Impacts of sputter-deposited platinum thickness on the performance of dye-sensitized solar cells

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ABSTRACT

The thickness of platinum thin film and surface roughness of the platinized counter electrode can be determined by sputtering time. A larger surface roughness is beneficial to the charge transfer efficiency and electrocatalytic activity of platinized counter electrode. When the sputtering time of 40 s is used, the dye-sensitized solar cell exhibits the largest short-circuit photocurrent density and the highest energy conversion efficiency of 6.81%. When the sputtering duration is over 80 s, both short-circuit photocurrent density and energy conversion efficiency are largely reduced. A thicker platinum film is not favorable for improving the performance of dye-sensitized solar cell. The optimum platinum thickness for sputter-deposited counter electrode approximates to 30 Å. The increase of peak height and peak area in cyclic voltammetric plot demonstrates larger active surface area and enhanced electrocatalytic activity of the platinized counter electrode. The dependence of short-circuit photocurrent density on platinum thickness has been further explored by electrochemical impedance spectroscopy. Corresponding charge transfer resistances at various platinum/electrolyte interfaces are obtained by simulation on the impedance spectra. This study has evidenced that the thickness of platinum greatly influences the electrocatalytic ability of platinized counter electrode and is certainly a significant factor for the performance of dye-sensitized solar cell.

1. Introduction

Dye-sensitized solar cell (DSSC) has been intensively investigated as a promising alternative to traditional silicon-based photovoltaic devices owing to its advantages of high solar to electric energy conversion efficiency, low production cost and simple fabrication processes [1–7]. The counter electrode (CE) is one of the most important components in a DSSC. If the CE is only a fluorine-doped tin oxide (FTO) conductive glass without a platinum (Pt) layer, the energy conversion efficiency (η) is very low (0.1%). This implies that the function of a CE depends essentially on Pt [8]. The task of a CE is to collect electrons arrived from the external circuit and transfer them back to the redox electrolyte, and then catalyze the reduction of I_3^- to I^-. The reduction of I^-/I_3^- redox species is employed to regenerate the sensitizer after electron injection. Therefore, CE materials with high conductivity and electrocatalytic activity are desirable [2]. Several different kinds of CE materials have been introduced to DSSCs, such as Pt [9–14], carbonaceous materials [8,15–18], conductive polymers [19–21], and metal compounds [22,23]. Low cost carbonaceous materials such as graphite [24,25], carbon black [26], porous carbon [27], carbon

nanotubes [28–30], and graphene [31,32], exhibit high chemical stability. However, carbonaceous films often need to be adhered to conductive substrates with binders, leading to problems of conductivity and stability in the electrolyte [18]. Accordingly, the η of the DSSCs with CEs fabricated by carbonaceous materials or conductive polymers usually reaches a bottleneck and can not be too high. Metals could be beneficial to obtain a high fill factor (FF) for large-scale DSSCs because of their low sheet resistances. However, it is difficult to use metals such as steel, copper and nickel, in liquid-type DSSCs since the I^-/I_3^- redox species in electrolyte are corrosive to the metals.

High electrocatalytic activity of the CE is important for a DSSC. A fast I_3^- reduction on CE results in minimum energy loss. As a noble metal, although Pt is subject to price variations, its electrocatalytic activity for I_3^- reduction is superior to other materials for use in the fabrication of CEs. Besides, the high corrosion stability in the electrolyte is another exceptional advantage of Pt. Thus a thin Pt layer coated on FTO conductive glass has been already widely used as the standard for the CE of DSSCs. Most of the DSSCs with η greater than 11% use Pt as catalyst on their CEs [4,33–36]. To fabricated platinized CEs with excellent electrocatalytic performance, some approaches have been developed. The CE for a DSSC is usually prepared by spreading drops of hydrogen hexachloroplatinate (H_2PtCl_6) isopropanol solution on FTO conductive substrate, followed by annealing at 500 °C. Compared to the thermal

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decomposition method to prepare Pt-coated CE, sputtering deposition to form an ultra-thin Pt layer on FTO conductive substrate in vacuum would be a more facile and faster way to obtain platinized CEs with excellent electrocatalytic activity. It has been illustrated in previous reports that Pt thickness has no significant influence on DSSC performance [37–39]. In this study, we have demonstrated that Pt thickness indeed apparently influences the short-circuit photocurrent density (J_{sc}) and η of DSSCs. A systematic and comparative investigation into the impacts of various sputtering times (different Pt thicknesses) on DSSC performance has been performed. The results have explicitly showed that a thicker Pt layer is unfavorable for DSSC performance. The DSSC with Pt sputtering duration of 40 s exhibited the largest J_{sc} of 15.01 mA cm^{-2} and the highest η of 6.65%. It has been concluded that the most appropriate thickness to form the sputter-deposited Pt CE for a DSSC is around 30 Å.

2. Experimental

2.1. Preparation of TiO$_2$ electrode and dye adsorption

Commercial FTO conductive glasses with sheet resistance of 7 Ω cm^{-2} were employed as the substrates for fabrication of DSSCs. The FTO conductive glasses were firstly cleaned with detergent, rinsed twice with de-ionized water, followed by ultrasonication in acetone and isopropyl alcohol baths sequentially, and finally dried by nitrogen gas flow. The nanoporous TiO$_2$ electrode was composed of three-layer TiO$_2$ nanoparticles. The diameter of the nanoparticles is 13 nm in the first two layers (Ti-nanoxide T/SP, solaronix) and 400 nm in the uppermost layer (Ti-Nanoxide R/SP, Solaronix). The nanoparticles of each layer were spread on clean FTO glass substrates by doctor blade method, followed by air-drying at room temperature and baking at 100 °C for 2 h, respectively, and then calcination at 500 °C for 60 min. The nanoporous TiO$_2$ electrode with an effective area of 0.5 × 0.5 cm^2 was pre-cleaned by oxygen plasma for 5 min before dye adsorption. Then it was immediately immersed in 0.3 mM dye solution (N719 in t-butanol/acetonitrile (1:1, v/v)) for 24 h. The plasma treatment could reduce oxygen vacancies which would provide electron traps and prevent electron transport on TiO$_2$ surfaces and create more hydrophilic surfaces beneficial for dye adsorption [40–46]. After drawn out from the dye solution and rinsed with acetonitrile, the dye-anchored TiO$_2$ was blow-dried with nitrogen gas and ready for use as the photoelectrode in the fabrication of DSSCs.

2.2. Preparation of Pt counter electrode

The FTO conductive glasses for preparation of Pt CEs were also cleaned by same processes as described above to obtain clean substrates. The deposition of Pt was achieved in vacuum by an ion sputter coater with the deposition rate of 0.75 Å s^{-1}. The sputtering times, 10 s, 40 s, 80 s and 120 s, were selected to fabricate uniform Pt ultra-thin films with different thicknesses so that a systematic and comparative study could be accomplished. After sputtering deposition, calcination was executed on the Pt CEs at 500 °C for 60 min. When cooling down to the room temperature, the Pt CEs were immediately used in the fabrication of DSSCs. The surface roughnesses of the sputter-deposited Pt ultra-thin films were examined by atomic force microscopy (AFM). The electrocatalytic activities of the Pt CEs with various thicknesses were examined by the potentiostat/galvanostat (CHI627C, CH Instruments, USA) using 1 mM I$_2$, 10 mM LiI and 0.1 M LiClO$_4$ in acetonitrile as the electrolyte to obtain cyclic voltammetry (CV) plots and chronoamperometric curves. The CV measurements were performed at a sweeping rate of 100 mV s^{-1}. The reflection spectra of Pt CEs were obtained by

Table 1
Thicknesses, R_q, and R_1 of Pt films obtained by various sputtering times.

	Sputtering time (s)			
	10	40	80	120
Pt thickness (Å)	7.5	30	60	90
R_q (nm)	38.5	40.4	36.7	37.1
R_1 (Ω)	5.64	4.65	5.88	7.57

a UV–Vis spectrophotometer equipped with an integrating sphere setup (U-3900H, Hitachi).

2.3. Fabrication and characterization of DSSCs

The DSSCs were of a sandwich type composed of a dye-adsorbed TiO$_2$ electrode, a polyimide spacer and a sputter-deposited Pt CE. The electrolyte solution prepared from 0.5 M LiI, 0.05 M I$_2$, 0.5 M TBP ($tert$-butylpyridine) and 0.5 M MPII (1-methyl-3-propylimidazolium iodide) in acetonitrile was injected into the narrow space between two electrodes by a microsyringe. The photovoltaic characterizations of DSSCs were completed by a solar simulator (SS50ABA, Photoemission Tech, Inc.) under AM 1.5 filter irradiation. The photocurrent–voltage properties were recorded by a source monitor (ADC 6240A) coupled with the Sunrise I–V measurement software under constant light intensity of 100 mW cm^{-2}. The Nyquist plots were achieved under dark in an open circuit by electrochemical impedance spectroscopy (EIS) measurements also using the potentiostat/galvanostat. The frequency range explored was 10^{-2} Hz to 10^5 Hz, and the ac amplitude was set as 10 mV between two electrodes.

3. Results and discussion

All the Pt ultra-thin films obtained by sputtering deposition for use as the CEs in DSSCs are uniform visually. The two-dimensional surface topography images of Pt ultra-thin films fabricated by various sputtering times have been examined by AFM, as shown in Fig. 1. The measurement area for AFM image of each Pt film is 5 μm × 5 μm. Since the deposition rate for sputtering is 0.75 Å s^{-1}, it can be calculated that the thicknesses of Pt ultra-thin films obtained by sputtering times of 10 s, 40 s, 80 s and 120 s are approximately 7.5 Å, 30 Å, 60 Å and 90 Å, respectively. Their average root mean square roughnesses (R_q) obtained by AFM measurements are 38.5 nm, 40.4 nm, 36.7 nm, and 37.1 nm, respectively, as displayed in Table 1. A larger R_q represents larger grain sizes and fewer grain boundaries in the Pt film, in which defects as electron traps would decrease and charge transport would be enhanced. Since the Pt ultra-thin film fabricated by sputtering time of 40 s has the largest R_q, it is expectable that the CE made of this Pt film would show the highest charge transfer efficiency leading to the largest J_{sc}, as revealed in Table 2. It is observed that R_q decreases apparently as sputtering duration for Pt deposition is longer than 80 s. Compared to sputtering time of 40 s, the Pt films fabricated by sputtering times of 80 s and 120 s would have smaller grain sizes and more grain boundaries containing more defects, resulting in worse

Table 2
Photovoltaic characteristics (J_{sc}, V_{oc}, FF and η) of the DSSCs with Pt CEs fabricated by various sputtering times.

Sputtering time (s)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)
10	14.43	0.71	0.61	6.24
40	15.22	0.71	0.63	6.81
80	13.42	0.72	0.62	5.96
120	12.42	0.73	0.62	5.62