

High-Performance dye-sensitized solar cells with various nanostructured materials as counter electrode

Xiaoguang Mei, Swee Jen Cho, Kuan Sun, Benhu Fan, and Jianyong Ouyang*

Department of Materials Science and Engineering, Faculty of Engineering, National University of Singapore, Singapore 117574, mseoj@nus.edu.sg

ABSTRACT

This paper reports high-performance dye-sensitized solar cells (DSCs) with two classes of nanostructured materials as counter electrode. The first one is nanostructured platinum (Pt) prepared by chemically reducing a Pt precursor with ethylene glycol (EG) at temperature below 200 °C. Two types of Pt structures, dense and porous Pt structures, were observed for the Pt deposited by EG reduction. The dense Pt structure is the result of Pt growth from the substrate immediately after the reduction, whereas the porous Pt structure originates from the precipitation of Pt nanoparticles. Pt deposited by this method could be used as the counter electrode of high-performance DSCs. The DSCs exhibited a power conversion efficiency (PCE) of 8.1%, quite close to that of the DSCs with Pt counter electrode prepared by the conventional pyrolysis. In addition, this low-temperature method enabled the Pt deposition on flexible substrate, which could be used as the flexible counter electrode for DSCs. The second types of materials are nanocomposites of multi-walled carbon nanotubes (MWCNTs) and poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) that is a conducting polymer. The composite films were prepared by spin-coating aqueous solutions of MWCNT/PEDOT:PSS composites. The devices exhibited a PCE of 6.5%.

Keywords: dye-sensitized solar cells, counter electrode, platinum, nanoparticles, carbon nanotubes

1 INTRODUCTION

Dye-sensitized solar cells (DSCs) have attracted strong attention due to the respectable energy conversion efficiency, the simple device fabrication process, and low cost [1]. Though lots of effort has been made in the work electrode, dye, and electrolyte, the counter electrode also plays a key role by catalyzing the reduction of the redox species. A high-performance DSC requires the counter electrode to be highly catalytic and high conductive. Hence, platinum (Pt), which is a good catalyst for the reduction of the redox species, such as triiodide/iodide, is usually used as the counter electrode of the DSC [2]. Various techniques have been developed for Pt deposition, including pyrolysis of Pt precursors, electrochemical deposition, electroless deposition, magnetron sputtering, e-beam evaporation, and

chemical vapor deposition [3-11]. Among these approaches, Pt fabricated by pyrolysis is the best as the counter electrode. However, the pyrolysis takes place at a temperature higher than 380 °C [8], which makes it unsuitable for the Pt deposition on materials of poor stability at high temperature, such as flexible materials like polymers. Flexible counter electrode is needed for flexible DSCs, which becomes more and more important in practical application [4-6].

It is important to develop a simple and effective method to deposit Pt at low temperature. Here, we will report the deposition of Pt on various substrates by chemically reducing a Pt precursor with EG [12]. Though polyol reduction of metal precursor has been extensively investigated for the preparation of various metal nanoparticles [13-15], there is not too much research work on the deposition of Pt film by polyol reduction, and there has been no report on the practical application of the Pt film deposited by polyol reduction. We also demonstrated high-performance DSCs with Pt counter electrode produced by the polyol reduction of a Pt precursor.

Another problem related to Pt is its high price. The noble Pt remarkably increases the cost of the DSC. Thus, other materials have also been investigated to replace Pt as the counter electrodes of the DSCs, such as carbon black, conductive polymers, and polymer/platinum composites [16,17]. Here, we will also report the application of nanocomposites of multi-walled carbon nanotubes (MWCNTs) and PEDOT:PSS as the counter electrode of DSCs [18]. The composite films were fabricated by solution processing.

2 EXPERIMENTAL

PEDOT:PSS was purchased from H. C. Starck. All other chemicals were purchased from Sigma-Aldrich and used without further purification. Glass, ITO coated polyethylene terephthalate (ITO/PET) films and fluorine-doped tin-oxide (FTO) coated glass were purchased from Corning, Sigma-Aldrich, and Flat Glass Business of the NSG group, respectively.

The EG solutions, which were used for the Pt deposition, were prepared by dissolving $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in EG under stirring for 5 min. A Pt film was deposited by dropping 400 μl EG solution of H_2PtCl_6 on a substrate of $2 \times 2 \text{ cm}^2$ on a hot plate at 180 °C. The Pt film was formed within 5 min. Then, the Pt film was cooled down to room

temperature in air, and subsequently was rinsed with ethanol for three times. Finally, the Pt film was dried at 60 °C for 10 min.

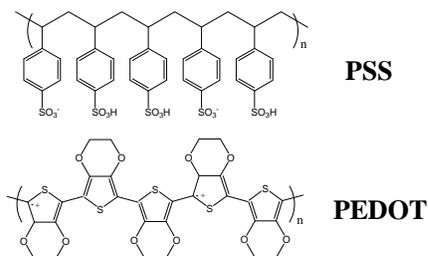
The MWCNTs, purchased from Sigma-Aldrich, were produced by the thermal chemical vapor deposition method by Arkema Inc. The specifications of the MWCNTs are: average outer diameter of 10~15nm, average length of 0.1~10µm, mean number of walls of 5~15, and > 90% carbon content. Solutions of MWCNT/PEDOT:PSS composites were prepared by dispersing MWCNTs in the aqueous PEDOT:PSS under ultrasonification. The weight ratio of the MWCNTs to the polymer is 2:1 in solution. The composite films were fabricated by spin coating the composite solution on FTO glass substrates. The composite films were dried at 110 °C on a hot plate for 30 min.

Scanning electron microscope (SEM) images and energy-dispersive X-ray spectra (EDX) were taken using Hitachi S-4100 scanning electron microscope, and atomic force microscope (AFM) images were acquired using a Veeco NanoScope IV Multi-Mode AFM with the tapping mode. X-ray diffractions (XRDs) were measured with a Bruker Bragg-Brentano theta X-ray diffractometer. The X-ray photoelectron spectra (XPS) were taken with an Axis Ultra DLD X-ray photoelectron spectrometer equipped with an Al K α X-ray source (1486.6 eV). The thickness of the deposited Pt films was determined by a Tencor P-10 Alpha-Step Profiler.

The DSCs were fabricated following the literature [19]. The photovoltaic performance of the devices was measured with a computer-programmed Keithley 2400 source/meter under Newport's Oriol class A solar simulator, which simulated the AM1.5 sunlight with energy density of 100 mW cm⁻² and was certified to the JIS C 8912 standard.

3 RESULTS AND DISCUSSION

3.1 Deposition of Pt films and their application as counter electrode of DSCs



Scheme 1 Chemical structure of PEDOT:PSS.

High-quality Pt films could be deposited on PEDOT:PSS/glass by the reduction of H₂PtCl₆ with EG. PEDOT:PSS (chemical structure shown in scheme 1), which is the most successful conducting polymer and has good thermal stability [20,21], was investigated as the substrate for Pt deposition by polyol reduction. The deposition was made by dropping 400 µl EG solution of

0.02 M H₂PtCl₆ on a PEDOT:PSS/glass of 2×2 cm² on a hot plate at 180 °C. The yellowish solution first turned to black, and then a smooth film distributed with black spots was formed on PEDOT:PSS. Fig. 1 shows a Pt film on PEDOT:PSS/glass fabricated by this method. Black spots were dispersed on the smooth Pt film.

Both the black spots and the smooth part were Pt as indicated by EDX. No Cl signal could be observed in the EDX, which indicates that H₂PtCl₆ completely converted into Pt. XPS of Pt suggests that both the black spots and the smooth part are zerovalent Pt.

The Pt film was further characterized by SEM. Two Pt structures were observed: porous and dense structures. The porous structure corresponding to the black spots on the Pt film was the aggregates of Pt nanoparticles (Fig. 1). The smooth part was dense and continuous Pt, whose morphology was revealed by AFM (Fig. 2) in higher magnification. The dense Pt has the grain size of about 50 nm. The dense Pt exhibited metallic luster with high reflection and had good adhesion to the PEDOT:PSS film. It could sustain a sonication process in an ultrasonic bath and the adhesive tape peel test. In contrast, the porous Pt had poor adhesion to the dense Pt. It was removed from the Pt film after the sonication in the ultrasonic bath or by the adhesive tape peel test.

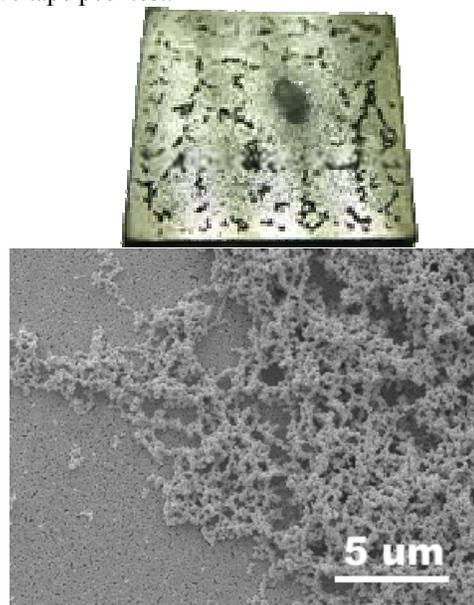


Fig. 1 Photograph (top) and SEM image (bottom) of a Pt film deposited on PEDOT:PSS/glass.

In terms of these experimental results, it is inferred that there are two Pt growing processes during the formation of the Pt film. One is the formation of the dense Pt on the PEDOT:PSS film immediately after the EG reduction of H₂PtCl₆. Pt grows from the substrate in this growing process. The other is the formation of Pt particles in solution [12-15]. The Pt nanoparticles aggregated in solution and became porous Pt on dense Pt after precipitation from the solution.

Besides the Pt formation on the PEDOT:PSS film during the EG reduction of H_2PtCl_6 , there was also interesting change on the PEDOT:PSS film. The PEDOT:PSS film had a conductivity of 0.4 S cm^{-1} before the Pt deposition. The conductivity of PEDOT:PSS increased to about 200 S cm^{-1} after the Pt deposition. This is consistent with the polyol treatment of the PEDOT:PSS film as reported in literature [22-24]. Thus, we can get a catalytic Pt film on a highly conductive polymer film through a simple process.

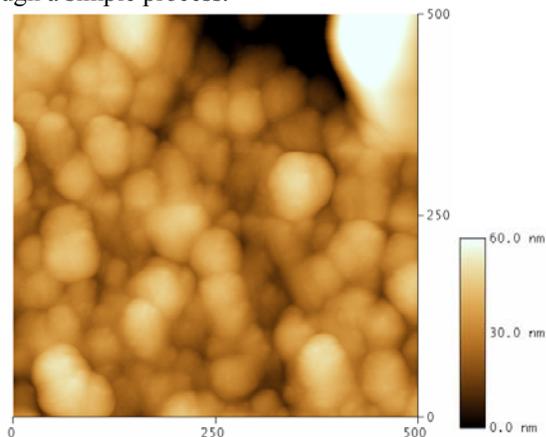


Fig. 2 AFM image of a Pt film deposited on PEDOT:PSS/glass. The unit is nm.

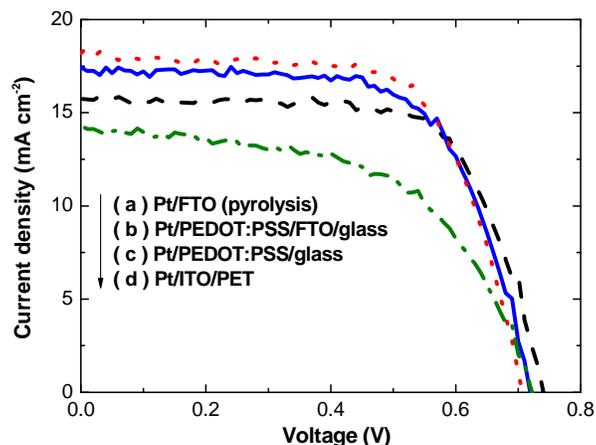


Fig. 3 Current density-voltage characteristics of dye-sensitized solar cells with different counter electrodes under AM 1.5 illumination. The counter electrodes are indicated in the figure. The Pt counter for (a) was deposited by pyrolysis of H_2PtCl_6 at $400 \text{ }^\circ\text{C}$, and the Pt counter electrodes for (b), (c) and (d) were deposited by EG reduction of $0.02 \text{ M H}_2\text{PtCl}_6$ solution at $180 \text{ }^\circ\text{C}$.

Pt deposited by EG reduction of H_2PtCl_6 at $180 \text{ }^\circ\text{C}$ was investigated as the counter electrode of DSCs. The Pt films were rinsed with ethanol three times to clean the surface and then dried at $60 \text{ }^\circ\text{C}$ for 10 min. The current-voltage curves of these DSCs under illumination of AM 1.5 (100 mW cm^{-2}) are shown in Fig. 3. The photovoltaic performance of a control DSC with the Pt counter electrode

prepared by pyrolysis of H_2PtCl_6 at $400 \text{ }^\circ\text{C}$ for 15 min on FTO glass is presented as well. The photovoltaic performance of these devices, including the open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), the fill factor (FF), and the energy conversion efficiency (η) are listed in Table 1. The DSC with Pt counter electrode deposited on PEDOT:PSS/FTO glass by EG reduction exhibited a photovoltaic efficiency of 8.4 %, almost the same as that (8.7 %) of the control DSC with Pt counter electrode on FTO glass prepared by pyrolysis

TABLE 1 Photovoltaic Performance of DSCs with Different Pt Counter Electrodes

counter electrode	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)
Pt/FTO ^a	18.19	710	0.68	8.7
Pt/PEDOT:PSS/FTO ^b	17.44	720	0.67	8.4
Pt/PEDOT:PSS/Glass ^b	15.75	740	0.69	8.1
Pt/ITO/PET ^b	14.30	720	0.56	5.8

^a Pt was prepared by pyrolysis of H_2PtCl_6 at $400 \text{ }^\circ\text{C}$ for 15 min. ^b Pt was prepared by EG reduction of $0.02 \text{ M H}_2\text{PtCl}_6$ at $180 \text{ }^\circ\text{C}$. It was rinsed with ethanol for three times and dried at $60 \text{ }^\circ\text{C}$ for 10 min.

Another interesting observation is the high photovoltaic efficiency by the DSC with Pt deposited on PEDOT:PSS/glass. The efficiency was 8.1 %, quite close to that of the DSCs with Pt counter electrode prepared by pyrolysis or EG reduction of H_2PtCl_6 on PEDOT:PSS/FTO glass. These results suggest that PEDOT:PSS/glass can replace FTO glass as the substrate for the counter electrode of DSCs. This will lower the cost of DSC, since FTO glass is the most expensive part of DSC [25,26].

The Pt deposition by the polyol reduction of H_2PtCl_6 at low temperature enables the Pt deposition on flexible substrates like polymers. Thus, flexible counter electrode can be readily realized by this method. We also fabricated DSCs with Pt counter electrode on flexible ITO/PET prepared by the EG reduction of $0.02 \text{ M H}_2\text{PtCl}_6$ solution at $180 \text{ }^\circ\text{C}$. The devices exhibited photovoltaic efficiency of 5.8 %. This preliminary efficiency was higher than that of DSCs with other flexible counter electrodes [5,6].

3.2 MWCNT/PEDOT:PSS as counter electrode of DSCs

Fig. 4 shows the SEM images of the MWCNT/PEDOT:PSS and MWCNT/PSSA composite films on FTO glass substrates. The MWCNTs formed a network in both composite films. The composite films were used as the counter electrodes of the DSCs.

The current (I)-voltage (V) curves of the DSCs with different counter electrodes are shown in Fig. 5. The DSC with the MWCNT/PEDOT:PSS counter electrode exhibited high photovoltaic performance: $J_{sc} = 15.5 \text{ mA cm}^{-2}$, $V_{oc} = 0.66 \text{ V}$, $FF = 0.63$, and $\eta = 6.5\%$. This performance is close to that of the DSC with the Pt counter electrode.

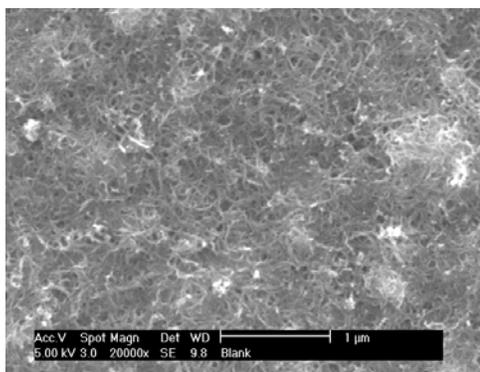


Fig. 4 SEM images of a MCNT/ PEDOT: PSS composite film.

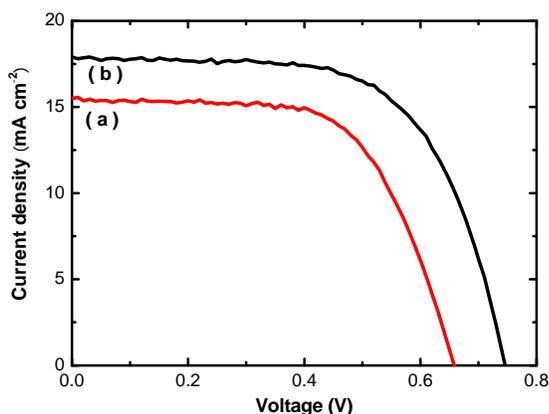


Fig. 5 Current-voltage curve of dye-sensitized solar cells with (a) a MWCNT/PEDOT:PSS composite film of 4.2 μm in thickness, and (b) Pt as the counter electrodes.

4 CONCLUSIONS

Nanostructured Pt films could be deposited by EG reduction of H_2PtCl_6 at low temperature. Both dense and porous Pt structures were observed. Pt deposited by this method could be used as the counter electrode for high-performance DSCs. This method enables the replacement of the expensive FTO glass with PEDOT:PSS/glass as the substrate of the counter electrode of DSCs and the preparation of flexible counter electrodes for high-performance DSCs. MWCNT/PEDOT:PSS films prepared by spin coating can be used as the counter electrode of DSC as well.

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REFERENCES

[1] B. Oregan and M. Grätzel, *Nature* 353, 737, 1991.
 [2] M. Grätzel, *J. Photochem. Photobiol. C* 4, 145, 2003.

[3] A. Hauch and A. Georg, *Electrochim. Acta* 46, 3457, 2001.
 [4] X. M. Fang, T. L. Ma, G. Q. Guan, M. Akiyama, T. Kida, and E. Abe, *J. Electroanal. Chem.* 570, 257, 2004.
 [5] T. Ma, X. Fang, M. Akiyama, K. Inoue, H. Noma, and E. Abe, *J. Electroanal. Chem.* 574, 77, 2004.
 [6] Y. Saito, W. Kubo, T. Kitamura, Y. Wada, and S. Yanagida, *J. Photochem. Photobiol. A: Chem.* 164, 153, 2004.
 [7] N. Papageorgiou, *Coord. Chem. Rev.* 248, 1421, 2004.
 [8] G. Khelashvili, S. Behrens, C. Weidenthaler, C. Vetter, A. Hinsch, R. Kern, K. Skupien, E. Dinjus, and H. Bönemann, *Thin Solid Films* 511–512, 342, 2006.
 [9] L. K. Kurihara, G. M. Chow, and P. E. Schoen, *Nanostruct. Mater.* 5, 607, 1995.
 [10] N. Papageorgiou, W. F. Maier, and M. Grätzel, *J. Electrochem. Soc.* 144, 876, 1997.
 [11] H. Bönemann, G. Khelashvili, S. Behrens, A. Hinsch, K. Skupien, and E. Dinjus, *J. Clust. Sci.* 18, 141, 2007.
 [12] K. Sun, B. Fan, and J. Ouyang, *J. Phys. Chem. C* 114, 4237, 2010.
 [13] S. E. Skrabalak, B. J. Wiley, M. Kim, E. V. Formo, and Y. N. Xia, *Nano Lett.* 8, 2077, 2008.
 [14] Y. Wang, J. W. Ren, K. Deng, L. L. Gui, and Y. Q. Tang, *Chem. Mater.* 12, 1622, 2000.
 [15] S. Komarneni, D. Li, B. Newalkar, H. Katsuki, and A. S. Bhalla, *Langmuir* 18, 5959, 2002.
 [16] T. N. Murakami and M. Grätzel, *Inorg. Chim. Acta* 361, 572, 2008.
 [17] Y. Saito, W. Kubo, T. Kitamura, Y. Wada, and S. Yanagida, *J. Photochem. Photobiol. A.* 164, 153, 2004.
 [18] B. Fan, X. Mei, K. Sun, and J. Ouyang, *Appl. Phys. Lett.* 93, 143103, 2008.
 [19] S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Pechy, and M. Grätzel, *Prog. Photovoltaics* 15, 603, 2007.
 [20] B. L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, and J. R. Reynolds, *Adv. Mater.* 12, 481, 2000.
 [21] Q. Pei, G. Zuccarello, M. Ahlskogt, and O. Inganäs, *Polymer* 35, 1347, 1994.
 [22] J. Ouyang, Q. Xu, C. W. Chu, Y. Yang, G. Li, and J. Shinar, *Polymer* 45, 8443, 2004.
 [23] J. Ouyang, C. W. Chu, F. C. Chen, Q. Xu, and Y. Yang, *Adv. Funct. Mater.* 15, 203, 2005.
 [24] J. Ouyang and Y. Yang, *Adv. Mater.* 18, 2141, 2006.
 [25] H. Greijer, L. Karlson, S. T. Lindquist, and A. Hagfeldt, *Renewable Energy* 23, 27, 2001.
 [26] G. Smestad, C. Binozzi, and R. Argazzi, *Sol. Energy Mater. Sol. Cells* 32, 259, 1994.