity does not increase significantly [15].

In this work, we fabricated DSSC devices using thermal treated PEDOT:PSS as counter electrodes. The photovoltaic properties of DSSC devices and the surface morphology of PEDOT:PSS counter electrodes were investigated.

II. EXPERIMENTAL

2.1. Materials

Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (BAYTRON® P VP CH 8000, PEDOT:PSS) was purchased from BAYER AG. Poly(ethylene oxide) (PEO, $M_w = 200{,}000$), iodide (I_2), acetonitrile (AN), propylene carbonate (PC), ethylene carbonate (EC), and tetrabutylammonium iodide (TBAI) were purchased from Sigma Aldrich Co., Ltd. *Cis*-di(thiocyanato)-N,N-bis(2,2′-bypyridil-4.4′-dicarboxylic acid)-ruthenium (II) complex (N3 dye), fluorine-doped SnO_2-layered (FTO) glass (15 ohm/sq), Pt-catalyst T/SP, Ti-Nanoxide HT/SP, and 1-propyl-3-methylimidazolium iodide (PMII) were purchased from Solaronix SA.

2.2. Measurements

Thicknesses of PEDOT:PSS films were measured by using a Alpha-step IQ. Photovoltaic performances of DSSC devices were measured by using a solar simulator (300 W simulator, models 81150) furnished with ARC Lamp power supply at AM 1.5, and the photointensity was $100\,mW/cm^2$. The active area of DSSC device measured by using a black mask was $0.25\,cm^2$. The surface morphology of PEDOT:PSS films were observed by using Atomic Force Microscope (AFM, Nanoscope IIIa®) in air.

2.3. Fabrications of DSSC Devices

We prepared the DSSC devices, sandwiched with working electrode using TiO_2 impregnated dye and counter electrode using thermal treated PEDOT:PSS as two electrodes. The DSSC device was fabricated as following process. The TiO_2 pastes (Ti-Nanoxide HT/SP) was spread on FTO glass by the doctor blade method. After heating

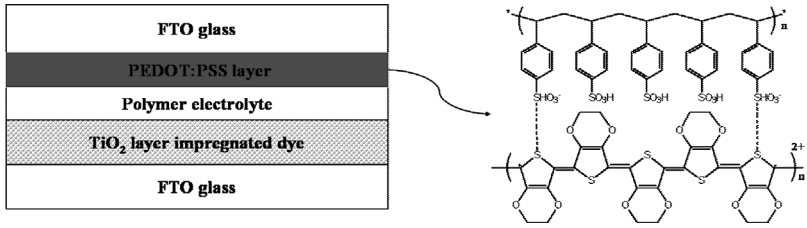

FIGURE 1 The schematic diagram of the DSSC device using PEDOT:PSS as counter electrode and the chemical structure of PEDOT:PSS.

up the FTO glass spread TiO_2 pastes to ca. 120°C for about 30 min and ca. 450°C for about 30 min as the controlled heating rate (5°C/min), it was cooled down from 450°C to 60°C as controlled cooling rate (5°C/min) to avoid cracking of the glass. The sensitizer N3 dye was dissolved in pure ethanol. The FTO glass deposited TiO_2 was dipped in ethanol solution at 45°C for 18 hours. Polymer electrolyte was consisted of PEO, 0.1 M of I_2, 0.3 M of PMII, and 0.2 M of TBAI in the solution of EC/PC/AN (4:1:5 v/v/v). The polymer electrolyte was casted on the TiO_2 deposited electrode impregnated dye, and dried in dry oven of 55°C for 4 hours.

To fabricate PEDOT:PSS counter electrodes, after PEDOT:PSS solution were spin-coated on FTO glass, PEDOT:PSS films were dried in dry oven at 120°C for 30 min. Then, the PEDOT:PSS films were thermally treated with 5°C/min of heating rate under various annealing conditions (at 45°C, 60°C, 80°C, 100°C, 120°C for 20 min or 720 min). To compare with the photovoltaic performances of DSSC devices, Pt counter electrode was prepared by the similar method of working electrode process. The Pt pastes (Pt-catalyst T/SP) were spread on FTO glass by the doctor blade method. After heating up the FTO glass spread Pt-catalyst T/SP to ca. 100°C for about 30 min and ca. 400°C for about 30 min as the controlled heating rate (5°C/min), it was cooled down from 400°C to 25°C as controlled cooling rate (5°C/min) to avoid cracking of the glass.

In assembling of DSSC devices, the working electrode and the counter electrode were clamped together. The structure of the DSSC device is shown in Figure 1.

III. RESULTS AND DISCUSSION

The I-V curves of DSSC devices using PEDOT:PSS films as counter electrodes are shown in Figures 2 and 3. The photovoltaic

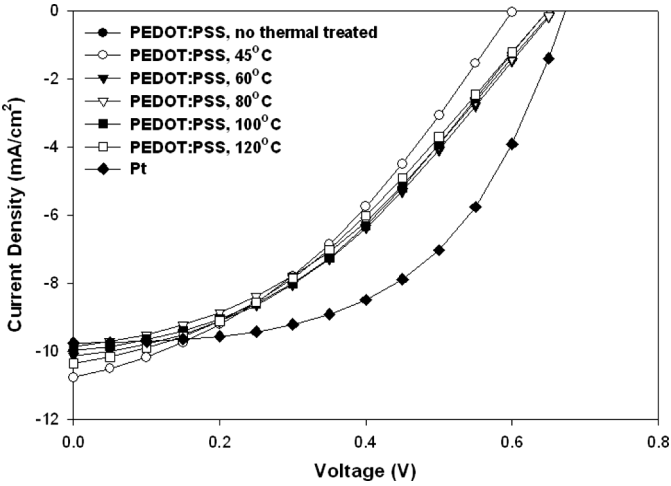

FIGURE 2 I-V curves of DSSC devices using thermal treated PEDOT:PSS for 20 min as counter electrodes under illumination at AM 1.5 condition.

characteristics of theirs are summarized in Table 1. The photovoltaic parameters of the cells such as open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and power conversion efficiency (η) were calculated from the analysis of I-V characteristics.

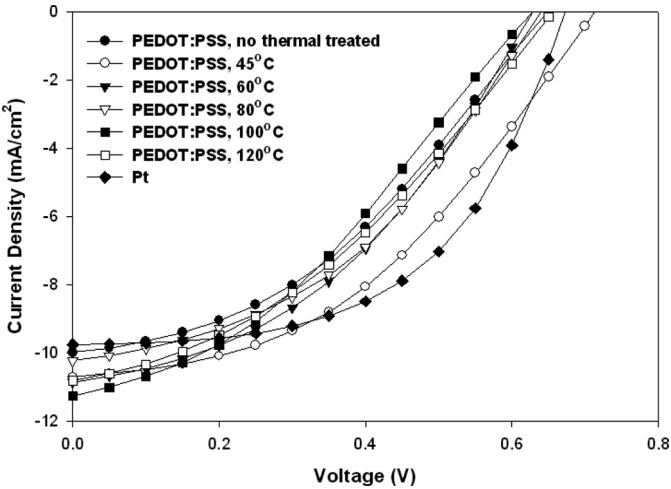

FIGURE 3 I-V curves of DSSC devices using thermal treated PEDOT:PSS for 720 min as counter electrodes under illumination at AM 1.5 condition.

TABLE 1 Photovoltaic Characteristics of DSSC Devices using PEDOT:PSS as Counter Electrodes[1)]

Counter electrode	Treatment condition		V_{oc}(V)	J_{sc} (mA/cm^2)	FF	η (%)
	Temperature (°C)	Time (min)				
PEDOT:PSS[2)]	–	–	0.65	10.78	0.36	2.49
	45		0.60	10.77	0.37	2.40
	60		0.65	9.99	0.39	2.54
	80	20	0.65	10.35	0.36	2.46
	100		0.66	10.14	0.38	2.56
	120		0.66	9.87	0.38	2.48
	45		0.71	10.71	0.42	3.22
	60		0.63	10.87	0.41	2.78
	80	720	0.64	10.23	0.41	2.71
	100		0.63	11.26	0.35	2.51
	120		0.65	10.81	0.37	2.60
Pt	–		0.67	9.75	0.54	3.55

[1)]All the devices were measured by solar simulator under illumination at AM 1.5 condition.

[2)]The thickness of PEDOT:PSS films measured by using Alpha-step IQ were about 110 nm.

To investigate the effect of thermally treatment of PEDOT:PSS counter electrode on the photovoltaic performances of DSSC devices, DSSC devices using thermal treated PEDOT:PSS as counter electrodes (at 45°C, 60°C, 80°C, 100°C, 120°C for 20 min or 720 min) were prepared. The V_{oc}, J_{sc}, FF, and η of DSSC device using no thermal treated PEDOT:PSS counter electrode were 0.65 V, 10.78 mA/cm^2, 0.36, and 2.49%, respectively. When PEDOT:PSS film was treated at 45°C for 720 min, the V_{oc} of the DSSC device was enhanced up to 0.71 V, the FF was 0.42, and the overall power conversion efficiency of device showed the best result of 3.22%. Compared to the photovoltaic result of DSSC device using Pt electrode, although there was little difference of the over all power conversion efficiency, 0.42 of FF in the DSSC device using PEDOT:PSS counter electrode showed lower value than 0.54 of Pt electrode. This result can be attributed to the report that the FF of DSSC device using an organic electrode such as PEDOT:PSS has relatively a low value, compared to DSSC devices using Pt electrode, due to the poor catalytic activity for I_3^- reduction per unit area and lower conductivity [5–7].

Meanwhile, the photovoltaic performances of DSSC devices using thermal treated PEDOT:PSS counter electrodes for 20 min were relatively lower values than those using thermal treated for long time.

There was not much difference with the DSSC device using no thermal treated PEDOT:PSS electrode. Regardless of the annealing temperature, the thermal treatment during the shorten time gave little effect on the photovoltaic performances of DSSC devices.

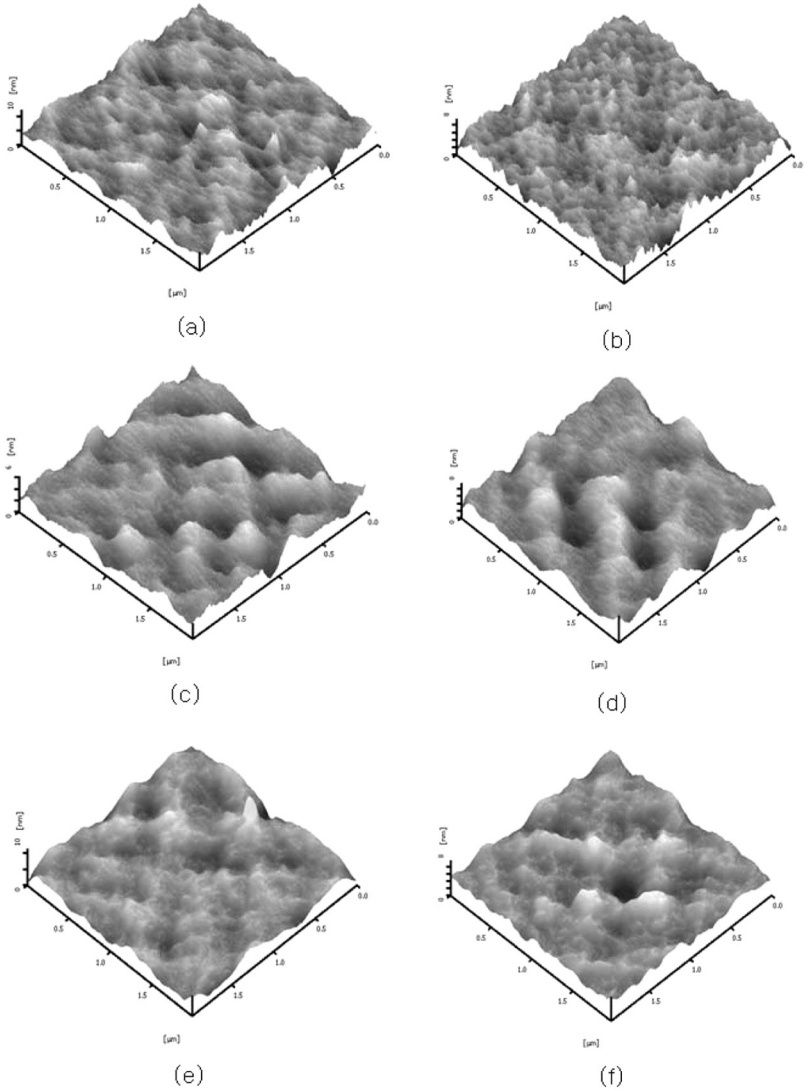

FIGURE 4 AFM images of (a) no thermal treated PEDOT:PSS film and (b), (c), (d), (e), (f) PEDOT:PSS film treated at 45°C, 60°C, 80°C, 100°C, 120°C for 720 min, respectively.

The change of the surface morphology of the PEDOT:PSS films before and after the thermal treatment was observed by AFM. Figure 4 are shown images of counter electrodes using (a) no thermal treated PEDOT:PSS and (b) ~ (f) thermal treated PEDOT:PSS for 720 min. The 110-nm-thick PEDOT:PSS film coated on the FTO glass was obtained with RMS of ca. 1.159, after the treatment of PEDOT:PSS films for 720 min, the thermal treated PEDOT:PSS films were ca. 0.978 (b), 0.917 (c), 1.342 (d), 0.868 (e), and 1.080 (f), respectively. As shown in Figure 4(b), after the thermal treatment of PEDOT:PSS film at 45°C for 720 min, the granular surface microstructure appeared, and the surface area of film increased. However, the more annealing temperature increase, the more granular surface microstructure disappeared and FF decreased. It was revealed that, the thermal treatment of PEDOT:PSS film resulted in the enhancement of power conversion efficiency of DSSC device, due to the increase of the surface area and the crystallinity of the PEDOT:PSS film during the thermal treatment.

To investigate the effect of the PEDOT:PSS film thickness of the counter electrode on the performance of DSSC, all the PEDOT:PSS films used were prepared by the spin coating method under same conditions. When the counter electrode was constructed of an FTO glass covered with 110-nm-thick PEDOT:PSS film, the V_{oc} and J_{sc} of the DSSC obtained to 0.71 V and 10.71 mA/cm^2, and the overall power conversion efficiency achieved 3.22%. As the PEDOT:PSS film thickness further increased, no apparent difference in V_{oc}, J_{sc}, and FF of the DSSCs were observed, as shown in Table 2.

Considering the durability and stability of the DSSC using organic counter electrode such as PEDOT:PSS and the concern that a small amount of PEDOT:PSS might dissolve in the electrolyte solution and complex formation with I^-/I_3^-, therefore, a too thin or too uneven

TABLE 2 Photovoltaic Characteristics of DSSC Devices using Different Thickness of PEDOT:PSS Films as Counter Electrodes[1)]

Thickness of counter electrode[2)] (nm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
80 ~ 90	0.70	10.71	0.39	2.95
110 ~ 120	0.71	10.71	0.42	3.22
800 ~ 900	0.66	11.37	0.40	3.03

[1)]All the devices were measured by solar simulator under illumination at AM 1.5 condition.

[2)]The thicknesses of PEDOT:PSS films were measured by using Alpha-step IQ. All the PEDOT:PSS films were thermally treated at 45°C for 720 min.

PEDOT:PSS film should be avoided in the fabrication of the DSSCs. Studies on the charge-transfer resistances at the interfaces of the electrolyte and counter electrodes and the optimization of the PEDOT:PSS film thickness are in progress.

IV. CONCLUSION

We successfully fabricated DSSC devices using PEDOT:PSS film as counter electrodes by spin coating method. The V_{oc}, J_{sc}, FF, and η of DSSC devices using no thermal treated PEDOT:PSS film as a counter electrode were 0.65 V, 10.78 mA/cm^2, 0.36, and 2.49%, respectively. In DSSC devices using thermal treated PEDOT:PSS film as a counter electrode at 45°C for 720 min, the overall power conversion efficiency was obtained the best result of 3.22%.

After the thermal treatment of PEDOT:PSS film at 45°C for 720 min, due to the increase of the surface area and the crystallinity of the PEDOT:PSS film, the power conversion efficiency of DSSC device increased from 2.49% to 3.22%.

As the PEDOT:PSS film thickness further increased, no apparent difference in V_{oc}, J_{sc}, and FF of the DSSCs using the PEDOT:PSS films as counter electrodes was observed.

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