



Effects of mesoscopic poly(3,4-ethylenedioxythiophene) films as counter electrodes for dye-sensitized solar cells

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ABSTRACT

Counter electrode coated with chemically polymerized poly(3,4-ethylenedioxythiophene) (PEDOT) in a dye-sensitized solar cell (DSSC) was studied. The surface morphology and the nature of I^-/I_3^- redox reaction based on PEDOT film were investigated using Atomic Force Microscopy and Cyclic Voltammetry, respectively. The performance of the DSSCs containing the PEDOT coated electrode was compared with sputtered-Pt electrode. We found that the root mean square roughness decreases and conductivity increases as the molar ratio of imidazole (Im)/EDOT in the PEDOT film increases. The DSSC containing the PEDOT coated on fluorine doped tin oxide glass with Im/EDOT molar ratio of 2.0, showed a conversion efficiency of 7.44% compared to that with sputtered-Pt electrode (7.77%). The high photocurrents were attributed to the large effective surface area of the electrode material resulting in good catalytic properties for I_3^- reduction. Therefore, the incorporation of a multi-walled carbon nanotube (MWCNT) in the PEDOT film, coated on various substrates was also investigated. The DSSC containing the PEDOT films with 0.6 wt.% of MWCNT on stainless steel as counter electrode had the best cell performance of 8.08% with short-circuit current density, open-circuit voltage and fill factor of 17.00 mA cm⁻², 720 mV and 0.66, respectively.

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1. Introduction

The demonstration of dye-sensitized solar cells (DSSCs) in 1991 introduced a most promising low cost light harvesting device, an alternative to traditional inorganic silicon solar cells [1]. Since then, great progress related to their performance has been made in this field. In order to further improve its efficiency, extensive research has been conducted on semiconductor nano-crystalline TiO₂ [2–5], dye molecules [6–10], electrolytes [11–14], and counter electrodes [15–17]. Although Pt as a counter electrode has high catalytic activity for reduction of I_3^- to I^- and conductivity, it is one of the most expensive components in the DSSCs. Therefore, development of counter electrodes with alternative materials is expected to reduce production costs of the DSSCs. Several carbonaceous materials such as carbon nanotubes, activated carbon, graphite, and carbon black had been employed as catalysts for counter electrodes in the DSSCs [17,18]. However, the internal resistance of a device increases with the thickness of the

counter electrodes, resulting in a low fill factor and efficiency. Recently, Murakami et al. employed carbon black as the counter electrode in the DSSCs and achieved a remarkable conversion efficiency of 9.1% under the light intensity of 100 mW cm⁻² [17].

Meanwhile, conducting polymers have also become one of the important candidates for counter electrode in the DSSCs. Among the numerous materials devised, the development of a polythiophene derivative and poly(3,4-ethylenedioxythiophene) (PEDOT), has presented a significant promise to meet the challenges of competing properties [19]. Yanagida et al. used chemically polymerized poly(3,4-ethylenedioxythiophene) (PEDOT) on fluorine doped tin oxide (FTO) glass as the counter electrode and obtained a conversion efficiency of ~3.6% under 100 mW cm⁻² [16], and also developed PEDOT-based solid-state electrolytes, with cell efficiency of <1% [20,21]. Muto et al. employed the addition of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS) with TiO₂ particles to improve the surface roughness, and incorporated this conductive film in plastic DSSC, where the efficiency had reached 4.38% [22].

In this paper, we report the employment of PEDOT film, as the counter electrode for the DSSC, prepared by oxidative polymerization of EDOT monomer using the method of spin coating on various substrates. The influences of various imidazole/EDOT ratios and

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percentages of multi-walled carbon nanotube (MWCNT) on the morphologies and conductivities of PEDOT films as well as on the cell performances of the DSSCs were examined.

2. Experimental

2.1. Materials

Anhydrous LiI, I₂, poly(ethylene glycol) (PEG) (MW 20,000), 4-tertiary butyl pyridine (TBP), tertiary butanol, and acetonitrile were purchased from Merck. Titanium (IV) tetraisopropoxide (>98%) was purchased from Acros and used as received. N3 dye (cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium (II)) was obtained from Solaronix (Aubonne, Switzerland). The multi-walled carbon nanotube (MWCNT) was purchased from Nanotech Port (Taiwan) and was oxidized in a concentrated 3:1 (v/v) acid mixture of H₂SO₄/HNO₃ under ultrasonication for 24 h at 50–60 °C to produce MWCNT with terminal –COOH groups [23].

2.2. Preparation of counter electrodes and TiO₂ electrodes

The PEDOT films were prepared by oxidative polymerization process [24]: solution A containing 0.434 g iron(III) toluenesulfonate (Fe(OTs)₃) in 0.25 ml methanol and solution B containing 0.05 g imidazole and 40 μl EDOT monomer in 0.25 ml methanol were mixed together, followed by spin casting on the ITO substrate and polymerization was carried out at 120 °C for 5 min. The resulting films were thoroughly washed with methanol for several times and dried with a nitrogen gun. Further, careful washing with methanol was done to remove the monomers and Fe³⁺ ion which will reduce the cell performance. The MWCNT was added in solution B if needed. The Pt (100 nm thick) sputtered onto the FTO glass was also used as the reference for comparative purpose. The structural nature was investigated using Atomic Force Microscopy in high mode (AFM, Digital Instruments, Dimension-3100 Multimode), and the AFM tip is a silicon-SPM sensor (tapping mode), thickness 4 μm, length 125 μm and width 30 μm. The surface morphology was measured by Scanning Electron Microscopy (SEM, Hitachi S-4700) under 10 kV operating voltage.

The TiO₂ nanoparticle preparation and electrode fabrication were carried out according to the literature [25], where the solution was concentrated to 13 wt.% and PEG was added to prevent film cracking during drying. The TiO₂ paste was coated onto FTO glass using a glass rod, and then sintered at 500 °C for 30 min.

2.3. Cell assembly and measurements of the DSSCs

An active area of 0.25 cm² was selected from the sintered TiO₂ electrode and immersed in a 3 × 10^{−4} M solution of N3 dye containing acetonitrile and tertiary butanol (in a volume ratio of 1:1) for 12 h. The cell was assembled with these two electrodes separated by the electrolyte composed of 0.5 M LiI/0.05 M I₂/0.5 M TBP in acetonitrile and an ionomer resin of 50 μm (Surlyn, Dupont).

The DSSCs were energized using a light source of a 450-W Xe lamp (#6266, Oriel) equipped with a water-based infrared filter and an AM 1.5 filter (#81075, Oriel). Photoelectrochemical characteristics and electrochemical impedance spectroscopic (EIS) measurements of the DSSCs were recorded with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie) under constant light illumination of 100 mW cm^{−2}. The applied bias voltage was set at an open-circuit voltage of the DSSCs, and the AC amplitude was 10 mV between the counter and working electrodes, in the frequency range of 10 mHz to 65 kHz. The impedance spectra were analyzed based on an equivalent circuit model [26].

3. Results and discussion

3.1. Characterizations of PEDOT films prepared with various imidazole/EDOT ratios

As depicted by Ha et al., the incorporation of imidazole during oxidative polymerization of EDOT into a polymer helps to reduce the reactivity of Fe(OTs)₃ leading to slow polymerization kinetics and low doping levels [24]. In order to see this effect, AFM images of PEDOT films incorporated with different ratios of Im/EDOT are shown in Fig. 1. Without the addition of imidazole, the high reactivity leads to thicker films as oligomers or polymers begin to form in the solution prior to spin coating (Fig. 1a). The fast polymerization kinetics may cause the precipitation of prepolymerized nanoscopic droplets onto the substrate, causing high surface roughness. Subsequently, with an increase in the concentration of imidazole, the conductivities of PEDOT films increase by simultaneously preventing over doping and promoting higher molecular weight chains due to the slowdown of the polymerization kinetics (Fig. 1b to e). The presence of imidazole preserves EDOT in monomeric form even after spin coating, and the polymerization after thermal treatment leads to smoother surface morphology by increasing connectivity between the domains. When the molar ratio of Im/EDOT was higher than 2.5, however, no polymerization had proceeded. The relationship between RMS roughness and conductivity of PEDOT films for different molar ratios of Im/EDOT is shown in Fig. 2. The conductivity values of the polymer film were obtained by the following relationship:

$$\sigma = 1 / (SR_t), \quad (1)$$

where σ is the film conductivity, SR is the surface resistance (Ohm square^{−1}) and t is the thickness of the film (cm). The average of at

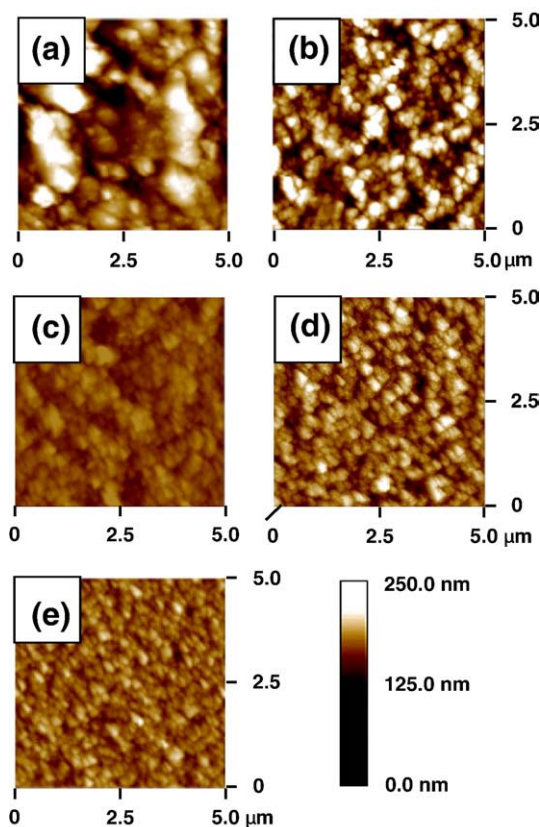


Fig. 1. AFM images of PEDOT films with various Im/EDOT molar ratios: (a) 0, (b) 1.0, (c) 1.5, (d) 2.0 and (e) 2.5.

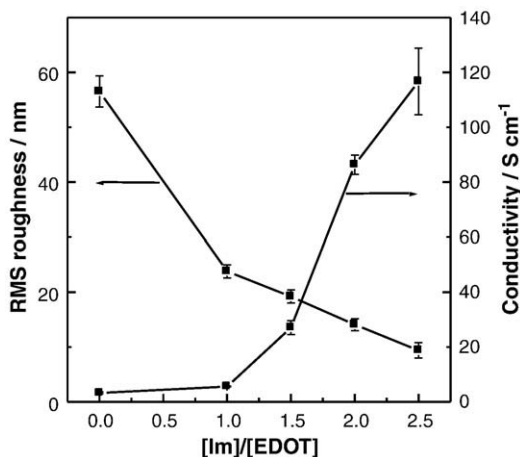


Fig. 2. The relationship of RMS roughness and conductivity of PEDOT films for different molar ratios of Im/EDOT.

least five measured values of surface resistance and film thickness at different locations of the polymer film was incorporated in the equation for getting a good conductivity.

It is noted that the order of RMS roughness (R_{rms} : values of those films, which reflect the degree of surface roughness) decreases with an increase in the molar ratio of Im/EDOT as measured by AFM. The PEDOT film without imidazole showed the largest R_{rms} value of ca. 58 nm over a 5×5 - μm area with low conductivity; however, with the increase in the molar ratio, the conductivities improve to a large extent. Meanwhile, the effects of polymer film thickness and conductivity on the different spinning conditions on glass substrate are shown in Fig. 3. It is found that the film thickness increases slightly with an increase in spin speed up to 4000 rpm and then drastically changes. On the other hand, the average conductivity of the film decreases from 2000 to 6000 rpm and the difference gets minimized between 6000 and 8000 rpm.

Cyclic voltammetry (CV) was used to analyze the relationship between ion diffusivity and reaction kinetics of an electrochemical system. Fig. 4 shows the CV of I^-/I_3^- redox couples on PEDOT film in acetonitrile containing LiI (10 mM), I_2 (1 mM) and $LiClO_4$ (0.1 M) as supporting electrolyte recorded at various scan rates ranging from 20 to 250 mV s^{-1} . The relationship between the anodic and cathodic peaks and square root of the scan rate is shown in the inset of Fig. 4. These two anodic and cathodic peaks represent the following reactions:

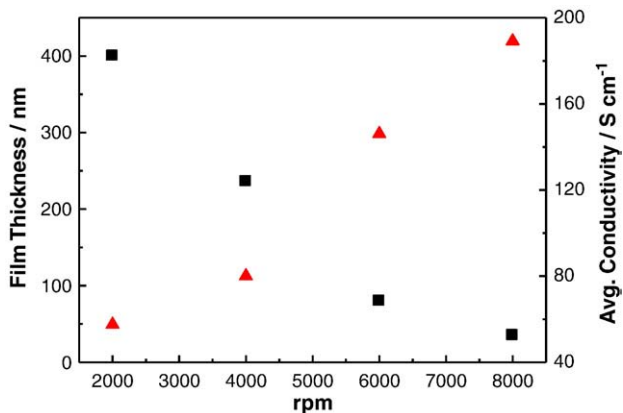


Fig. 3. The relationship between polymer film thickness and conductivity.

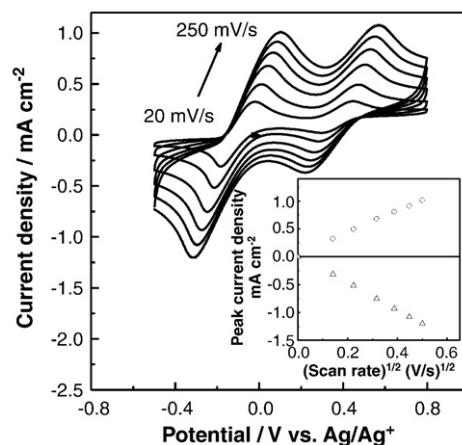


Fig. 4. The CVs of iodide species on PEDOT film in acetonitrile solution containing 10 mM LiI, 1 mM I_2 and 0.1 M $LiClO_4$ taken at various scan rates ranging from 20 to 250 mV s^{-1} . The peak current as a function of scan rate is shown in the inset of Fig. 3.



The linear relationship indicates the diffusion limitation of the redox reaction on PEDOT film [16,27]. Similar to Pt electrode, the redox reaction at the PEDOT surface was slightly affected by the adsorption of iodide species under these conditions. It also suggests that there is no specific interaction between I^-/I_3^- and the PEDOT film on the surface of the electrode.

3.2. Influences of the PEDOT films as the counter electrode on the performances of DSSCs

The J - V curves of the DSSCs based on PEDOT counter electrodes prepared with various Im/EDOT molar ratios along with Pt and PEDOT-PSS and the dependence of various parameters such as V_{OC} (open-circuit voltage), FF (fill factor), J_{SC} (short-circuit current density) and conversion efficiency of the DSSCs on the various molar ratios of Im/EDOT are shown in Figs. 5 and 6 respectively. The DSSC with a PEDOT (Im/EDOT = 2.0) counter electrode had the highest J_{SC} and FF, with a good conversion efficiency of 7.44%, in comparison to 7.77% obtained for the cell prepared with the sputtered-Pt electrode. The PEDOT film having both the molar ratios of 0 and 2.0 represented a good J_{SC} value due to higher surface roughness and conductivity, respectively (Fig. 6). The FF and V_{OC}

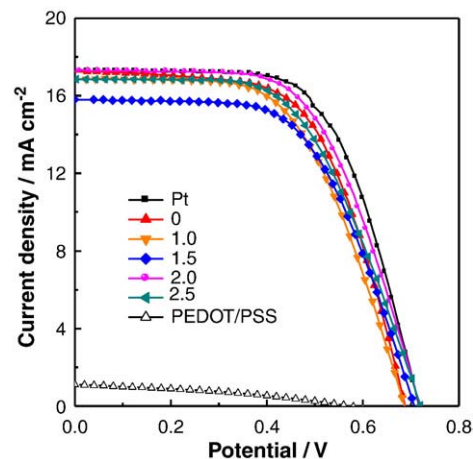


Fig. 5. The J - V curves of the DSSCs based on PEDOT counter electrodes prepared with various Im/EDOT molar ratios. Pt and PEDOT-PSS electrodes are also taken for comparison.

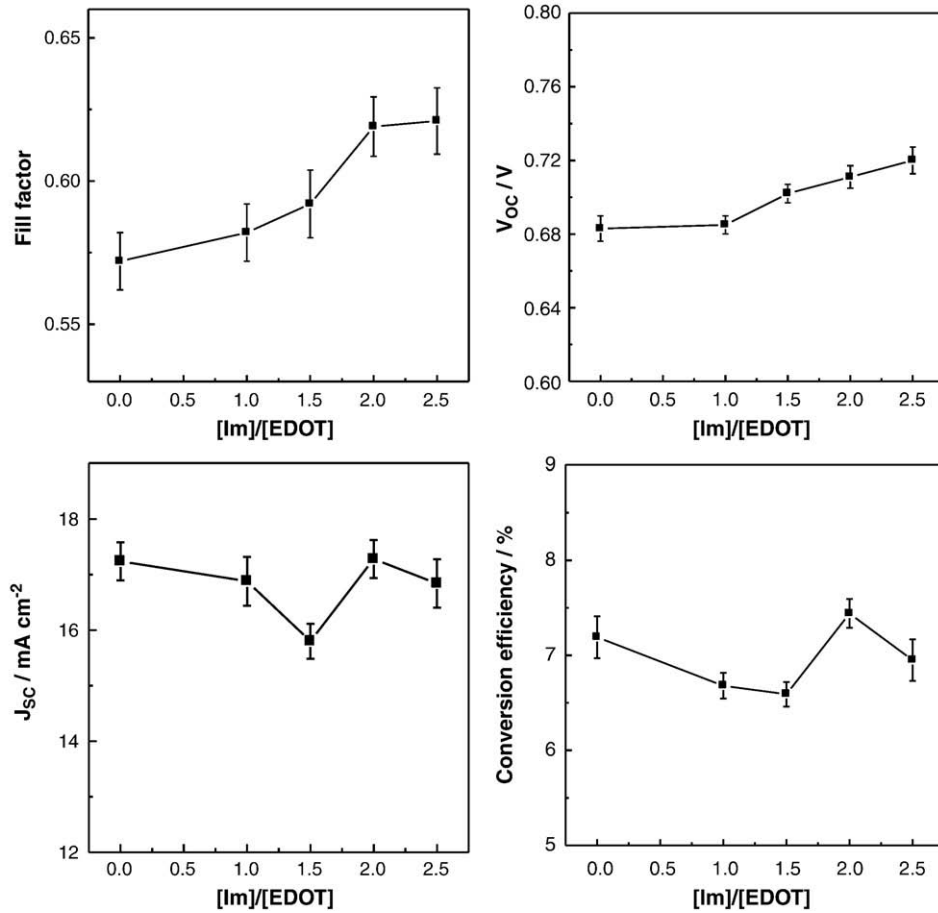


Fig. 6. The dependence of V_{oc} , FF, J_{sc} and conversion efficiency of the DSSCs on the various molar ratios of Im/EDOT.

increase with an increase in the ratios of Im/EDOT due to the reduction of IR drops of devices with the improvement of conductivity and better adhesion of the PEDOT films on substrates (Fig. 6). The PEDOT-PSS, as counter electrode, showed a poor cell performance (Fig. 5). Consequently, the rougher the PEDOT film is, the higher the value of J_{sc} will be.

3.3. Effect of addition of MWCNT into the PEDOT film on the performance of the DSSC

The other important factors such as good catalytic activity and the better adhesion with substrate can also lead to better performance in the DSSCs. Towards this goal, the MWCNT, was incorporated into PEDOT film which is expected to further improve the conductivity and surface roughness simultaneously. The TEM image of the MWCNT is shown in Fig. 7(a). The effect of addition of various percentages of MWCNT with different spin rates on the conductivities of PEDOT film having Im/EDOT molar ratio of 2.0 is given in Table 1. From the table, it is noted that the low spin rate decreases surface resistance. Meanwhile, when the amounts of MWCNT in PEDOT film increase to 0.6 wt.%, the surface resistances decrease to ca. $64 \Omega \text{ sq.}^{-1}$; further an increase in the amounts of MWCNT results in the increase of film resistance, which may be due to the aggregation of MWCNT leading to the formation of less amount of PEDOT on the substrate.

The SEM images of PEDOT films with and without 0.6 wt.% MWCNT are shown in Fig. 7(b) and (c) respectively for comparison. The figures reveal that the MWCNT is well distributed in PEDOT film with a high roughness. Furthermore, the influence of photovoltaic performances of the DSSCs with PEDOT film as counter electrodes containing 0.6 wt.% of MWCNT and molar ratio of Im/EDOT as 2.0,

coated with various spin rates on different substrates was also investigated, and their detailed performances are listed in Table 2. In the beginning, we have tried not only to use PEDOT film as a catalytic layer but also as a conducting layer to substitute for the ITO or FTO layer on substrates. Unfortunately, this idea led to a poor result in the study. It is found that only PEDOT coated glass substrate (0.6 wt.% MWCNT) film with low spin rate of 370 rpm can get a J_{sc} of 16.05 mA cm^{-2} but still with a very poor FF of 0.35. This may be correlated with the high serial resistance (R_s) of a device based on glass substrate. Because the series resistance (R_s) of the cell is considered to have the sheet resistance (R_{sh}) of the electrode substrate, the resistance of the counter electrode and the resistance of electrolyte, can directly influence the FF of J - V curves. The J - V characteristics of the DSSC can also be treated by Eq. (4),

$$J = J_{sc} - J_0 [\exp(qV + R_s J / nkT) - 1], \quad (4)$$

as those of a p - n junction solar cell [28], the relationship between the R_s and the J_{sc} is comprehensible.

Regarding the performance of the DSSCs with glass substrate, devoid of conductive layer on it, the electron collection may be affected and resulted in low J_{sc} when we use a thin PEDOT film as counter electrode. As for the PEDOT (0.6 wt.% MWCNT) films coated on FTO glass and stainless steel are concerned, better performances were obtained for the DSSCs based on PEDOT containing 0.6 wt.% MWCNT when compared to pure PEDOT films. Films obtained by the spin coating speed of 370 rpm show an efficiency of 8.08%. The higher FF of 0.66 in DSSC based on stainless steel is due to the high conductivity of the substrate and good adhesion with PEDOT films. The corrosion stability of stainless steel examined by Ma et al. [29],

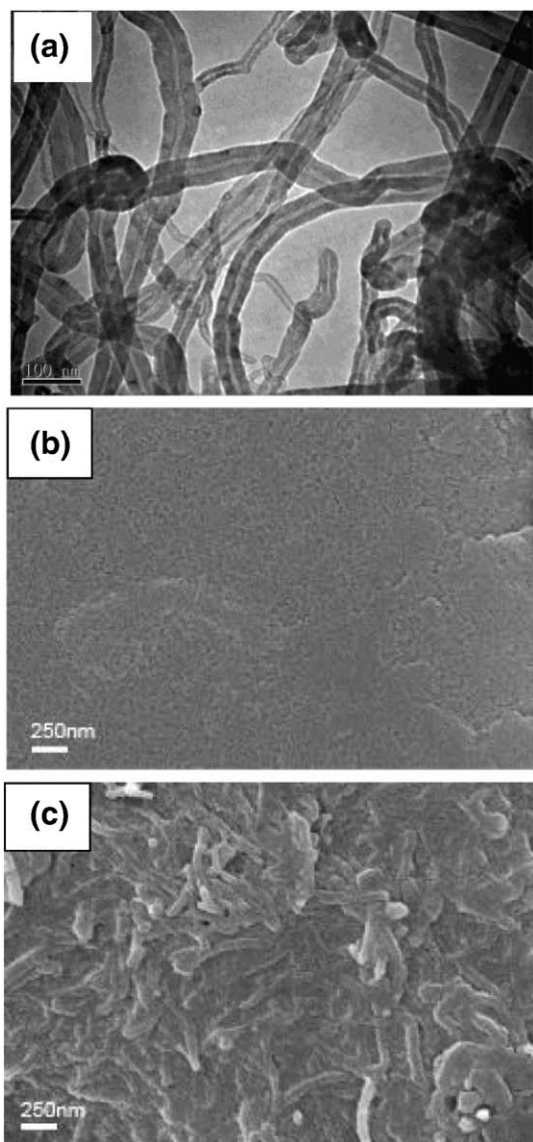


Fig. 7. (a) The TEM image of MWCNT. The SEM images of PEDOT film in the absence (b) and (c) presence of 0.6 wt.% MWCNT.

reported that the stainless steel had a better stability in the electrolyte solution for 3 months, than polystyrene film, Cu and Al foils. It is clear that the cells using only bare FTO glass and stainless steel as the counter electrodes without catalyst, performed with the efficiency of 0.02 and 0.16%, respectively. The necessity of depositing an effective catalyst onto the substrates can easily be appreciated from the above results.

The EIS analysis of the DSSCs with counter electrode of PEDOT films containing 0.6 wt.% MWCNT on stainless steel substrates are

Table 1

The effect of addition of various percentages of MWCNT with different spin rates on the conductivities of PEDOT film. The molar ratio of Im/EDOT is 2.0. The data were the average values obtained for three samples.

Im/EDOT (molar ratio)	370 rpm ($\Omega \text{ sq.}^{-1}$)	500 rpm ($\Omega \text{ sq.}^{-1}$)	1000 rpm ($\Omega \text{ sq.}^{-1}$)
2.0 (without MWCNT)	317.5±18	390.1±16	646.5±16
2.0 (0.2 wt.% MWCNT)	191.7±15	259.7±12	639.0±10
2.0 (0.4 wt.% MWCNT)	108.7±15	149.6±11	271.9±11
2.0 (0.6 wt.% MWCNT)	64.3±13	125.1±10	244.2±10
2.0 (0.8 wt.% MWCNT)	119.6±25	123.5±13	298.1±12

Table 2

Photovoltaic performances of DSSCs having PEDOT counter electrode containing 0.6 wt.% MWCNT coated with various spin rates on glass, FTO glass and stainless steel under illumination of 100 mW cm^{-2} . The molar ratio of Im/EDOT is 2.0. Impedance parameters in partial have also been given here. The data were the average values obtained for three samples.

Sample	J_{SC} (mA cm^{-2})	V_{OC} (mV)	FF	η (%)	R_S (Ω)	R_{ct1} (Ω)
370 rpm ^a	16.05	700	0.35	3.93±0.5	~88	~15
500 rpm ^a	14.20	680	0.36	3.38±0.5	~95	~16
1000 rpm ^a	6.36	690	0.26	1.68±0.5	~240	~40
370 rpm ^b	17.28	720	0.62	7.71±0.3	~22	~5
500 rpm ^b	17.30	720	0.63	7.84±0.3	~23	~6
1000 rpm ^b	16.52	715	0.59	6.97±0.3	~23	~18
370 rpm ^c	17.00	720	0.66	8.08±0.3	~17	~4
500 rpm ^c	16.80	710	0.65	7.75±0.3	~17	~7
1000 rpm ^c	14.52	700	0.60	6.10±0.3	~18	~20
only FTO ^d	1.10	485	0.08	0.04±0.4	N/A	N/A
only S.S. ^e	2.18	600	0.12	0.16±0.4	N/A	N/A

^a PEDOT films were coated on glass.

^b PEDOT films were coated on FTO glass.

^c PEDOT films were coated on stainless steel.

^d Only FTO glass.

^e S.S. means stainless steel (SUS 304).

shown in Fig. 8 and partial parameters are listed in Table 2. It shows that under identical values of R_S values of ca. 17 Ω , and the R_{ct1} , the electrochemical reaction at the counter electrode interface in the high-frequency region (10^3 – 10^5 Hz) increases from ca. 4 to 20 Ω with an increase in the spin rate. The DSSC with the lowest R_{ct1} value of ca. 4 Ω showed the best result of 8.08%, with J_{SC} , V_{OC} and FF of 17.00 mA cm^{-2} , 720 mV and 0.66, respectively, due to the high active surface area and good catalytic property for the reduction of I_3^- to I^- .

4. Conclusion

The employment of PEDOT films as counter electrodes on various substrates prepared under different conditions on the performance of platinum-free DSSCs were studied. The resulting PEDOT counter electrodes showed excellent catalytic behavior in DSSC leading to good cell performance. The CV measurement involving the I^-/I_3^- redox reaction suggests that no specific interaction between I^-/I_3^- and the PEDOT electrode occurred, as in the case of the Pt electrode. The DSSC based on counter electrode of PEDOT film containing 0.6 wt.% MWCNT coated with a spin rate of 370 rpm on stainless steel had the best conversion efficiency of 8.08%, with J_{SC} , V_{OC} , and FF values of 17.00 mA cm^{-2} , 720 mV and 0.66, respectively.

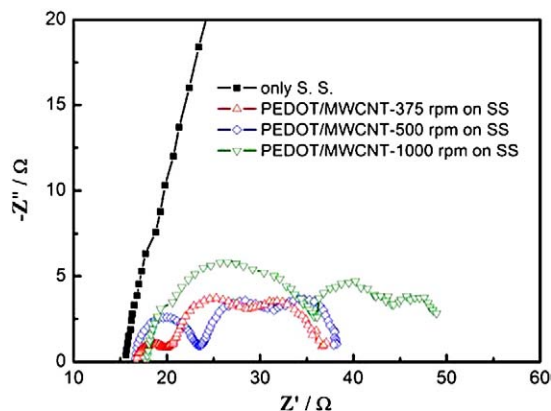


Fig. 8. EIS measurements of the DSSCs based on PEDOT films containing 0.6 wt.% MWCNT coated on stainless steel substrate.

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References

- [1] B. O'Regan, M. Grätzel, *Nature* 353 (1991) 737.
- [2] C.J. Barbe, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, M. Grätzel, *J. Am. Ceram. Soc.* 80 (1997) 3157.
- [3] Z.S. Wang, C.H. Huang, Y.Y. Haung, Y.J. Hou, P.H. Xie, B.W. Zhang, H.M. Cheng, *Chem. Mater.* 13 (2001) 678.
- [4] Z.S. Wang, H. Kawauchi, T. Kashima, H. Arakawa, *Coord. Chem. Rev.* 248 (2004) 1381.
- [5] K.S. Raja, V.K. Mahajan, M. Misra, *J. Power Sources* 159 (2006) 1258.
- [6] M.K. Nazeeruddin, P. Pechy, T. Renouard, S.M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, C. Le, E. Costa, V. Shklover, L. Spiccia, G.B. Deacon, C.A. Bignozzi, M. Grätzel, *J. Am. Chem. Soc.* 123 (2001) 1613.
- [7] T. Renouard, R.A. Fallahpour, M.K. Nazeeruddin, R. Humphry-Baker, S.I. Gorelsky, A.B.P. Lever, M. Grätzel, *Inorg. Chem.* 41 (2002) 367.
- [8] Z.S. Wang, Y. Cui, Y. Dan-oh, C. Kasada, A. Shinpo, K. Hara, *J. Phys. Chem. C* 111 (2007) 7224.
- [9] P. Wang, S.M. Zakeeruddin, J.E. Moser, R. Humphry-Baker, P. Comte, V. Aranyos, A. Hagfeldt, M.K. Nazeeruddin, M. Grätzel, *Adv. Mater.* 16 (2004) 1806.
- [10] C.Y. Chen, S.J. Wu, C.C. Wu, J.G. Chen, K.C. Ho, *Angew. Chem. Int. Ed.* 45 (2006) 5822.
- [11] X. Zhang, H. Yang, H.M. Xiong, F.Y. Li, Y.Y. Xia, *J. Power Sources* 160 (2006) 1451.
- [12] J.Y. Kim, T.H. Kim, D.Y. Kim, N.G. Park, K.D. Ahn, *J. Power Sources* 175 (2008) 692.
- [13] J. Wu, Z. Lan, J. Lin, M. Huang, P. Li, *J. Power Sources* 173 (2007) 585.
- [14] F. Cecchet, A.M. Gioacchini, M. Marcaccio, F. Paolucci, S. Roffia, M. Alebbi, C.A. Bignozzi, *J. Phys. Chem. B* 106 (2002) 3926.
- [15] C.H. Yoon, R. Vittal, J. Lee, W.S. Chae, K.J. Kim, *Electrochim. Acta* 53 (2008) 2890.
- [16] Y. Saito, W. Kubo, T. Kitamura, Y. Wada, S. Yanagida, *J. Photochem. Photobiol. A: Chem.* 164 (2004) 153.
- [17] T.N. Murakami, S. Ito, Q. Wang, M.K. Nazeeruddin, T. Bessho, I. Cesar, P. Liska, R. Humphry-Baker, P. Comte, P. Pechy, M. Grätzel, *J. Electrochem. Soc.* 153 (2006) A2255.
- [18] K. Suzuki, M. Yamamoto, M. Kumagai, S. Yanagida, *Chem. Lett.* 32 (2003) 28.
- [19] B.L. Groenedaal, F. Jonas, D. Freitag, H. Pielartzik, J.R. Reynolds, *Adv. Mater.* 12 (2000) 481.
- [20] N. Fukuri, Y. Saito, W. Kubo, G.K.R. Senadeera, T. Kitamura, Y. Wada, S. Yanagida, *J. Electrochem. Soc.* 151 (2004) A1745.
- [21] R. Senadeera, N. Fukuri, Y. Saito, T. Kitamura, Y. Wada, S. Yanagida, *Chem. Commun.* (2005) 2259.
- [22] T. Muto, M. Ikegami, K. Kobayashi, T. Miyasaka, *Chem. Lett.* 36 (2007) 804.
- [23] K.M. Lee, C.W. Hu, H.W. Chen, K.C. Ho, *Sol. Energy Mater. Sol. Cells* 92 (2008) 1628.
- [24] Y.H. Ha, N. Nikolov, S.K. Pollack, J. Mastrangelo, B.D. Martin, R. Shashidhar, *Adv. Funct. Mater.* 14 (2004) 615.
- [25] M.K. Nazeeruddin, R. Humphry-Baker, P. Liska, M. Grätzel, *J. Phys. Chem. B* 107 (2003) 8981.
- [26] M.C. Bernard, H. Cachet, P. Falaras, A. Hugot-Le Goff, M. Kalbac, I. Lukes, N.T. Oanh, T. Stergiopoulos, I. Arabatzi, *J. Electrochem. Soc.* 150 (2003) E155.
- [27] A. Hauch, A. Georg, *Electrochim. Acta* 46 (2001) 3457.
- [28] M. Matsumoto, Y. Wada, T. Kitamura, K. Shigaki, T. Inoue, M. Ikeda, S. Yanagida, *Bull. Chem. Soc. Jpn.* 74 (2001) 387.
- [29] T. Ma, X. Fang, M. Akiyama, K. Inoue, H. Noma, E. Abe, *J. Electroanal. Chem.* 574 (2004) 77.