

The simple and easy way to manufacture counter electrode for dye-sensitized solar cells

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ABSTRACT

We previously developed poly-N-vinyl-2-pyrrolidone (PVP)-capped Pt nanoclusters on ITO glass via a simple “2-step dip coating process” as counter electrode for DSSC. This new counter electrode was examined by transmission electron microscopy (TEM), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and current-voltage curve (*I*–*V* curve).

The TEM results revealed that PVP-capped Pt nanoclusters' size is about 3 nm, and the amount of Pt deposited on ITO glass is about 5 μg/cm². Comparing with sputtered Pt and Solaronix thermal cluster Pt-catalyst T/SP, the PVP-capped Pt counter electrode has lower amount of Pt deposited on TCO glass, more positive potential of tri-iodide reduction, and better performance for the charge-transfer resistance (*R*_{CT}) and the cell efficiency (*η*).

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention for its low cost of raw material and manufacture equipment, and the high conversion efficiencies (~10%) [1–3]. Basically, the dye-sensitized solar cells' system consists of nanocrystalline semiconductor film on transparent conductive oxide (TCO) glass as the photoanode; cathode are usually made of platinum that is vacuum deposited on conducting glasses to reduce the overpotential for reduction of tri-iodide to iodide in redox electrolyte, and an iodide/tri-iodide redox couple in a proper mediator as the electrolyte. The working principle of DSSCs is explained below: under illumination, the photoexcitation of dye lead to charge separation, and the separated charge injects into the conduction band of porous TiO₂, and then passes through the external circuit. Simultaneously, the oxidized dye is reduced by the iodide ion and returns to its ground state. The tri-iodide formed by the oxidation of iodide ion is reduced back to iodide ion on the counter electrode. The reaction occurs on the counter electrode is: $I_3^- + 2e^- \rightarrow 3I^-$. Therefore, the catalytic activity of counter electrode of DSSCs is one of the main requests for the overall smooth reaction within the cell.

To lower the overpotential for reduction of I_3^- to I^- in redox electrolyte, platinum (Pt) is the most common catalyst material coated

on TCO (ITO, ATO, FTO) glass [4,5]. Various methods have been used for the formation of Pt thin layer, in which sputtering is the most common method. However, sputtering requires ultra-high vacuum environment and uses more amount of platinum to produce one flat surface while the amount of Pt necessary to obtain the desired catalytic effect is very small [6]. The thermal decomposition of platinum was developed by Papageorgiou et al. [4]. It was made by spin-coated 5 mM H₂PtCl₆ IPA solution on the TCO substrate, and reducing the Pt precursor in the air furnace at 380 °C for 30 min. Although the thermal cluster Pt has many advantages, such as, low Pt loading, the superior catalytic activity, and good mechanical stability, it requires heating up to 380 °C, which is energy consumptive and not suitable for production.

In addition, carbon [7] and conducting polymer [8] were also proposed to be the catalyst for tri-iodide reaction in DSSCs, but these new materials are still in early stage of development. Because of its low catalytic activity compared with platinum, it requires a thick porous film to obtain an acceptable catalytic effect, and the mechanical stability is still in concerned.

Recently, PVP-capped Pt nanoclusters deposited on TCO glass as the counter electrode for DSSCs was developed by Wei et al. [9,10]. It showed the good catalytic performance and ultralow Pt loading by using this cheap wet process to manufacture the DSSC counter electrode. In this article, we extended this “two step dip coating” process to manufacture the Pt counter electrode, and compared its performance with the sputtered Pt and the Solaronix thermal cluster Pt-catalyst T/SP.

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2. Experiments

2.1. Materials and reagents

Indium tin oxide (ITO glass $7 \Omega/\square$, uni-onward corp.), Stibium-doped tin oxide (ATO glass $13 \Omega/\square$, Geomatec Co., Ltd.) TiO_2 paste (PST-18NR & PST-400C, Catalysts & Chemical Ind. Co., Ltd.), surlyn[®] (50 μm , DuPont), 3-MPN (Acros), LiI (Acros), DMPII (Solaronix SA), Iodide (I_2 , J.T. Baker), TBAI (Merck), TBP (Aldrich), LiClO_4 (Acros), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Alfa aesar), NaBH_4 (Acros), PVP (M.W.8000, Acros), Conditioner (Rockwood Electrochemicals Asia, Ltd.), N719 (Everlight group), Pt-catalyst T/SP (Solaronix SA).

2.2. Sample preparation

2.2.1. PVP-capped Pt nanoclusters suspension

First, PVP with a molecular weight of 8000 was dissolved in deionized water under stirring. Second, H_2PtCl_6 precursor was dissolved into this solution. After that, the reductant NaBH_4 solution was gradually added. The color of the solution quickly changed from brown to black, indicating the formation of PVP-capped Pt nanoparticles. The reaction was completed within 30 min at room temperature.

2.2.2. Preparation of the PVP-capped Pt nanoclusters counter electrode

The “two step dip coating” process is described below: The ITO glass ($1.5 \times 1.5 \text{ cm}^2$) was immersed into conditioner for 5 min followed by activation with PVP-capped Pt nanoclusters for 5 min. Before each step, the ITO glass was rinsed with deionized water, and finally dried in open air, then heated in furnace at 270°C for 10 min. The preparation flowchart is shown in Fig. 1.

2.2.3. Preparation of the Solaronix thermal cluster Pt-catalyst T/SP counter electrode

The Pt-catalyst T/SP (Solaronix SA) was screen-printed on ATO glass for 10 times to increase the thickness of Pt film. Between each print, the Pt film was dried for 3 min at room temperature, and heated for 3 min at 130°C . Finally, the ATO glass was heated for 30 min at 400°C .

2.2.4. Preparation of the porous TiO_2 photoanode

The TiO_2 paste from CCIC was screen-printed on ATO glass for several times until the thickness of TiO_2 film is about $7 \mu\text{m}$. After that, the TiO_2 film was sintered at 500°C for 30 min. Dye impregnation was done by immersing the TiO_2 photoanode in a 0.4 mM N719 ethanol solution at 40°C for 12 h.

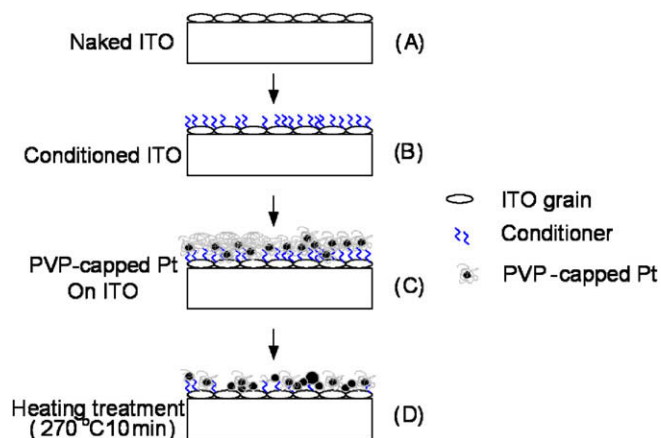


Fig. 1. The flowchart of the “two step” wet process to manufacture the counter electrode.

2.3. Characterization

The particle size of PVP-capped Pt nanoclusters was measured by Transmission Electron Microscope (TEM, Philips Tecnai 20). The size distribution was calculated with 500 different particles. In order to determine the catalytic activity toward tri-iodide reduction, the electrochemical Impedance spectroscopy (EIS) was measured by applying alternating current voltage ranging between 50 kHz and 0.1 Hz with 5 mV amplitude in a symmetric cell (Auto Lab PGSTAT320N). The electrolyte for ac-impedance test contains 0.2 M DMPII, 0.2 M LiI, 0.2 M TBAI, 0.05 M I_2 , 0.5 M TBP in 3-MPN solution. The sealant is 50 μm thermoplastic hot-melt sealing surlyn. The cyclic voltammetry was taken place in there-electrode system (Auto Lab PGSTAT320N). The working electrode is 0.5 cm^2 PVP-capped Pt, sputtered Pt, or Solaronix thermal cluster Pt-catalyst T/SP on TCO glass, the reference electrode is Platinum wire ($\Phi = 0.3 \text{ mm}$), and the counter electrode is a Platinum plate (1 cm^2). The electrolyte for CV test consists of 50 mM LiI, 10 mM I_2 , 500 mM LiClO_4 in 3-MPN solution. The scan rate is 5 mV/s. Photocurrent–voltage (I – V) curves was measured with a Keithley 2400 source meter under illumination by a YAMASHITA DENSO YSS-150A solar simulator ($\text{AM}1.5$, $100 \text{ mW}/\text{cm}^2$). The electrolyte for I – V test is the same as ac-impedance test.

3. Results and discussion

3.1. The TEM result

Fig. 2 shows that the particle size of PVP-capped Pt nanoclusters is about 3 nm. Because of its nanosize, the surface to volume ratio is much higher than the bulk material. Therefore, comparing with the same amount of platinum usage, the PVP-capped Pt nanoclusters has more surface area, on the other words, more active sites to catalyze the tri-iodide reduction reaction. This speculation can be confirmed by the Pt loading and CV result.

3.2. The Pt loading on TCO glass

Table 1 shows that the amount of PVP-capped Pt deposited on TCO glass is similar to Solaronix Pt-catalyst T/SP and much lower than sputtered Pt.

3.3. The Cyclic voltammetry results

The cyclic voltammetry result was illustrated in Fig. 3, and Table 2 summarized the cathodic peak current (I_{pc}) and cathodic peak potential (E_{pc}) data related to tri-iodide reduction. The reaction occurs on the counter electrode in DSSCs is: $\text{I}_3^- + 2e^- \rightarrow 3\text{I}^-$. Therefore, we only considered the cathodic reaction here. Based on the same working area (0.5 cm^2), the value of cathodic peak current (I_{pc}) of PVP-capped Pt nanoclusters electrode is much larger than sputtered Pt and Solaronix thermal cluster Pt-catalyst T/SP electrode. It means that more tri-iodide ion can be reduced to iodide ion on the PVP-capped Pt nanoclusters electrode surface than others. In addition, Table 1 shows that the amount of PVP-capped Pt deposited on TCO glass is almost the same as Solaronix Pt-catalyst T/SP, and much lower than sputtered Pt. This result indirectly demonstrated that the PVP-capped Pt nanoclusters electrode provided larger surface area to catalyze the tri-iodide reduction because of its nanosize, and acquired the large cathodic current.

In addition, the cathodic peak potential (E_{pc}) of PVP-capped Pt nanoclusters and sputtered Pt electrode is almost the same but more positive than the Solaronix thermal cluster Pt-catalyst T/SP's. It indicates that the overpotential for reduction of I_3^- to I^- of

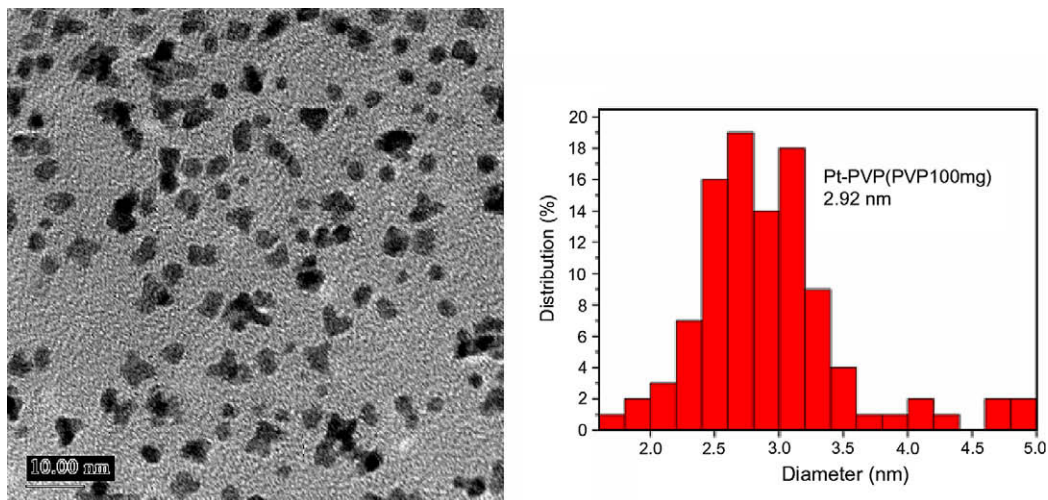


Fig. 2. Typical TEM images and size distributions of PVP-capped Pt nanoclusters (scale bar: 10 nm).

Table 1
The amount of Pt loading on TCO glass.

	Pt ($\mu\text{g}/\text{cm}^2$)
PVP-capped Pt	4.65
Solaronix Pt-catalyst T/SP	4.935
Sputtered Pt	600

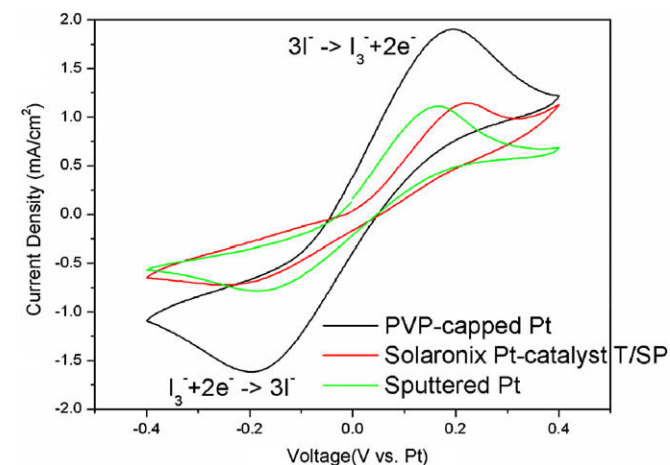


Fig. 3. The cyclic voltammety of various Pt electrode. Scan rate: 5 mV/s.

Table 2
The I_{pc} and E_{pc} data related to I_3^- reduction with various Pt electrode from cyclic voltammety.

	I_{pc} (mA/cm^2)	E_{pc} (vs. Pt) (V)
PVP-capped Pt	-1.618	-0.193
Solaronix Pt-catalyst T/SP	-0.724	-0.244
Sputtered Pt	-0.786	-0.183

PVP-capped Pt nanoclusters and sputtered Pt electrode is much smaller than the Solaronix thermal cluster Pt-catalyst T/SP's.

3.4. The electrochemical impedance spectroscopy (EIS) analysis

The electrochemical impedance spectroscopy (EIS) was measured with a symmetry cell. The result is shown in Fig. 4, which

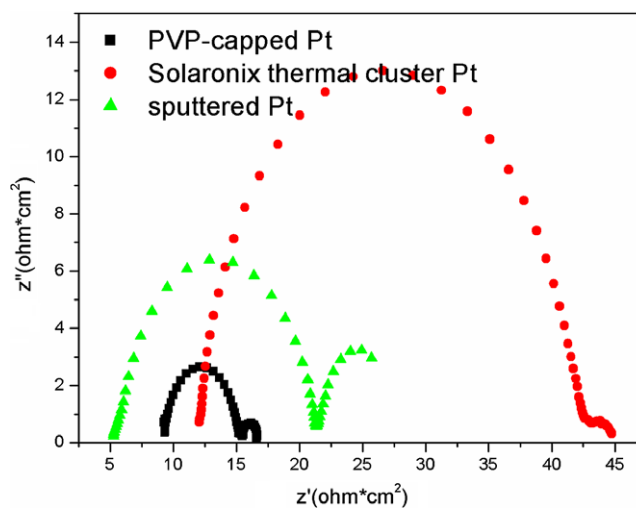


Fig. 4. The Nyquist plots of various Pt electrodes.

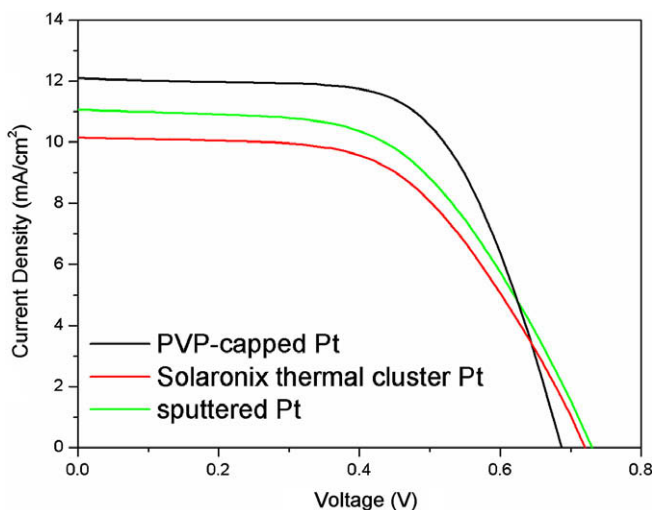


Fig. 5. The I–V curves of DSSCs with various Pt counter electrodes.

Table 3The I - V curve data of DSSCs with various Pt counter electrode.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η (%)
PVP-capped Pt	0.69	12.11	0.64	5.28
Solaronix Pt-catalyst T/SP	0.72	10.15	0.54	4.09
Sputtered Pt	0.73	11.06	0.55	4.45

is Nyquist plot including series resistance (R_s) at the high-frequency region, a charge-transfer resistance (R_{CT}) at the medium-frequency region, and a Nernst diffusion resistance (R_D) at the low-frequency region.

By using varied of TCO substrate, the series resistance (R_s) of these electrodes is different from each other. The mirror-like sputtered Pt electrode has the smallest R_s ($5.3 \Omega \times \text{cm}^2$) for its metallic conductivity. The R_s of the PVP-capped Pt nanoclusters deposited on ITO glass ($7 \Omega/\square$) is $9.3 \Omega \times \text{cm}^2$, and the R_s of Solaronix thermal cluster Pt-catalyst T/SP printed on ATO glass ($13 \Omega/\square$) is $12.1 \Omega \times \text{cm}^2$.

The R_{CT} represents the resistance relating to the electron transfer of the tri-iodide reduction. Therefore, it can stand for the catalytic activity of the counter electrode in DSSCs. According to Fig. 4, R_{CT} of PVP-capped Pt nanoclusters electrode, sputtered platinum electrode, and Solaronix thermal cluster Pt-catalyst T/SP electrode is 3.1, 8, and $15.2 \Omega \times \text{cm}^2$ respectively. It means that the PVP-capped Pt nanoclusters electrode's catalytic activity is much superior to others.

3.5. The photocurrent–voltage (I - V) curves

Fig. 5 is the I - V characteristics of the DSSCs, and the results are summarized in Table 3. The performance of the PVP-capped Pt nanoclusters counter electrode shows the short circuit current (J_{sc}) is 12.11 mA/cm^2 , open circuit voltage (V_{oc}) is 0.69 V, fill factor (FF) is 0.64 and cell efficiency is 5.28%. Compared to the I - V curves with sputtered Pt and Solaronix thermal cluster Pt-catalyst T/SP as

the counter electrode, the performance of PVP-capped Pt nanoclusters counter electrode has better performance.

4. Conclusions

Our “2-step dip coating process” is a simple and fast procedure to manufacture the counter electrode for DSSCs. The R_{CT} of PVP-capped Pt nanoclusters counter electrode is about $3 \Omega \times \text{cm}^2$, and the I - V characteristics shows great performance. In addition, the PVP-capped Pt nanoclusters counter electrode is transparent and low Pt usage which is suitable for DSSCs.

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