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# *In situ* growth of mirror-like platinum as highlyefficient counter electrode with light harvesting function for dye-sensitized solar cells<sup>†</sup>

Nan Nan Zhang,‡<sup>a</sup> Bo Zhang,‡<sup>ab</sup> Yu Hang Li,<sup>b</sup> Yu Hou,<sup>b</sup> Shuang Yang,<sup>b</sup> Ju Hua Zhong<sup>\*a</sup> and Hua Gui Yang<sup>\*b</sup>

In this work, we prepared a continuous nanostructured Pt-mirror film with metallic lustre and good adhesion to the F-doped tin oxide conducting glass (FTO) substrate through a simple *in situ* growth method, which retains a good catalytic activity and more importantly, exhibits significant light reflection for light-harvesting. The dye-sensitized solar cells (DSCs) fabricated with Pt-M CE exhibited superior photovoltaic performance compared with the conventional Pt CE. The enhancements of the short-circuit current density and energy conversion efficiency are 15.3% and 18.5%, respectively. Such significant enhancement of the short-circuit current density was found to be related to the excellent light reflection and high catalytic activity of the Pt-M CE. This has been proved by ultraviolet and visible reflection spectra (UV/Vis), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV).

# 1. Introduction

Dye-sensitized solar cells (DSCs) have been recognized as a promising candidate for the next-generation photovoltaic devices due to their low manufacturing cost and high power conversion efficiency in contrast with conventional silicon solar cells. They have been attracting much attention since Grätzel and co-workers developed them in 1991.<sup>1</sup> A typical DSC consists of a dye-sensitized nanocrystalline TiO<sub>2</sub> photoanode, an electrolyte containing the iodide/triiodide ( $I^-/I_3^-$ ) redox couple, and a counter electrode (CE). In a DSC system, the CE plays a crucial role as it collects the electrons flowing from the external circuit

‡ These authors contributed equally to this work.

and catalyzes the reduction of  $I_3^-$  to  $I^-$ , realizing the regeneration of the sensitizer.<sup>2–4</sup> Platinum (Pt) has been a cornerstone material for CEs because of its superior electrocatalytic activity, high electrical conductivity and good stability.<sup>5</sup>

Considering that simple, low-cost fabrication processes are of pivotal interest for the commercialization of DSCs, much effort has been made to either replace Pt with cost-effective alternative materials or develop easy methods to obtain Pt CEs with high catalytic activity.6-8 The potential alternative should be endowed with high catalytic activity for  $I_3^-$  reduction, good electrical conductivity, low sheet resistance and ready availability. In previous studies, plenty of less expensive materials were used as a replacement of Pt, with similar catalytic activity, such as conducting polymers,<sup>9,10</sup> carbon-based materials (including graphite, multi-walled carbon nonotubes, singlewalled carbon nanotubes, carbon black, carbon fiber, mesoporous carbon, and fullerene),11-17 Pt-dispersed hybrid materials,<sup>18</sup> metal nitrides,<sup>19,20</sup> metal sulfides,<sup>21,22</sup> metal oxides,<sup>23,24</sup> etc. However, the fact remains that there are few alternatives good enough to replace Pt CE in DSC systems. Pt is still the primary material as CE of DSCs in terms of the photovoltaic performance.25-27

One way to further enhance the energy conversion efficiency of the cell is the application of a reflector on the CE, aiming at reflecting unabsorbed photons back into the absorbing film, to ensure that more photons that enter the cell are efficiently transformed into useful charges. By lengthening the optical path length in the cell, via altering the reflectivity of the CE, the collected current density can be increased.28-30 Diau et al.25 reported mirror-like Pt CE through cyclic electro-deposition, and applied the CE as the reflector and also retained the high catalytic activity of Pt. Herein, we propose a facile strategy to prepare Pt-mirror film with metallic lustre in situ on FTO substrate at low temperature and use it directly as CE to assemble DSCs without any further treatments. High energy conversion efficiency ( $\eta$ ) of 7.49% is achieved for the DSC with prepared Pt-M CE, much higher than that of the cell with conventional Pt CE (6.32%).

<sup>&</sup>lt;sup>a</sup>Department of Physics, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, China. E-mail: jhzhong@ecust.edu.cn; Fax: +86 21-6425-1493; Tel: +86 21-6425-1493

<sup>&</sup>lt;sup>b</sup>Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, China. E-mail: hgyang@ecust.edu.cn; Fax: +86 21-6425-2127; Tel: +86 21-6425-2127

<sup>†</sup> Electronic supplementary information (ESI) available: ICP-AES of the Pt and Pt-M CE; photovoltaic performance of the DSCs with different amounts of conventional Pt.

## 2. Experimental

### 2.1. Materials

Hexachloroplatinic acid ( $H_2$ PtCl<sub>6</sub>, AR), methylamine solution (30%), and *N*,*N*-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Poly(vinylpyrrolidone) (PVP) (K30, AR) was obtained from Sigma-Aldrich. All chemicals were used as received.

### 2.2. Preparation of Pt-mirror and Pt counter electrodes

In a typical experiment, Pt-M CE was prepared *via* a novel twostep method. Firstly, a thin layer of gold (Au) film was coated on a FTO substrate by using a Hitachi E-1010 ion sputter at a pressure of 10 Pa and current density of 15 mA for 20 s. The Au seeds prepared above enable the Pt nanoparticles' growth to start from the FTO substrate. Secondly, 1.0 mL H<sub>2</sub>PtCl<sub>6</sub> (20 mg mL<sup>-1</sup>), 0.4 g poly(vinylpyrrolidone) and 0.2 mL methylamine solution were mixed together with 20 mL *N*,*N*-dimethylformamide. The resulting homogeneous yellow solution was transferred to a Teflon-lined stainless-steel autoclave with a capacity of 50 mL and the processed substrate containing Au seeds was immersed into the reaction mixture.<sup>31</sup> The sealed vessel was heated to 160 °C and held at this temperature for 11 h.

The conventional Pt CE was prepared by drop-casting  $0.5 \text{ mM H}_2\text{PtCl}_6/\text{ethanol solution on the clean FTO substrate. It was then annealed in a muffle furnace at 450 °C for 30 min.$ 

#### 2.3. Fabrication of dye-sensitized solar cells

The DSCs were fabricated through the conventional process following our previous report.32 The paste composed of TiO2 nanoparticles was coated on a TiCl4-treated FTO substrate by screen printing. Then the pre-prepared films were annealed according to the programmed procedure: heating at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and finally at 500 °C for 15 min. Another TiCl<sub>4</sub> treatment was carried out followed by sintering at 500 °C for 30 min. The prepared TiO<sub>2</sub> films were transferred to a 5 imes 10<sup>-4</sup> M solution of N719 dye in acetonitrile/tert-butyl alcohol (V/V = 1/1) for 24 h. The dyecovered TiO<sub>2</sub> electrode and counter electrode were sealed with a hot-melt gasket of 25 µm. The electrolyte, composed of 0.60 M 1butyl-3-methylimidazolium iodide, 0.03 M I2, 0.50 M 4-tert-butyl pyridine and 0.10 M guanidinium thiocyanate in acetonitrile, was filled into the internal space of the cell via vacuum backfilling.

### 2.4. Characterization

The optical reflection spectra of the samples were recorded on an ultraviolet and visible spectrophotometer (UV/Vis) (CARY 500). The microscopic surface morphology of the Pt and Ptmirror films were investigated by field emission scanning electron microscopy (SEM, HITACHI S4800). The photocurrentvoltage tests of the devices were performed under one sun condition using a solar light simulator (Oriel, 91160, AM 1.5 globe), and the characteristics were measured with a digital source meter (Keithley 2601, USA). The power of the simulated light was calibrated to 100 mM cm<sup>-2</sup> using a Newport Oriel PV reference cell system (model 91150 V). The incident photon to current conversion efficiencies (IPCE) of the corresponding DSCs were recorded with a system consisting of a model SR830 DSP Lock-In Amplifer and model SR540 Optical Chopper (Stanford Research Corporation, U.S.A), a 7IL/PX 150 xenon lamp and power supply, and a 7ISW301 spectrometer. The Pt loading amounts of the two CEs were tested by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Varian 710 ES). The electrochemical impedance spectroscopy (EIS) experiment was measured with full cells in the dark by using an electrochemical workstation (Parstat 2273, Princeton), with the frequency range from 1 MHz to 100 mHz with an AC modulation signal of 10 mV and bias DC voltage of 0.60 V. The curves were fitted by the ZSimpWin software. Cyclic voltammetry (CV) was conducted in a three-electrode system in an acetonitrile solution of 0.1 M LiClO<sub>4</sub>, 10 mM LiI and 1 mM I<sub>2</sub> at a scanning rate of 50 mVs<sup>-1</sup> using an electrochemical workstation (CHI 650, Chenhua). The working electrodes were Pt-mirror and Pt loaded FTO substrates, the CE was a Pt foil, and the Ag/Ag<sup>+</sup> couple was employed as reference electrode.

### 3. Results and discussion

### 3.1. Optical measurement

The Pt mirror was deposited on the FTO substrate by a twostep process at a relatively low temperature. Typically, the FTO containing a thin layer of Au seeds prepared by sputtering deposition was immersed into the reaction mixture. After being heated at 160 °C for 11 h, high-quality Pt film exhibiting a metallic lustre was obtained. The light-reflecting properties of the Pt-M and Pt CE were evaluated from UV/Vis reflection spectra. As shown in Fig. 1, the Pt film we prepared with a mirror-like surface shows reflectivity of approximately 30-55% in the range 300-800 nm, and the reflectivity increases as the wavelength increases. On the other hand, the conventional Pt CE only has a reflectivity of less than 10%. The inset digital photograph shows a clear image reflected by the Pt-M CE.



Fig. 1 The UV/Vis reflection spectra of the Pt and Pt-M electrodes.

#### 3.2. Morphology characterization

Fig. 2 shows the SEM images of the Pt and Pt-mirror films deposited on the FTO substrate. It is clear from Fig. 2(a) that the Pt film prepared through the conventional method had a porous structure and the Pt nanoparticles formed a continuous network covered on the FTO substrate. By contrast, the Pt-mirror film had a dense structure as shown in Fig. 2(b). This dense structure is mainly due to the *in situ* growth of Pt nanoparticles.<sup>8,33,34</sup> The Pt nanoparticles aggregated on the rough FTO substrate and formed an uneven film with a morphology similar to that of bare FTO (Fig. 2(e)). Fig. 2(c) and (d) display the boundary morphologies of the Pt and Pt-mirror deposited FTO substrate, respectively.

### 3.3. Schematic diagram

According to the literature,<sup>35</sup> the most commonly used N719 dye does not absorb red or longer wavelengths well which gives the dye its distinct reddish color. While the Pt-M can reflect the long wavelength well as shown in Fig. 1, and indicates that a significant fraction of residual light can be redirected by the Ptmirror film, which could lead to an increased utilization of solar light in DSCs if it is used as the CE in DSCs. Fig. 3 gives a plausible schematic diagram of DSC structures with Pt and Pt-M CEs showing the reflecting of incident light.

### 3.4. Photovoltaic performance

To investigate the reflecting effect on the photovoltaic performance, the Pt-M CE was subsequently assembled into DSCs, and compared to the DSCs using conventional Pt CE. Fig. 4 shows the photocurrent–voltage (*J–V*) curves of two DSCs fabricated with Pt and Pt-M CE. The corresponding photovoltaic parameters are summarized in Table 1. Under 1 sun illumination (100 mW cm<sup>-2</sup>, AM 1.5 G), the DSC using Pt-M as a CE exhibited an extraordinarily high energy conversion efficiency ( $\eta$ ) of 7.49%, while the one with conventional Pt CE showed only 6.32%. Compared with Pt CE, DSCs using Pt-M as CE have higher short-circuit current density ( $J_{sc} = 18.50 \text{ mA cm}^{-2}$ ), opencircuit voltage ( $V_{oc} = 700 \text{ mV}$ ), and fill factor (FF = 0.58), and the



Fig. 3 Schematic diagram of the DSCs with a conventional transparent Pt CE (left) and a Pt-M CE (right) reflecting the incident light.

parameters of the cell using Pt CE are  $J_{sc} = 16.04$  mA cm<sup>-2</sup>,  $V_{\rm oc} = 687$  mV, and FF = 0.56. In general, sunlight is harvested by the dye molecules in a DSC system, but the incident photons might not have been captured completely. The Pt-M CE with excellent light reflection can reflect the residual incident photons to return to the dye-covered TiO<sub>2</sub> electrode, making a dye sensitizer film that can harvest more incoming light. The  $J_{sc}$ of the DSC using Pt-M CE improves 15.3%. The high  $J_{sc}$ ,  $V_{oc}$ , and FF yield an overall energy conversion efficiency. We measured the IPCE spectra of the DSCs with Pt CE and Pt-M CE, as shown in Fig. 5. The IPCE results were consistent with the photovoltaic performance of the DSCs. In the wavelength region of 350-700 nm, the DSC with Pt-M CE produced greater IPCE values than that with Pt CE, indicating that the Pt-mirror film conferred improved light-utilization efficiency. In order to eliminate the influence of the mass amount of Pt and illustrate the light reflection of the Pt-M CE, the Pt loading amount of the two CEs and the photovoltaic performance of the DSCs with different mass amounts of conventional Pt were explored (see Fig. S1 and Table S1 in ESI<sup>†</sup>). There was no obvious enhancement of the  $\eta$  values when a greater amount of the conventional Pt was used. The  $\eta$  value of the cell with 2F Pt was 6.48%. In the meantime, the  $\eta$  value of the DSC with Pt-M is 7.49%, but the mass amount of Pt of the Pt-M is smaller than that of the 2F Pt. Moreover, the  $J_{\rm sc}$  (18.50 mA cm<sup>-2</sup>) of the DSC with Pt-M is much higher than that of the 2F Pt (16.11 mA  $\text{cm}^{-2}$ ). According to the analysis above, it also concluded that the Pt-M prepared by our method facilitates to improve the performance of the DSCs.



**Fig. 2** SEM images of Pt film (a), Pt-mirror film (b) and bare FTO substrate (e) with a high magnification, (c and d) the boundaries of Pt/ FTO, and Pt-mirror/FTO with a low magnification.



Fig. 4 J-V characteristics of the DSCs with Pt CE and Pt-M CE under 100 mW cm<sup>-2</sup>, AM 1.5 G illumination.

Table 1Photovoltaic performance parameters of the DSCs based ondifferent CEs and the simulated EIS parameters of the full cells fabri-<br/>cated with the CEs<sup>a</sup>

| CE   | $J_{\rm sc}$ (mA cm <sup>-2</sup> ) | $V_{\rm oc}$ (mV) | FF   | $\eta$ (%) | $R_{\rm s}\left(\Omega\right)$ | $R_{\mathrm{ct1}}\left(\Omega\right)$ | $E_{\rm pp} \left( {\rm mV} \right)$ |
|------|-------------------------------------|-------------------|------|------------|--------------------------------|---------------------------------------|--------------------------------------|
| Pt   | 16.04                               | 687               | 0.56 | 6.32       | 12.46                          | 3.81                                  | 456                                  |
| Pt-M | 18.50                               | 700               | 0.58 | 7.49       | 10.01                          | 3.48                                  | 427                                  |

 $^a$   $J_{\rm sc}$ : Short-circuit photocurrent density;  $V_{\rm oc}$ : open-circuit voltage; FF: fill factor;  $\eta$ : energy-conversion efficiency;  $R_{\rm s}$ : series resistance;  $R_{\rm ct1}$ : charge-transfer resistance of the counter-electrode/electrolyte interface;  $E_{\rm pp}$ : peak to peak separation.



Fig. 5 IPCE spectra of the DSCs with Pt CE and Pt-M CE.

### 3.5. Electrochemical measurements

As Diau *et al.* reported,<sup>25</sup> the catalytic activity of Pt is strongly affected by the morphology of the nanostructure, so we further investigated the electrochemical catalytic performance of the Ptmirror electrode in the following parts. Firstly, EIS were carried out with full cells (anode//electrolyte//CE) in the dark at a bias direct current (DC) voltage of 0.60 V and 10 mV of amplitude over the frequency range of 0.1 Hz to 1 MHz. Fig. 6 shows the Nyquist plots of the full cells. An equivalent circuit model used to fit the experimental EIS data is inset in Fig. 6. The EIS parameters were determined by fitting the impedance spectra using the ZSimpWin software, and are summarized in Table 1.

The charge-transfer resistance ( $R_{ct1}$ ) indicates the electron transfer resistance of the counter-electrode/electrolyte interface and thus varies inversely with the  $I_3^-$  reduction activity.<sup>21</sup> It can be calculated from the diameter of the semicircle in the high frequency region in the Nyquist plot. The high-frequency intercept on the real axis represents the series resistance ( $R_s$ ), which is mainly composed of the bulk resistance of CE materials, FTO substrate, and contact resistance, *etc.* From Table 1, it can be seen that Pt-M CE owns  $R_{ct1}$  of 3.48  $\Omega$ , smaller than that of conventional Pt CE (3.81  $\Omega$ ), which means the Pt-M has a higher catalytic activity which is of benefit to the increase of the conversion efficiency of DSCs. In the mean time, the  $R_s$  of Pt-M CE (10.01  $\Omega$ ) is slightly smaller that of Pt CE (12.46  $\Omega$ ), which may be attributed to the fact that the Pt nanoparticles of Ptmirror film had good adhesion to the FTO substrate.



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Fig. 6 EIS data of the full cells. The inset gives the equivalent circuit of the cells.

To measure the catalytic activities of the CEs independently, CV tests were performed. Fig. 7 shows the CVs of Pt-M, and Pt electrodes. Two typical pairs of oxidation and reduction peaks are clearly observed for both electrodes.<sup>36</sup> In addition, the profile of the pairs of redox peaks of the two kinds of CEs are very similar since they are all for FTO substrates loaded with Pt. The left and right pairs correspond to the reactions described by eqn (1) and eqn (2), respectively. We only focus on the left cathodic peak since the CE of the cell is responsible for catalyzing  $I_3^-$  reduction.

$$I_3^- + 2e^- \leftrightarrow 3I^- \tag{1}$$

$$3I_2 + 2e^- \leftrightarrow 2I_3^- \tag{2}$$

The peak to peak separation  $(E_{pp})$ , which is negatively correlated with the standard electrochemical rate constant of a redox reaction, is an important parameter for analyzing the catalytic activity of the CE. The Pt-mirror has a smaller  $E_{pp}$ (427 mV) than that of Pt (456 mV), suggesting that the intrinsic electrocatalytic activity of  $I_3^-$  on the Pt-M CE is better than



Fig. 7 CV curves of  $I^-/I_3^-$  redox couple for Pt CE and Pt-M CE.

conventional Pt CE, which is in accordance with the results of  $R_{ct1}$  from EIS analysis.<sup>36</sup> According to the literature,<sup>37</sup> the photovoltage lies in the difference between the potential of dyesensitized TiO<sub>2</sub> film and the redox equilibrium potential of electrolyte. On the condition of the same dye-sensitized TiO<sub>2</sub> film electrode, the difference of  $V_{\rm oc}$  arises from the  $I^-/I_3^-$  redox equilibrium potential on Pt-M and Pt CEs. From Fig. 7, it is clear that there is a positive shift of redox equilibrium potential on Ptmirror film compared with Pt film which results in a higher  $V_{oc}$ . It is well known that a larger enclosed redox reaction area of CV curve means a higher electrochemically active surface area of an electrode.38 As shown in Fig. 7, Pt-M CE has a smaller redox reaction area than Pt CE, and especially a lower cathodic peak current density for I<sub>3</sub><sup>-</sup> reduction, which indicates that Pt-M CE has a smaller active area meaning less reaction active sites for  $I_3^-$  reduction due to its dense structure of the film compared with Pt CE.<sup>39</sup> Even though the active surface area of Pt-M CE is slightly inferior to that of conventional Pt CE, the high intrinsic catalytic activity for  $I_3^-$  reduction makes up for it, and also the Pt-M CE acts as a reflector to enhance the light-harvesting of the sensitizing dye when assembled in the DSCs. The bifunctional Pt-M CE compensates for its smaller active surface area, and meanwhile brings a higher energy conversion efficiency than conventional Pt CE.

### 4. Conclusions

In summary, a mirror-like Pt film could be facilely deposited on the FTO substrate at low temperature by *in situ* growth method. The film deposited by this method had a dense structure and good adhesion to the FTO due to the Pt nanoparticles grown from the substrate. Pt-M CE shows impressive improvement of catalytic activity for  $I_3^-$  reduction, with a high energy conversion efficiency of 7.49% in a DSC system, achieving an 18.5% enhancement compared to the conventional Pt CE (6.32%). The enhanced  $J_{sc}$  is rationalized by the high light reflection of the film which facilitates improved light-harvesting of the dye. The Pt-M CE possesses low  $R_s$ ,  $R_{ct1}$ ,  $E_{pp}$ , and high light reflection; the synergistic effect of these properties leads to the enhancement in all photovoltaic performance metrics including current density, voltage, fill factor and energy conversion efficiency.

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