An optimum morphology of platinum nanoparticles with excellent electrocatalytic activity for a highly efficient dye-sensitized solar cell

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ABSTRACT

Remarkable morphology of platinum (Pt) nanostructures from submicron clusters, by way of nanoclusters, to nanoparticles (NPs) was obtained through controlling the heating rate of thermo-decomposition of Pt precursor molecules. Uniform and dense distribution of Pt-NPs was obtained on FTO glass substrate prepared at the heating rate lower than $1.2\,°C\,min^{-1}$. The highest electrocatalytic performance, which corresponded to the lowest charge transfer resistance of $0.86\,\Omega\,cm^2$, was achieved with the counter electrode prepared at the heating rate of $1.2\,°C\,min^{-1}$ during sintering. The heating rate during sintering proved to be a sensitive parameter for determining the morphology of Pt-NPs formed on the surface of FTO glass substrate, which subsequently influenced the catalytic activity of the Pt-NPs and subsequently the photovoltaic performance of a dye-sensitized solar cell (DSC). The highest conversion efficiency of the DSC prepared with the heating rate of $1.2\,°C\,min^{-1}$ was 9.30% with fill factor of 67.21%, J_{sc} of $18.14\,mA\,cm^{-2}$, and V_{oc} of $762.5\,mV$.

1. Introduction

Dye-sensitized solar cells can achieve comparatively high conversion efficiency with low fabrication cost [1]. A DSC consists primarily of a working electrode, an electrolyte, and a counter electrode. Although the working electrode has the greatest potential to improve the efficiency of DSCs, the CE also has an important role of regenerating iodide from triiodide. Both high conductivity and excellent catalysis are required for this purpose.

Platinum has been almost always used as a CE material for DSC [1–7] because of its catalytic functionality, high conductivity and chemical stability under acid/base environments [2]. Generally, there are two methods of coating Pt on a conductive substrate, such as Pt-sputtering [2–5] and thermal decomposition (TD) of chloroplatinic acid hydrate [6,7]. Pt-sputtering method, however, uses a large amount of expensive Pt and needs vacuum equipment which causes high processing cost. Although TD method uses a small amount of Pt ($5–10\,\mu g\,cm^{-2}$), low electric conductivity can result in a decrease of energy conversion efficiency of DSCs [8,9] due to agglomeration of Pt nanoparticles (Pt-NPs) on the FTO glass substrate and poor uniformity of Pt films [10,11].

Recently, a homogeneous Pt CE with high quality was prepared through the TD method of Pt precursor solution containing a small amount of polyvinyl pyrrolidone (PVP) [7]. Although the uniformity

of Pt films was achieved, the problem of the agglomeration of Pt-NPs on FTO glass substrate does still not have been solved yet.

In this study, we report a successful TD method to prepare uniformly dispersed Pt-NPs without any agglomeration on the CE, through controlling the heating rate during the sintering process. Careful control of the heating rate allows us to obtain an optimum morphology of Pt-NPs, which results in excellent electrocatalytic activity for the I_3^-/I^- redox reaction, and further improves the photovoltaic performance of DSCs with a Pt-NPs CE.

2. Experimental

2.1. Materials

FTO glass for use as a transparent conducting electrode was purchased from Pilkington, USA ($\sim$8 Ohm $\square^{-1}$). These substrates were used after cleaning by sonic treatment in acetone (Fluka). Nonporous TiO_2 paste and ruthenium based-dye (N719) were purchased from Solaronix, Switzerland. The dye was adsorbed from a 0.3 mM solution in a mixed solvent of acetonitrile (Sigma–Aldrich) and tert-butylalcohol (Aldrich) with a volume ratio of 1:1. The electrolyte was a solution of 0.60 M 1-methyl-3-butylimidazolium iodide (Sigma–Aldrich), 0.03 M I_2 (Sigma–Aldrich), 0.10 M guanidinium thiocyanate (Sigma–Aldrich), and 0.50 M 4-tert-butylpyridine (Aldrich) in a mixed solvent of acetonitrile (Sigma–Aldrich), and valeronitrile, with a volume ratio of 85:15.

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2.2. Preparation of CEs

A Pt precursor solution containing 10 mM $H_2PtCl_6 \cdot xH_2O$ in iso-propanol was prepared first. 8 μl of Pt precursor was deposited on 2×2 cm^2 specimens of FTO glass, and the solvent was allowed to evaporate at 70 °C for 10 min. Then, the specimens were kept at 400 °C for 15 min [6] after heating them with different heating rates of 3, 2, 1.5, 1.2, 1, and 0.85 °C min^{-1}.

2.3. Preparation of TiO$_2$ working electrode and assembly of the DSC

The preparation of TiO$_2$ working electrode and the assembly of DSC were carried out as described in previous studies [4,5].

2.4. Measurements

The morphologies of the Pt CE were analyzed by high-resolution scanning electron microscopy (HRSEM, JEOL JSM-7000F). Sheet resistances were measured using a four-point probe setup (CMT-SR 1000 N, Advanced Instrument Technology, Inc.). Photocurrent-voltage characteristics were measured with an electrochemical interface and impedance analyzer (IVIUM Technologies, Ivium-Stat) under illumination from a Sun 3000 solar simulator with a 1000 W mercury-based Xe arc lamp and AM 1.5 G filters. The light intensity was calibrated with a silicon photodiode. Cyclic voltammograms (CVs) were obtained as in previous studies [4,5]. The electrochemical impedance spectroscopy (EIS) of a symmetric dummy cell was performed under open-circuit condition. The measured frequency range was 100 kHz to 100 mHz with perturbation amplitude of 5 mV [12]. The obtained spectra were fitted using Z-View software (v3.2c, Scribner Associates, Inc.) with reference to the proposed equivalent circuit. Tafel measurements were performed with a scanning rate of 5 mV s^{-1} in the potential range of 0.6 V to -0.6 V [12]. The data were analyzed with IviumStat to calculate the exchange current density.

3. Results and discussion

3.1. Morphology of Pt-NPs CEs

There exists Lewis acid-base interaction between the $H_2PtCl_6 \cdot xH_2O$ and fluorine-doped SnO$_2$ because F atoms can provide free electron pairs due to their hybrid orbital configuration of $2s^2 2p^5$ [13], and $H_2PtCl_6 \cdot xH_2O$ is a kind of acid [7]. Thus, $H_2PtCl_6 \cdot xH_2O$ could be well spread over the FTO glass substrate, forming a thin layer. According to Schweizer and Kerr [14], $H_2PtCl_6 \cdot xH_2O$ can be converted to PtCl$_2$ before decomposition to Pt-NPs. The structure of highly crystalline β-PtCl$_2$ contains discrete Pt$_6$Cl$_{12}$ units, which are volatile [15,16]. The volatility of Pt$_6$Cl$_{12}$ in the TD to metallic Pt offers an explanation for the ease of dispersing Pt as small crystallites on high-surface-area catalysts and catalyst supports [14]. The amount of Pt "missing" in the thermo-gravimetric analysis (TGA) has also been observed to vary with sample size, heating rate, and gas flow rate [14]. These previous studies emphasize the importance of heating rate in TD processes.

The chlorine-containing platinum species, if present at temperatures higher than 250 °C, can be poorly dispersed catalysts because of agglomeration [17]. Thus, the time for heating process is a decisive factor for controlling the amount of chlorine. Fig. 1 shows the morphologies of Pt-NPs CEs prepared with different heating rates during sintering. Fig. 1 (a) presents a HRSEM image of Pt-NPs CE prepared with a heating rate of 3 °C min^{-1}. A few submicron clusters of Pt ionic species were observed on the surface of FTO glass. Fig. 1(b) presents a HRSEM image of Pt-NPs CE prepared

Counter electrode	Sheet resistance/$\Omega \ \square^{-1}$
3/°C min^{-1}	8.039 ± 0.074
2/°C min^{-1}	7.843 ± 0.008
1.5/°C min^{-1}	7.781 ± 0.017
1.2/°C min^{-1}	7.602 ± 0.015
1/°C min^{-1}	7.705 ± 0.003
0.85/°C min^{-1}	7.731 ± 0.004

with a heating rate of 2 °C min^{-1}. Pt-NPs formed clusters at the valley between SnO$_2$ particles on the surface of FTO glass. Fig. 1(c) presents a HRSEM image of Pt-NPs CE prepared with a heating rate of 1.5 °C min^{-1}. Pt-NPs not only formed clusters at the valley between SnO$_2$ particles but were also individually deposited on the surface of SnO$_2$ particles without any aggregation. The fast heating rate in the TD process represents a short time of decomposing chlorine, suggesting plausible agglomeration of Pt ionic species not yet fully converted into Pt-NPs. In contrast to the fast heating rate, the slow heating rate in the TD process means that there is enough time for decomposing chlorine, which results in high yield of Pt-NPs. Fig. 1(d), (e) and (f) present HRSEM images of Pt-NPs with heating rates of 1.2 °C min^{-1}, 1 °C min^{-1}, and 0.85 °C min^{-1}, respectively. All Pt-NPs were independently deposited on the surface of FTO glass without any aggregation. The size and distribution of Pt-NPs, however, became more uniform with decreasing heating rate from 1.2 °C min^{-1} to 0.85 °C min^{-1}. This is because long treatment time could facilitate the migration of the Pt ionic species through surface diffusion as well as the conversion of Pt ionic species into Pt-NPs. Thus, the distribution of Pt-NPs prepared with the heating rate of 1.2 °C min^{-1} was more localized at the grain boundary between SnO$_2$ crystals. The Pt-NPs localized at the boundary, while independently deposited on the surface of FTO glass, can act as bridges for facilitating electron conductivity, as well as catalysts for enhancing charge transfer between Pt surface and electrolytes, because the CE prepared at the heating rate of 1.2 °C min^{-1} reveals the smallest sheet resistance as shown in Table 1. Furthermore, excessive treatment time could also increase the amount of Pt "missing" during the TD process due to the formation of volatile Pt$_6$Cl$_{12}$ units.

3.2. Electrochemical catalytic activity of Pt-NPs CEs

Cyclic voltammetry was conducted using a conventional three-electrode system in acetonitrile solution [4,5]. Pt-NPs CEs prepared by TD method with different heating rate during sintering were used as working electrodes, with Pt mesh as a counter electrode, and Hg/Hg^{2+} in acetonitrile served as a reference electrode. The data were recorded from 900 mV to −900 mV with a scan rate of 50 mV s^{-1}.

As shown in Fig. 2(a), there exist two anodic current peaks (I_{pa1}: $3I^- = I_3^- + 2e^-$, I_{pa2}: $2I_3^- = 3I^- + 2e^-$) and two cathodic current peaks (I_{pc1}: $3I^- + 2e^- = 2I_3^-$, I_{pc2}: $I_3^- + 2e^- = 3I^-$). The different morphologies of Pt-NPs CEs prepared by TD method with different heating rates during the sintering process show an obvious influence on the electrochemical catalytic activity of I_3^- reduction on the surface of Pt-NPs CEs. Although the oxidation and reduction peaks of I^-/I_3^- on the Pt-NPs CEs look similar, increased peak current density was observed when Pt-NPs CE was prepared with a suitable heating rate in the sintering process. The higher peak current density indicates higher catalytic activity of the Pt-NPs CEs [4,5,7]. Fig. 2(b) shows the cathodic current peaks (I_{pc2}) of Pt-NPs CEs prepared by TD with different heating rates in sintering, and a maximum value was obtained at the heating rate of 1.2 °C min^{-1}. The reason for this may be related to the different morphologies of Pt-NPs CEs [18,19], which can be determined by the size and distribution of Pt-NPs on FTO glass as mentioned.