

Nanostructured Platinum Films Deposited by Polyol Reduction of a Platinum Precursor and Their Application as Counter Electrode of Dye-Sensitized Solar Cells

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Platinum precursors such as H_2PtCl_6 can be reduced to platinum (Pt) by polyols at temperatures below 200 °C. This method was developed to deposit nanostructured Pt films on various substrates through a solution process. High-quality Pt films with good adhesion to substrate were obtained on substrates like conducting polymer films, indium tin oxide (ITO), and polyimide by dropping a solution of H_2PtCl_6 in ethylene glycol (EG). Two types of Pt structures, that is, 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. This Pt growth from the substrate can produce a continuous nanostructured Pt film with metallic luster and good adhesion to the substrate. The porous Pt structure is the result of the nucleation of Pt in solution. The Pt nucleation in solution gives rise to Pt particle formation. These Pt particles aggregate and finally precipitate as porous Pt on the dense Pt. The quality of the Pt film was affected by the experimental conditions, such as substrate, concentration, and pH value of H_2PtCl_6 solution in EG, and temperature during the reduction. Pt deposited by this method could be used as the counter electrode of high-performance dye-sensitized solar cells (DSCs). The DSCs exhibited a light-to-electricity conversion efficiency 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.

1. Introduction

Deposition of metal films is always an important subject due to the wide applications of the metal films. New approaches which can overcome some problems in conventional metal deposition techniques may bring strong impact not only on the deposition but also on the applications of the metal films. Chemical reduction of metal salts can produce pure metal at low temperature. But it has been extensively used for preparation of metal nanoparticles and rarely for the deposition of the metal films, since the metal nucleation and growth usually occurs in solution. If the metal nucleation and growth can start from substrate, high-quality metal films can be fabricated through such a simple process at low temperature. Pt has many important applications due to its good chemical stability and excellent catalysis, particularly in energy-related systems, such as in DSCs and fuel cells.^{1–4} In these applications, Pt is usually deposited on substrates. Various techniques have been developed for Pt deposition. It can be deposited from pure Pt metal by magnetron sputtering or e-beam evaporation.^{5–12} It can also be produced from solution of its salts, such as by electrochemical deposition, electroless deposition, or pyrolysis at high temperature.^{13–21} Lewis et al. also reported the deposition of Pt films from platinum organic complexes by chemical vapor deposition.²² The performance of Pt is strongly affected by deposition techniques, and there are some limitations for these techniques in some applications. For example, the magnetron sputtering or e-beam evaporation requires high vacuum and high power because of the high melting point of Pt. These requirements

substantially increase the cost for Pt deposition. On the other hand, a conductive substrate with good stability in the electrolyte solution is needed for the electrochemical deposition of Pt, and electroless deposition requires a layer of an active metal on the substrate. In addition, the DSCs with Pt counter electrode prepared by sputtering or electrodeposition exhibits photovoltaic performance inferior to the ones with Pt counter electrode prepared by pyrolysis.¹² The problem for the pyrolysis is that the conversion from a Pt salt to metallic Pt takes place at a temperature higher than 380 °C,¹⁹ which makes it unsuitable for the Pt deposition on materials of poor stability at high temperature, such as flexible materials like polymers. A flexible counter electrode is needed for flexible DSCs, which becomes more and more important in practical application.^{6–11}

It is important to develop a simple and effective method to deposit Pt at low temperature. One possible way is to deposit Pt through the reduction of platinum salts by a simple chemical process, such as polyol reduction of Pt salts. Though polyol reduction of metal precursor has been extensively investigated for the preparation of various metal nanoparticles,^{23–25} there are only a few reports on the deposition of metal films by polyol reduction of metal precursors. Kurihara et al. very briefly reported the depositions of metals, including Co, Ni, Rh, Re, W, Pt, and Au, on various nonconductive substrates, including Pyrex, Kapton, Teflon, graphite fiber, aluminum nitride, carbon fibers, and alumina fibers, by immersing the substrates into the reaction mixture of metal salts.¹⁷ The deposited metal films had a nanocrystallite structure with the average crystallite sizes of tens of nanometers. Depositions of Cu on aluminum nitride and Ni–Co alloys on copper were reported as well.^{26–30} The polyol reduction of Pt precursors has been regarded as an interesting

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and simple deposition technique to produce Pt films on substrates.^{19,21} However, no follow-up work was reported for the deposition of Pt film by polyol reduction. In addition, there has been no report on the practical application of the Pt film deposited by polyol reduction. Here, we reported the deposition of high-quality Pt films on conducting substrates, including conducting polymer films and ITO, by the polyol reduction of H_2PtCl_6 at low temperature. We also demonstrated high-performance DSCs with Pt counter electrode produced by this method.

2. Experimental Section

2.1. Materials and Pt Deposition: Conducting Poly(3,4-ethylenedioxythiophene). Poly(styrenesulfonate) (PEDOT:PSS, Baytron P) was purchased from H. C. Starck. The PEDOT:PSS concentration was 1.3% by weight. All chemicals, including polyvinyl alcohol (average $M_w = 89\,000$ – $98\,000$, 99+% hydrolyzed), poly(4-styrenesulfonic acid) ($M_w \approx 75\,000$, 18 wt % in water), EG (Fluka, purum, $\geq 98.0\%$), and chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, ACS reagent, $\geq 37.50\%$ Pt basis) were purchased from Sigma-Aldrich and used without further purification. Glass, ITO coated polyethylene terephthalate (ITO/PET) films (surface resistivity of $45\ \Omega/\text{sq}$), and fluorine-doped tin-oxide (FTO) coated glass (Pilkington, surface resistivity of $15\ \Omega/\text{sq}$), which were used as the substrates, were purchased from Corning, Sigma-Aldrich, and Flat Glass Business of the NSG group, respectively. Polyimide films were obtained from 3M.

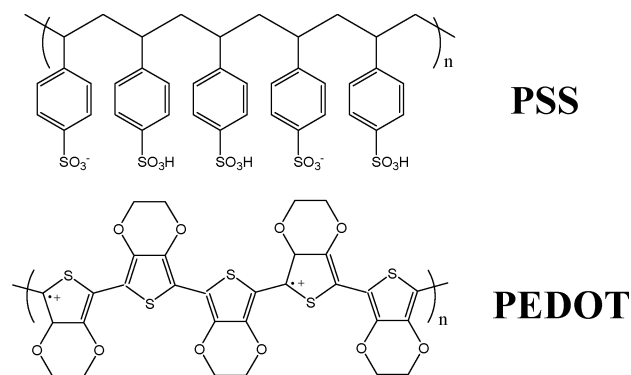
Glass, FTO glass, and ITO/PET were used as substrate for Pt deposition or polymer films. Glass and FTO glass were sequentially cleaned with detergent, DI water, acetone, and isopropyl alcohol. Each cleaning step was carried out under sonication in a Branson 1510 ultrasonic bath for 20 min. PEDOT:PSS films on glass or FTO glass were prepared by spin coating the PEDOT:PSS aqueous solution at 2000 rpm for 1 min and subsequently dried at $110\ ^\circ\text{C}$ for 30 min. Other polymer films, including polyvinyl alcohol and poly(4-styrenesulfonic acid), were prepared on glass substrate from the respective aqueous solution of 1% by weight polymer by the same process.

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. Solutions with H_2PtCl_6 concentrations varying from 0.002 to 0.1 M were prepared. A Pt film was deposited by dropping $400\ \mu\text{L}$ of EG solution of H_2PtCl_6 on a substrate of $2 \times 2\ \text{cm}^2$ on a hot plate at $180\ ^\circ\text{C}$. The Pt film was formed within 5 min. Then, the Pt film was cooled to room temperature in air, and subsequently was rinsed with ethanol three times. Finally, the Pt film was dried at $60\ ^\circ\text{C}$ for 10 min.

2.2. Characterization of Pt Films. Two methods, sonication and adhesive tape peel test,¹⁷ were carried out to investigate the adhesion of the Pt films on various substrates. The former test was performed by sonicating the substrate coated with Pt in water in a Branson 1510 ultrasonic bath for 5 min, and the latter was done by sticking a Unipex adhesive tape on the Pt film deposited on the substrate and then peeling off the tape.

Scanning electron microscope (SEM) images and energy-dispersive X-ray spectra (EDX) of the Pt films were taken with a Hitachi S-4100 scanning electron microscope, and atomic force microscope (AFM) images were acquired with 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).

SCHEME 1: Chemical Structure of PEDOT:PSS



The thickness of the deposited Pt films was determined by a Tencor P-10 Alpha-Step Profiler.

2.3. Fabrication and Characterization of Dye-Sensitized Solar Cells. The DSCs were fabricated following the literature and our early report.^{31,32} The photovoltaic performance of the devices was measured with a computer-programmed Keithley 2400 source/meter under Newport's Oriel class A solar simulator, which simulated the AM1.5 sunlight with energy density of $100\ \text{mW cm}^{-2}$ and was certified to the JIS C 8912 standard. Electrochemical impedance spectroscopy (EIS) was performed on DSCs under 1.5 AM illumination with electrochemical station Autolab potentiostat 302.N and FRA2. The frequency range was from 100 kHz down to 0.01 Hz, and the amplitude of the ac voltage was 10 mV. A bias of 0.6 V was applied on the DSCs during the EIS study. The catalysis of Pt prepared by EG reduction was investigated by electrochemical impedance spectroscopy (EIS) on symmetric test cells under a bias of 0 V, using an Autolab PGSTAT302N potentiostats. The electrolyte in the cells is the same as that in the DSCs. The frequency range was from 100 kHz down to 0.01 Hz, and the amplitude of the ac voltage was 10 mV. The charge-transfer resistances were obtained by fitting the ac impedance data with the Zview program.

3. Results and Discussion

3.1. Deposition and Characterization of Pt Films. High-quality Pt films could be deposited on PEDOT:PSS/glass by the reduction of H_2PtCl_6 with EG. EG was selected as the solvent and the reductant of H_2PtCl_6 , since EG had low boiling point and low viscosity among the polyols and the other products from the EG reduction of H_2PtCl_6 were simple and readily removed.²³ PEDOT:PSS (chemical structure shown in Scheme 1), which is the most successful conducting polymer and has good thermal stability,^{33,34} was investigated as the substrate for Pt deposition by polyol reduction. The deposition was made by dropping a $400\ \mu\text{L}$ EG solution of 0.02 M H_2PtCl_6 on a PEDOT:PSS/glass of $2 \times 2\ \text{cm}^2$ on a hot plate at $180\ ^\circ\text{C}$. The yellowish solution first turned black, and then a smooth film distributed with black spots was formed on PEDOT:PSS. The inset of Figure 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 (Figure 1). No Cl signal could be observed in the EDX, and the other signals, including C, O, Na, and Si, were from PEDOT:PSS or glass. Hence, H_2PtCl_6 completely converted into Pt. This is further confirmed by an XPS survey for binding energy from 30 to 1100 eV (Figure 2a). No XPS signal of Cl was detected as well. Moreover, as shown in Figure 2b, XPS

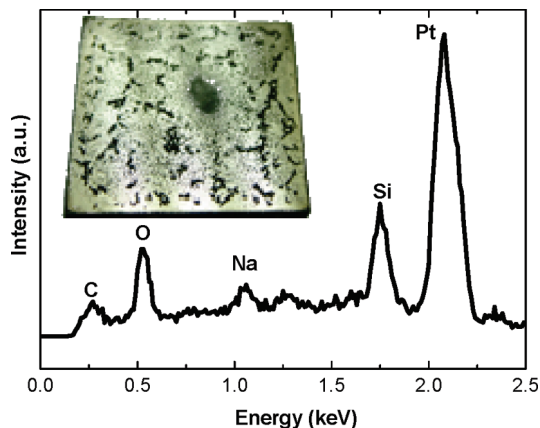


Figure 1. Photograph (inset) and EDX of a Pt film on PEDOT:PSS/glass fabricated by EG reduction of 0.02 M H_2PtCl_6 solution at 180 °C.

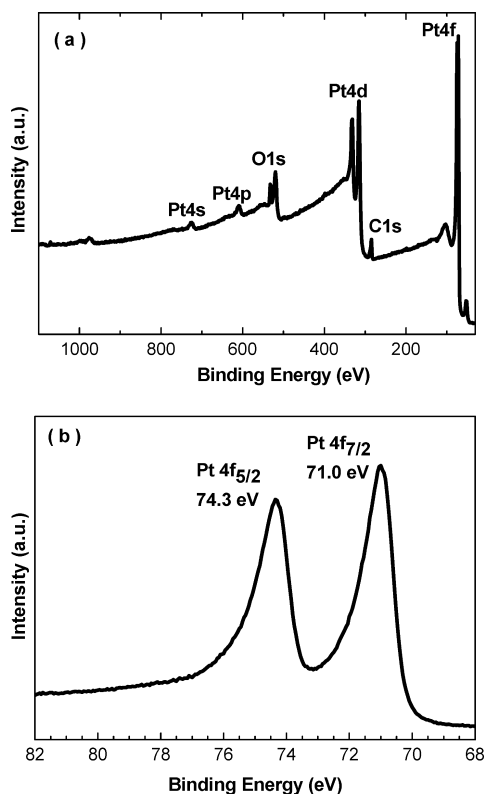


Figure 2. XPS (a) survey and (b) narrow scan of a Pt film on PEDOT:PSS/glass fabricated by EG reduction of 0.02 M H_2PtCl_6 solution at 180 °C.

scans in the narrow range of Pt suggest that both the black spots and the smooth part are zerovalent Pt.^{15,20}

The Pt film was also characterized by SEM. Two Pt structures were observed: porous and dense structures. The porous structure in the SEM picture, which corresponded to the black spots on the Pt film, was the aggregates of Pt nanoparticles (Figure 3a). The smooth part was dense and continuous Pt, whose morphology was revealed by SEM (Figure 3b) and AFM (Figure 4) in higher magnifications. The AFM image indicates that 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.

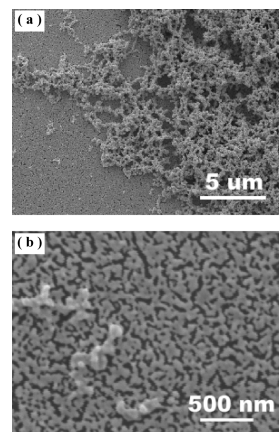


Figure 3. SEM images of a Pt film deposited on PEDOT:PSS/glass by EG reduction of 0.02 M H_2PtCl_6 solution at 180 °C. Image b shows the smooth part in image a with higher magnification.

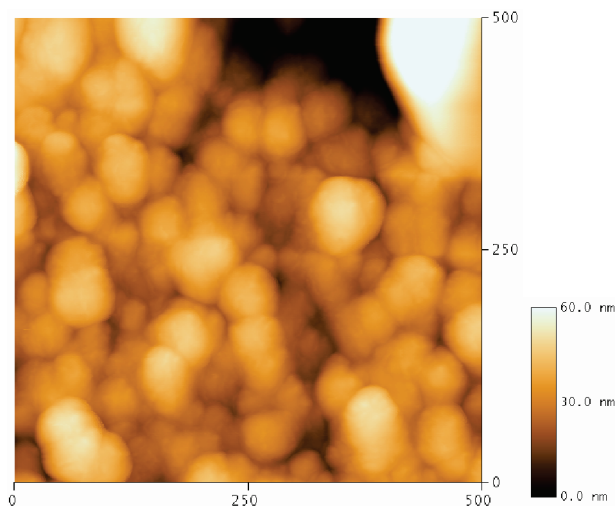


Figure 4. AFM image of a Pt film deposited on PEDOT:PSS/glass by EG reduction of 0.02 M H_2PtCl_6 solution at 180 °C. The unit is nm.

Products other than Pt, including H_2O , HCl , and CO_2 , vaporized during this process, and other compounds adsorbed on Pt were washed away with ethanol.²³ The XRD of a cleaned Pt film suggests that it has a crystal structure as normal Pt metal (Figure 5).

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 H_2PtCl_6 . Pt grows from the substrate in this growing process. The other is the formation of Pt particles in solution.^{23–25} The Pt nanoparticles aggregated in solution and became porous Pt on dense Pt after precipitation from the solution.

The porous Pt did not homogeneously deposit on the dense Pt. It had a wide distribution in thickness, which could be from 0 up to 1 μm . It was also difficult to control its thickness. On the other hand, the thickness of the dense Pt part could be controlled by the solution volume. The dense Pt part, deposited by dropping a 400 μL EG solution of 0.02 M H_2PtCl_6 on a PEDOT:PSS/glass of $2 \times 2 \text{ cm}^2$ on a hot plate at 180 °C, had a thickness of about 160 nm. As shown in Figure 6, the thickness of the dense Pt part almost linearly increases with the increasing H_2PtCl_6 solution volume.

Besides the Pt formation on the PEDOT:PSS film during the EG reduction of H_2PtCl_6 , there was also an interesting change

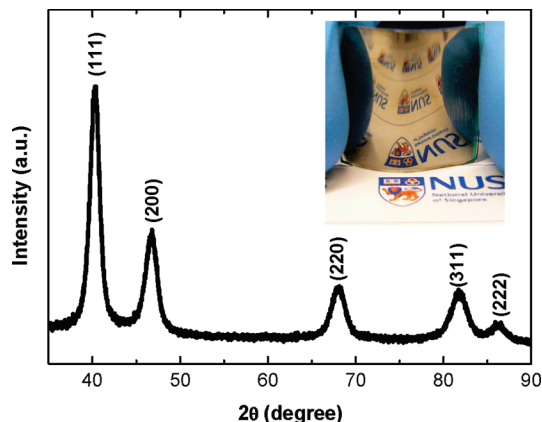


Figure 5. XRD of a Pt film deposited on PEDOT:PSS/glass by EG reduction of 0.02 M H_2PtCl_6 solution at 180 °C. The inset is a Pt film deposited on ITO/PET after sonication for 10 min, which shows the high reflection and the flexibility of the Pt film. The blue color in the picture is from the lab glove.

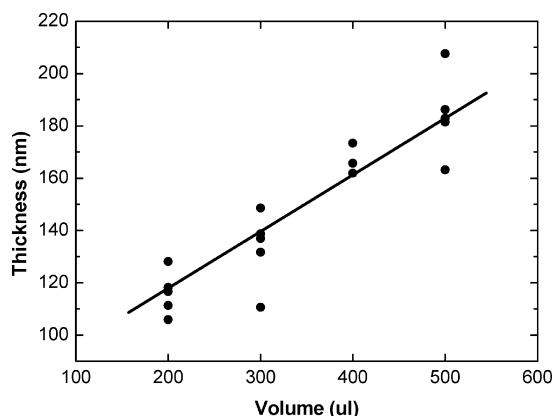


Figure 6. Dependence of the thickness of the smooth Pt part on volume of H_2PtCl_6 solution in EG. The Pt films were fabricated by dropping 0.02 M H_2PtCl_6 /EG solution on $2 \times 2 \text{ cm}^2$ PEDOT:PSS/glass at 180 °C. The dots are experimental results, which are simulated by the straight line.

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 the literature.^{35–40} Thus, we can obtain a catalytic Pt film on a highly conductive polymer film through a simple process. The high conductivity for the substrate is important for some applications, such as counter electrode of dye-sensitized solar cells.^{31,32}

Other conductive substrates were also investigated for the Pt deposition by the polyol reduction. Continuous Pt films could also be deposited on conductive ITO substrate. The inset of Figure 5 shows the picture of a Pt film deposited on a flexible ITO/PET substrate by EG reduction of 0.02 M H_2PtCl_6 solution at 180 °C, of which the black spots, that is, the porous Pt structure, were removed after a sonication in an ultrasonic bath for 5 min. The Pt/ITO/PET film exhibited metallic luster with high reflection and had high flexibility. Though continuous Pt films could form on conductive FTO glass, the adhesion to the substrate was quite poor.

Insulating polymers were also investigated as the substrates for Pt deposition through the same process. Continuous Pt films with metallic luster could be produced on polyimide, while discontinuous Pt films without metallic luster were obtained on substrates like poly(vinyl alcohol), poly(4-styrenesulfonic acid),

poly(methyl methacrylate), and Teflon. Thus, the quality of the Pt film deposited by polyol reduction strongly depends on the interaction between Pt and the substrate. Presumably, Pt could have strong interaction with the conjugated PEDOT chains in PEDOT:PSS.

Our method of dropping EG solution of a Pt precursor on substrate is different from that reported by Kurihara et al.¹⁷ In their report, the nonconductive substrates were immersed into the reaction mixture of metal precursors in polyol. We prepared Pt films on nonconductive polyimide by the two methods and found that the Pt films fabricated by our method were more homogeneous and metallically lustrous and had higher conductivity.

3.2. Factors Affecting the Quality of Pt Films. Skrabalak et al. studied the mechanism for the EG reduction of metal precursors in solution and concluded that the reduction is due to the conversion of EG into a reductant, glycolaldehyde, when heated in air.²³ Thus, it is not surprising that the quality of the Pt films produced by EG reduction of H_2PtCl_6 is affected by other experimental conditions besides the substrate, including concentration and pH value of H_2PtCl_6 solution in EG and temperature during the EG reduction. Even air flowing condition has an effect on the quality of the Pt film.

The quality of the Pt films was affected by the rate of EG reduction of H_2PtCl_6 . High-quality Pt films could be deposited through the reduction of H_2PtCl_6 with EG, since the generation of glycolaldehyde from EG is a slow process. When acetaldehyde was used to replace EG, the reduction of H_2PtCl_6 was much more rigorous, and Pt deposited on the substrate was principally porous Pt. More rigorous reduction generates Pt particles in solution more rapidly, resulting into more porous Pt deposited on the substrate. In fact, rigorous reduction of Pt salt was used to fabricate porous Pt by Yang et al.⁴¹ The effect of the reduction rate on the quality of the Pt films is similar to that on the silver films by the Tollens reaction.⁴²

The temperature during the reduction of H_2PtCl_6 is another factor affecting the quality of the Pt films. Pt films were prepared by dropping a 400 μL EG solution of 0.02 M H_2PtCl_6 on $2 \times 2 \text{ cm}^2$ PEDOT:PSS/glass substrates at different temperatures, 120, 140, 160, 180, and 200 °C. The pictures of these Pt films were shown in Figure 7a. The EG reduction of H_2PtCl_6 at 120 °C resulted into a dark film without metallic luster. Its SEM image indicates a discontinuous film (Figure 7b). Cl and ionic Pt were observed in the XPS (Figure 8), which indicate that H_2PtCl_6 was not completely reduced at this temperature. Wang et al. also pointed out that the polyol reduction of Pt salts took place at a temperature above 120 °C.²⁴ The Pt films became continuous and exhibited metallic luster when deposited at temperatures of 140 °C and above (Figure 7c). Another phenomenon related to the reduction temperature is the observation of more black spots, that is, porous Pt, on the Pt films deposited at higher temperature. Obviously, this is related to the higher reduction rate at higher temperature. The temperature effect can be understood in terms of the polyol reduction mechanism as reported by Skrabalak et al.²³ The conversion of EG into glycolaldehyde is affected by temperature. It is small at temperatures below 140 °C and increases with increasing temperature. Thus, the temperature can affect the reduction rate of H_2PtCl_6 , the nucleation, and the growth kinetics of Pt.

The pH value of the H_2PtCl_6 solution in EG also affected the quality of the Pt films, since the pH value had an effect on the reduction of Pt precursors.^{23,24} NaOH was added into an EG solution of 0.02 M H_2PtCl_6 to adjust the pH value of the solution from 2 to 10. The Pt film deposited from the basic

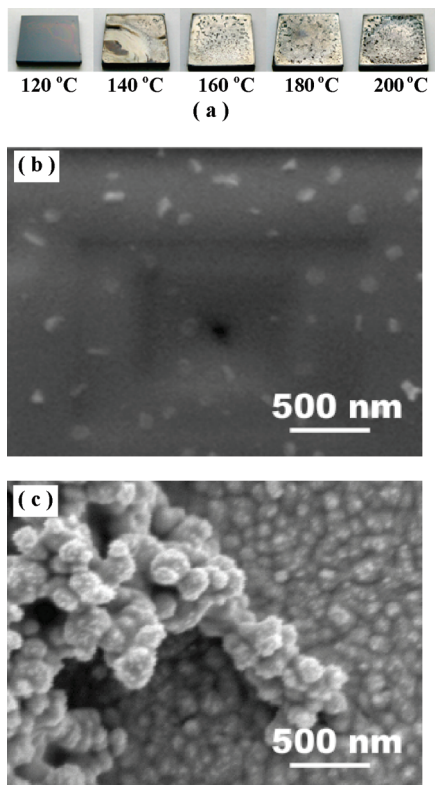


Figure 7. Pt films on PEDOT:PSS/glass deposited by EG reduction of 0.02 M H_2PtCl_6 solution at different temperatures: (a) pictures of Pt films with the deposition temperatures indicated; (b, c) SEM images of Pt films deposited at 120 and 140 °C, respectively.

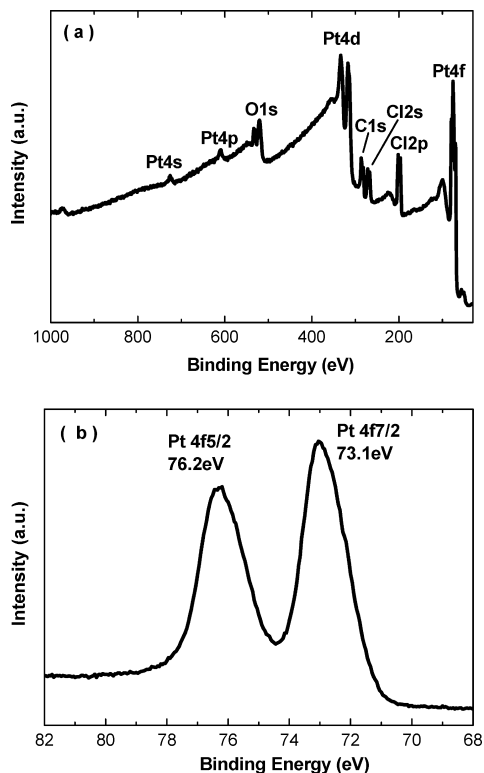


Figure 8. XPS (a) survey and (b) narrow scan of Pt on PEDOT:PSS/glass deposited by EG reduction of 0.02 M H_2PtCl_6 solution at 120 °C.

solution was less uniform than that from the acidic solution, that is, the acidic solution produced Pt films of higher uniformity. Presumably, this is related to the stability of the Pt

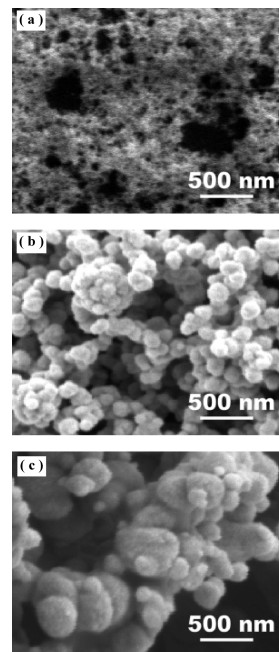


Figure 9. SEM images of Pt films on PEDOT:PSS/glass. The Pt films were deposited from a EG solution of (a) 0.002, (b) 0.01, and (c) 0.1 M H_2PtCl_6 at 180 °C, respectively.

particles in EG solution, since Pt particles with small size and good stability can be produced in basic EG solution.²⁴ In addition, the addition of NaOH into EG solution of H_2PtCl_6 affects the Pt microstructure formation and accelerates the oxidation of EG into glycolaldehyde.²³ Thus, more Pt nanoparticles with good stability are formed in basic EG solution, while more Pt grows from the substrate and becomes a continuous film in acidic EG solution.

The concentration of H_2PtCl_6 in EG has an effect on the quality of the Pt film as well. The SEM images of Pt films deposited from three EG solutions of different H_2PtCl_6 concentrations indicate that a EG solution of higher H_2PtCl_6 concentration produced Pt particles with larger size and wider size distribution (Figure 9). This is consistent with the effect of the H_2PtCl_6 concentration on the size of Pt nanoparticles produced by polyol reduction.²⁴

The environment, particularly the air flowing condition, affected the quality of the Pt film as well. We found that the Pt film became more inhomogeneous, such as formation of “coffee rings”, when it was deposited in a fume hood with air flow than outside without air flow.

3.3. Pt as Counter Electrode of Dye-Sensitized Solar Cells.

DSCs provide cheap and renewable energy and are very promising to be commercialized in the near future. They require a counter electrode with good conductivity and excellent catalysis, since the redox species regenerate on the counter electrode.^{1,2} Many materials, including Pt, graphites, activated carbons, conducting polymers, carbon nanotubes, and composites of conducting polymer and carbon nanotube, have been investigated as the counter electrode. Among them Pt is still the best material as the counter electrode of DSCs in terms of the photovoltaic performance.^{31,43–46} A couple of deposition techniques, such as magnetron sputtering, electrochemical deposition, chemical vapor deposition, and pyrolysis, have been studied.^{5–22} The DSCs with Pt counter electrode by the pyrolysis of H_2PtCl_6 at a temperature higher than 380 °C exhibit the best photovoltaic efficiency. Although a Pt counter electrode prepared by polyol reduction of Pt precursor was mentioned by Khelash-

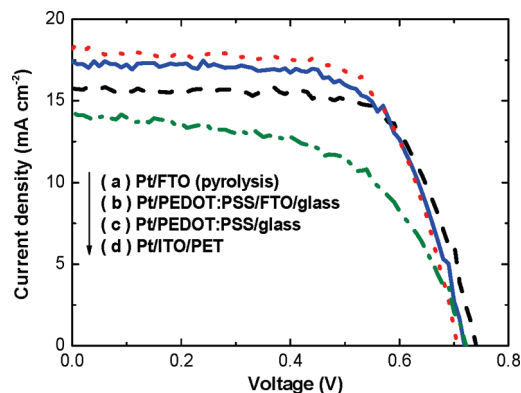


Figure 10. Current density–voltage characteristics of dye-sensitized solar cells with different counter electrodes under AM 1.5 illumination. The counter electrodes are indicated in the figure. The Pt counter for (a) was deposited by pyrolysis of H_2PtCl_6 at 400 °C, and the Pt counter electrodes for (b–d) were deposited by EG reduction of 0.02 M H_2PtCl_6 solution at 180 °C.

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 glass (pyrolysis) ^a	18.19	710	0.68	8.7
Pt/PEDOT:PSS/FTO glass ^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 °C for 15 min.

^b Pt was prepared by EG reduction of 0.02 M H_2PtCl_6 at 180 °C. It was rinsed with ethanol three times and dried at 60 °C for 10 min.

vili et al., their platinum materials were actually Pt powders generated in solution by polyol reduction, and no photovoltaic performance was reported.^{19,21}

Pt deposited by EG reduction of H_2PtCl_6 at 180 °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 °C for 10 min. The current–voltage curves of these DSCs under illumination of AM 1.5 (100 mW cm^{-2}) are shown in Figure 10. Two types of rigid substrates, PEDOT:PSS/FTO glass and PEDOT:PSS/glass, were used for the Pt deposition by EG reduction of H_2PtCl_6 . The former substrate was used because FTO glass was usually exploited as the substrate for the Pt counter electrode prepared by pyrolysis of Pt salts. The photovoltaic performance of a control DSC with the Pt counter electrode prepared by pyrolysis of H_2PtCl_6 at 400 °C for 15 min on FTO glass is presented as well. The photovoltaic performance of these devices, including the open-circuit voltage (V_{oc}), the 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. It is worth pointing out that the cleanness of the Pt films affects the photovoltaic performance of the dye-sensitized solar cells since the regeneration of the redox species takes place at the surface of the Pt films. When an as-prepared Pt film without the ethanol rinse process was used as the counter electrode of DSC, J_{sc} and V_{oc} decreased to 15.2 mA cm^{-2} and 0.69 V, respectively. The energy conversion efficiency decreased to 7.3%.

Another interesting observation is the high photovoltaic efficiency by the DSC with Pt deposited on PEDOT:PSS/glass.

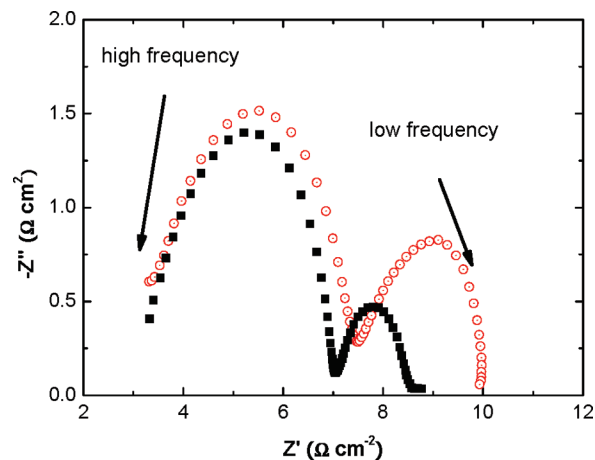


Figure 11. Nyquist plots of symmetrical cells with Pt prepared by pyrolysis (open circles) and Pt by EG reduced on PEDOT:PSS/FTO (solid squares) as the two electrodes.

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. The high performance of this device was also related to the high conductivity of the PEDOT:PSS film, which was actually enhanced from 10^{-1} S cm^{-1} to 10^2 S cm^{-1} by EG during the Pt deposition.^{35–40} In addition, we investigated the application of Pt prepared by EG reduction of H_2PtCl_6 as the counter electrode of DSCs with a device area larger than 5 cm^2 (fabrication and photovoltaic performance of large-area DSCs are given in the Supporting Information). The large-area DSCs exhibited comparable photovoltaic performance with the control devices with Pt prepared by pyrolysis as the counter electrode. 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.^{47,48}

The Pt deposition by the polyol reduction of H_2PtCl_6 at low temperature enables the Pt deposition on flexible substrates like polymers. Thus, a 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 M H_2PtCl_6 solution at 180 °C. The devices exhibited photovoltaic efficiency of 5.8%. This preliminary efficiency was higher than that of DSCs with other flexible counter electrodes.^{7–11}

The redox species I^-/I_3^- regenerate through the reduction of triiodide on the Pt counter electrode of DSCs. It is strongly dependent on the catalysis of Pt. Pt prepared by the EG reduction was characterized by the ac impedance spectroscopy on symmetrical cells with Pt as the two electrodes to understand its catalysis of Pt on the reduction of triiodide (Figure 11). The semicircle at the high-frequency range corresponds to the charge transfer of the triiodide reduction on Pt.^{49,50} The charge-transfer resistance (R_{CT}) on Pt prepared by EG reduction was 2.28 $\Omega \text{ cm}^2$, which is lower than that (3.74 $\Omega \text{ cm}^2$) with Pt by pyrolysis. Thus, Pt prepared by EG reduction effectively catalyzes the reduction of triiodide. This accounts for the high performance of the DSCs with the EG-reduced Pt as the counter electrode.

There may be two concerns on the stability of Pt on PEDOT:PSS/FTO glass as the counter electrode of DSCs. One concern is about the adhesion of Pt on PEDOT:PSS/FTO glass in the electrolyte of DSCs over time. Pt may detach from PEDOT:PSS if it has a poor adhesion. Another concern is related to the stability in the conductivity of the PEDOT:PSS film on FTO glass. PEDOT:PSS has been widely used as the buffer layer in

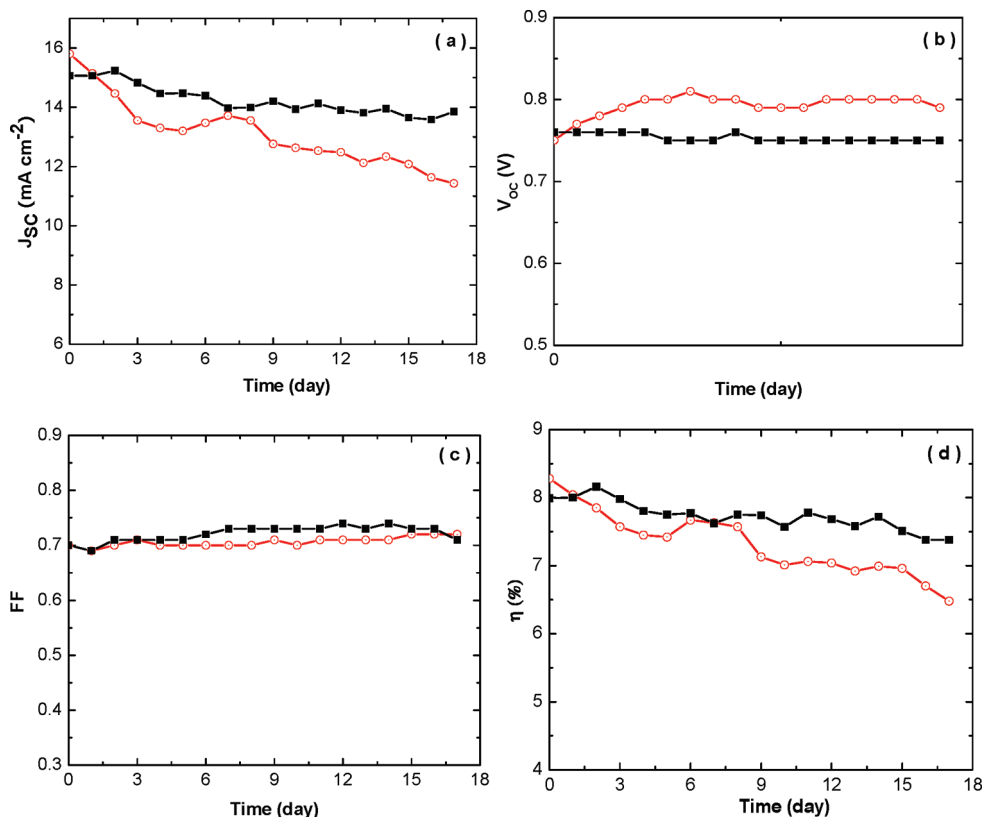


Figure 12. Variations of (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) η with time for DSCs with Pt counter electrode prepared by pyrolysis (open circles) and by EG reduction of H_2PtCl_6 on PEDOT:PSS/FTO (solid squares).

organic electronic devices, including polymer photovoltaic cells and polymer light-emitting diodes.⁵¹ It was observed that PEDOT:PSS was volatile and brought problems on the stability of those devices.^{52–54} We studied the variation of the photovoltaic performance with time for DSCs using Pt prepared by EG reduction of H_2PtCl_6 as the counter electrode (Figure 12). Those devices were sealed and stored in ambient air. The device with Pt prepared by EG reduction of H_2PtCl_6 as the counter electrode exhibited good stability: J_{sc} decreased from 15.06 mA cm^{-2} to 13.85 mA cm^{-2} after 17 days, that is, less than 10% decrease, whereas V_{oc} and FF were almost flat against time. η slightly decreased from 8.0% to 7.4% after 17 days. The stability in the photovoltaic performance of the DSC is comparable or even better than the control device with Pt prepared by pyrolysis as the counter electrode.

The stability in the catalytic properties of Pt as the counter electrode of DSCs was investigated by ac impedance spectroscopy. R_{CT} of the triiodide reduction on Pt prepared by EG reduction of H_2PtCl_6 was 2.45 $\Omega \text{ cm}^2$ just after the device fabrication. It increased to 3.38 $\Omega \text{ cm}^2$ after 17 days (Figure 13). The change in the R_{CT} value over time was similar to that on Pt prepared by pyrolysis, whose R_{CT} increased from 3.52 $\Omega \text{ cm}^2$ to 4.78 $\Omega \text{ cm}^2$ after 17 days.

4. Conclusions

In conclusion, nanostructured Pt films could be deposited on flexible and rigid conducting substrates, including PEDOT:PSS film and ITO, by EG reduction of H_2PtCl_6 at low temperature. Both dense and porous Pt structures were observed. The dense Pt results from the Pt growth from the substrate, while the porous Pt is due to the Pt particles formed in solution. The quality of the Pt film was affected by many factors, such as substrate, pH value and concentration of the H_2PtCl_6 solution in EG, and

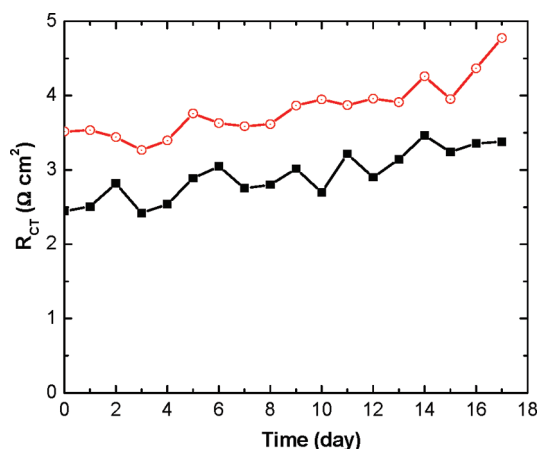


Figure 13. Variations of the charge transfer resistances (R_{CT}) with time for DSCs with Pt counter electrode prepared by pyrolysis (open circles) and by EG reduction of H_2PtCl_6 on PEDOT:PSS/FTO (solid squares).

temperature during EG reduction. 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.

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Supporting Information Available: Fabrication and photovoltaic performance of DSCs with device areas larger than 5 cm^2 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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