

## Platinum Nanoparticles on Flexible Carbon Fiber Paper without Transparent Conducting Oxide Glass as Counter Electrode for Dye-sensitized Solar Cells

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Flexible carbon fiber paper deposited with platinum nanoparticles was applied as counter electrode for dye-sensitized solar cells (DSSCs). Compared to others, such as sputtered-Pt or PVP-capped Pt nanoparticles on TCO glass, not only does this counter electrode has good conductivity without using TCO glass but also flexible and shows good adhesion. Acceptable charge-transfer resistance of 5.25  $\Omega\text{-cm}^2$  is obtained. Current-voltage characteristics of the DSSC are 0.71 V on  $V_{OC}$ , 9.44 mA/cm<sup>2</sup> on  $J_{SC}$ , 0.61 on FF and 4.13% cell efficiency under AM 1.5, 100 mW/cm<sup>2</sup> illumination. Additionally, spinning technology can be applied to produce this low cost counter electrode.

**Keywords:** DSSC; Counter electrode; Flexible carbon fiber; Platinum.

### INTRODUCTION

Much attention has been paid to the development of dye-sensitized solar cells (DSSCs) because it is a low-cost photovoltaic device that has a short time for energy pay-back.<sup>1-5</sup> Generally, a DSSC consists of a noncrystalline titanium dioxide (TiO<sub>2</sub>) modified with dye as anode electrode, a platinum counter electrode, and an electrolyte with the dissolved iodide ion/tri-iodide ion ( $I^-/I_3^-$ ) redox couple between the electrodes. To lower the overpotential for reduction of  $I_3^-$  to  $I^-$  in redox electrolyte, platinum is the most common catalyst material coated on TCO (ITO, ATO, FTO) glass,<sup>6-9</sup> which occupy almost 25~35% for overall price of DSSCs. Various methods have been used for the formation of Pt thin layer, in which the sputtering is the most common method. However, sputtering requires ultra-high vacuum environment and use more amount of platinum to form one flat surface while the amount of Pt necessary to obtain the desired catalytic activity is very small.<sup>10</sup> In addition, carbon<sup>11</sup> and conducting polymer<sup>12</sup> were also proposed to be the catalyst for tri-iodide reduction in DSSCs. However, these new materials are still in early stage of development because it requires a thick porous

film coated on the substrate to obtain an acceptable catalytic effect.

Recently, PVP-capped Pt nanoparticles deposited on TCO glass as the counter electrode for DSSCs was developed by Wei et al.<sup>13,14</sup> It showed a positive result for  $R_{CT}$  and DSSCs properties by using this cheaper wet process. However, the adhesion between Pt nanoparticles and ITO glass surface is not good enough, and the durability test for the cells might be another issue. The reason is supposed to be that smooth glass surface can not provide good adsorbability for PVP-capped Pt nanoparticles. If raising temperature of thermal treatment to enhance adhesion, sheet resistance of ITO glass will increase. According to heat-resistant, ATO or FTO may be suitable but more expensive.

As mentioned above, we develop a new method combining carbon fiber paper with PVP-capped Pt nanoparticles without using TCO glass substrate as the counter electrode for DSSCs. The carbon fiber paper is originally used as the thermal insulation material, and not only has good electric conductivity ( $2 \Omega/\square$ ) but also high corrosion stability against iodine in the electrolyte. The surface of car-

bon fiber paper is rough enough to provide physical bonding with Pt nanoparticles. Therefore, the adhesion problem will be improved.

## EXPERIMENTAL

### Materials and Reagents

Carbon fiber paper (KUREHA, E-704  $2 \Omega/\square$ ), Fluorine-doped tin oxide (FTO glass NSG  $13 \Omega/\square$  3.2 mm, Pilkington  $15 \Omega/\square$  2.2 mm), Indium Tin Oxide (ITO glass Ritek  $6 \Omega/\square$  0.7 mm)  $\text{TiO}_2$  paste (Catalysts & chemical Ind. Co. Ltd.), surlyn® (50  $\mu\text{m}$ , DuPont), 3-Methoxypropionitrile (3-MPN, Acros), Lithium iodide (LiI, Acros), 1,2-dimethyl-3-propylimidazolium iodide (DMPII, Solaronix SA), Iodide ( $\text{I}_2$ , J. T. Baker), Tetra-n-butyl-ammonium iodide (TBAI, Merck), 4-tert-butylpyridine (tBP, Aldrich), Lithium perchlorate ( $\text{LiClO}_4$ , Acros), hexachloroplatinate (IV) hexadrate Dihydrogen ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , Alfa aesar), Sodium borohydride ( $\text{NaBH}_4$ , Acros), polyvinylpyrrolidone (PVP M.W. 8000, Acros), Conditioner (ML-371, OMGroup), *cis*-di(thiocyanato)-*N,N'*-bis(2,2'-bipyridyl)-4-carboxylic acid-4'-tetrabutylammonium carboxylate ruthenium (II) (N-719, Everlight group), lithium battery separator (Tonen chemical Co.).

### Sample Preparation

#### PVP-capped Pt nanoparticles suspension

First, PVP with a molecular weight of 8000 was dissolved in deionized water under stirring. Second,  $\text{H}_2\text{PtCl}_6$  precursors was dissolved into this solution. After that, the reductant  $\text{NaBH}_4$  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 minutes at room temperature.

#### Preparation of the PVP-capped Pt nanoparticles counter electrode

The “two-step dip coating” process is described below: The FTO glass ( $1.5 \times 1.5 \text{ cm}^2$ ) or carbon fiber paper was immersed into 1% conditioner for 5 minutes at  $60^\circ\text{C}$  followed by activation with PVP-capped Pt nanoclusters for 5 minutes at  $40^\circ\text{C}$ . Before each step, the FTO glass was rinsed with deionized water, and finally dried in open air, then heated in furnace at  $270^\circ\text{C}$  for 10 minutes. The preparation flowchart is shown in Fig. 1.

#### Preparation of the porous $\text{TiO}_2$ photoanode

The  $\text{TiO}_2$  paste from CCIC was screen-printed on FTO glass for several times until the thickness of  $\text{TiO}_2$  film is about 11  $\mu\text{m}$ . After that, the  $\text{TiO}_2$  film was sintered at  $500^\circ\text{C}$  for 30 minutes. Dye impregnation was done by immersing the  $\text{TiO}_2$  photoanode in a 0.4 mM N719 ethanol solution at  $40^\circ\text{C}$  for 12 hours.

$^\circ\text{C}$  for 30 minutes. Dye impregnation was done by immersing the  $\text{TiO}_2$  photoanode in a 0.4 mM N719 ethanol solution at  $40^\circ\text{C}$  for 12 hours.

### Cell assembling

The photoanode after dyeing was assembled with three different cathodes, involving sputtered Pt, Pt/ITO glass, and Pt/C paper counter electrode. Unfortunately, we did not have proper sealing method to seal the Pt/C paper at this moment. Therefore, we put a piece of separator, which was widely used in lithium battery, to make sure the cell was not in short current condition. All cells were measured in this way.

### Characterization

The images of Pt nanoparticles on carbon fiber paper were measured by Field Emission gun scanning Electron Microscope (FEG-SEM, JEOL, JSM-6330F). Platinum loading on carbon fiber paper is measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis. 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 100 kHz to 0.1 Hz with 5 mV amplitude in a symmetric cell (Autolab PGSTAT320N). The electrolyte for ac-impedance test contains 0.2 M DMPII, 0.2 M LiI, 0.2 M TBAI, 0.05 M  $\text{I}_2$ , 0.5 M TBP in 3-MPN solution. The sealant is 50  $\mu\text{m}$  thermoplastic hot-melt sealing surlyn. Photocurrent-voltage (I-V) character-

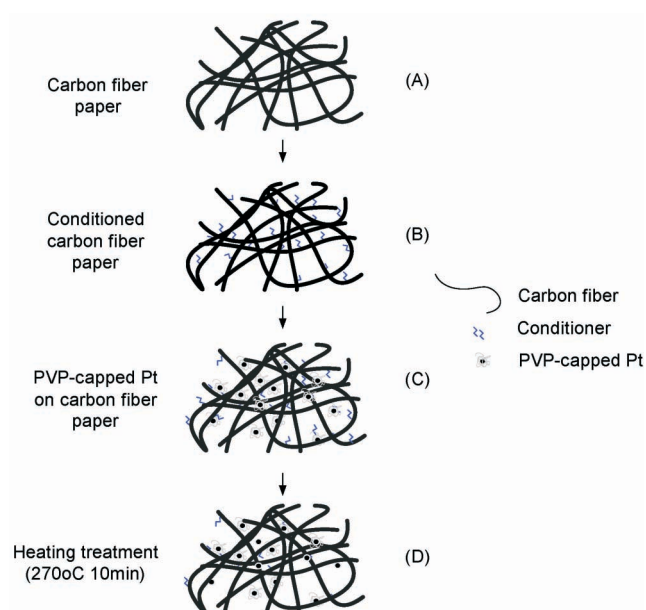


Fig. 1. The flowchart of the “Two step” wet process to manufacture the counter electrode.

istic was measured with a Keithley 2400 source meter under illumination by a YAMASHITA DENSO YSS-150A solar simulator (AM1.5, 100 mW/cm<sup>2</sup>). The electrolyte for I-V test is the same as ac-impedance test.

## RESULTS AND DISCUSSION

### The SEM Image

Fig. 2(b) is the SEM picture showing that Pt nanoparticles deposited on the carbon fiber's surface, which was not observed from the pure carbon fiber paper (Fig. 2(a)). It is clear indicated that the Pt nanoparticles were deposited on the carbon fiber's surface by the two step dip coating.

### The Pt loading on different substrate

Table 1 shows that the amount of PVP-capped Pt deposited on carbon fiber paper is more than on TCO glass. It is because that the surface area of carbon fiber paper is larger than TCO glass, the amount of Pt deposited on it is more than TCO glass. In addition, both PVP-capped Pt on TCO glass and carbon fiber are much lower than sputtered Pt.

### The electrochemical Impedance spectroscopy (EIS) Analysis

Electrochemical Impedance spectroscopy (EIS) was measured with the symmetric cell. This symmetric cell con-

Table 1. The amount of Pt loading on different substrate

	Pt ( $\mu\text{g}/\text{cm}^2$ )
PVP-capped Pt on TCO	4.65
PVP-capped Pt on carbon fiber	6.51
Sputtered Pt on TCO	600

sisting of two identical Pt/C papers of which two bare glasses (not TCO glass) are in the back to confine liquid electrolyte. The ac-impedance result is shown in Fig. 3, which is Nyquist plot including series resistance ( $R_s$ ), charge-transfer resistance ( $R_{CT}$ ) and Nernst diffusion resistance ( $R_D$ ).  $R_{CT}$  of pure carbon paper is around  $2 \text{ k}\Omega \times \text{cm}^2$ , it reveals that the catalytic activity of pure carbon fiber paper is not good enough for the tri-iodide reduction. After depositing the Pt nanoparticles,  $R_{CT}$  of carbon fiber paper is decreased from 2k to  $5.25 \Omega \times \text{cm}^2$ , meaning that the Pt nanoparticles effectively improve entire catalytic activity. Moreover, the value of  $R_{CT}$  for sputtered Pt, Pt/C paper and Pt/ITO glass are 7.75, 5.25 and  $5.5 \Omega \times \text{cm}^2$ , respectively. It could be explained that the catalytic activity of Pt nanoparticles no matter on carbon fiber paper or ITO glass is better than sputtered Pt because of nano-scale particles provides larger surface area than bulk material. Furthermore, sheet resistance of carbon fiber paper is  $2 \Omega/\square$ , and ITO glass is  $7 \Omega/\square$ . Therefore,  $R_s$  of Pt/C paper is closed to sputtered Pt and is lower than Pt/ITO glass. Thus, Pt/C paper not only has good  $R_{CT}$  performance but also has low  $R_s$ .

### The Photocurrent-voltage (I-V) characteristics

In addition to Electrochemical Impedance Spectros-

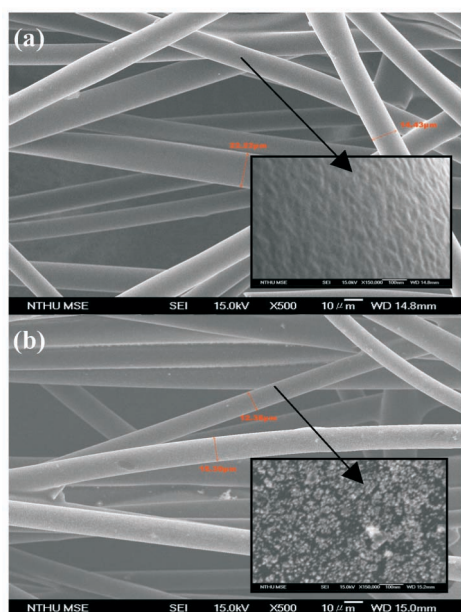


Fig. 2. SEM pictures of (a) carbon fiber paper. (b) carbon fiber paper with Pt nanoparticles.

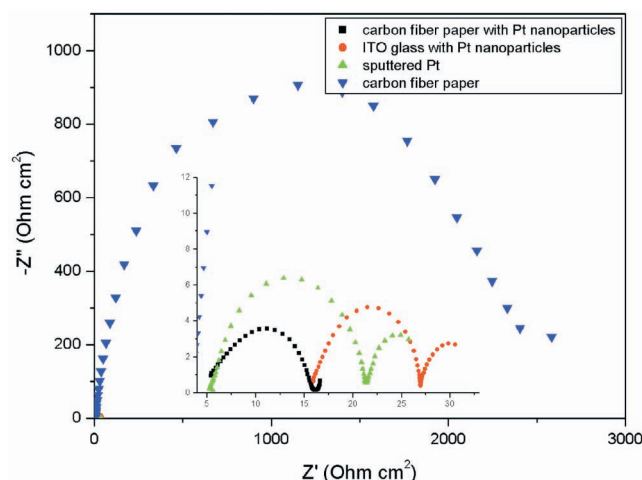


Fig. 3. Electrochemical impedance spectrum of a symmetric test cell, cell area =  $0.5 \text{ cm}^2$ .

Table 2. The I-V curve data of DSSCs with various Pt counter electrode

	$V_{OC}$ (V)	$J_{SC}$ (mA/cm <sup>2</sup> )	FF	$\eta$ (%)
PVP-capped Pt on carbon fiber paper	0.71	9.44	0.61	4.13
PVP-capped Pt on TCO	0.63	10.77	0.59	4.01
Sputtered Pt on TCO	0.65	9.96	0.61	3.94
Carbon fiber paper	0.63	7.29	0.27	1.24

copy, Photocurrent-voltage (I-V) characteristic is important to DSSC behavior. Fig. 4 is the I-V characteristics of DSSC under 1 sun illumination, and the results are summarized in Table 2. The prepared cell of Pt/C paper shows a short circuit current ( $J_{sc}$ ) of 9.44 mA/cm<sup>2</sup>,  $V_{oc}$  of 0.71 V, fill factor (FF) of 0.61 and cell efficiency of 4.13%. Compared to the DSSC employing a sputtered Pt electrode or Pt/ITO glass, the  $J_{sc}$  is lower. It infers that carbon fiber with many fine branches cause more electron recombination for  $J_{sc}$  elimination or the electrolyte leakage while measuring I-V curve. Nevertheless, the DSSC with Pt/C paper cathode has similar performance with sputtered Pt and Pt/ITO glass.

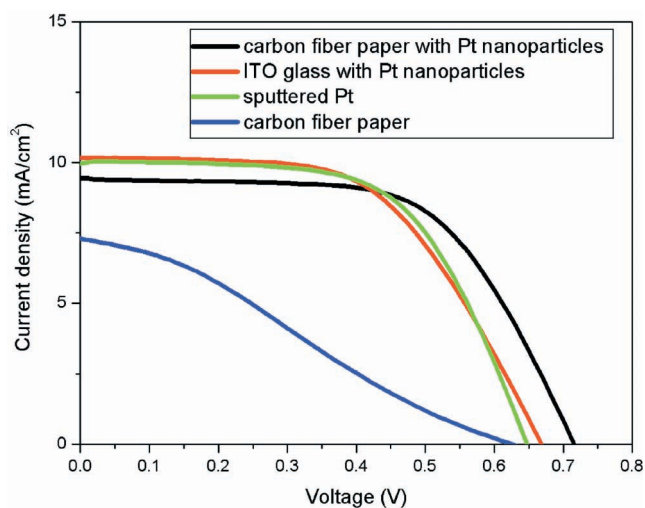


Fig. 4. Current-voltage characteristics of DSSCs employed 3 types of counter electrodes.

## CONCLUSIONS

In conclusion, carbon fiber paper with Pt nanoparticles is introduced in DSSC as counter electrode without TCO substrate. Not only acceptable catalytic activity does it have, but also has low sheet resistance, cheap cost and flexibility. In addition, the production steps can carry out by continuous spinning technology under ambient conditions in the future. Hence mass production will be much easier and less expensive.

## ACKNOWLEDGEMENT

The authors would like to thank the Tripod tech. corp. and the National Science Council (97-2221-E-007-079-MY3).

Received November 26, 2009.

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