

PREPARATION AND PROPERTIES OF FLEXIBLE DYE-SENSITIZED SOLAR CELLS

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Introduction

Recently, flexible DSCs have been developed to replace the rigid DSCs composed of conductive glass substrates. The advantages of low cost, light-weight and less shape limitations for the flexible devices have attracted considerable interests due to the potential of practical applications and the acceleration of the commercialization of DSCs. The flexible substrates, such as conductive polymeric films or metal sheets were used for the working electrodes and counter electrodes. It has been reported that Ti substrates have been used as a flexible metal substrate to fabricate DSCs[1,2]. A high conversion efficiency of 7.2% was achieved for flexible cells produced via screen-printing technology [2], indicating that the Ti substrate is a promising metal substrate for fabrication of flexible DSCs with high efficiency. In this work Flexible DSC comprised of a nanocrystalline TiO₂ film electrode based on Ti-metal substrate and a counter-electrode based on plastic substrate was investigated.

Experimental

Preparation of counter electrode by chemical reduction.

H₂PtCl₆ was dissolved in terpineol with concentration of 0.4 wt%, 0.6 wt%, 0.8 wt% and 1.0 wt% to prepare the paste. The pastes were screen printed on the ITO-PEN surface using a 200 mesh screen and then dried at 80 °C for 2 h. Then the H₂PtCl₆/ITO-PEN electrodes were immersed in 10mM NaBH₄ aqueous solution at 40 °C to reduce Pt ions. After 2 h, the electrodes were taken out from the NaBH₄ solution and rinsed with distilled water. Then the common pressure hydrothermal process was applied. The electrodes were placed in a non-sealed container filled with water at 100 °C for 4 h to remove organic residues then to dry them at 80 °C for 2 h giving transparent Pt CEs (Pt/ITO-PEN).

Preparation of counter electrode by electrochemical reduction. Two-step constant current electrodeposition of Pt was carried out by using ITO-PEN substrate as a cathode, a clean FTO conductive glass as an anode, a 5 mM H₂PtCl₆ aqueous solution containing 0.1 M LiClO₄ as an electrolyte on a Solartron SI 1287 electrochemical interface system. The first step was performed at the large cathodic current I₁ with short duration of t₁ and the second step was followed at the small cathodic current I₂ with long duration of t₂, the total charge amount of two steps is fixed at 38 mC.

Preparation of working electrode by electrophoretic deposition. For electrophoretic deposition of the nanocrystalline TiO₂ films on Ti substrates, a suspension was prepared with 0.5 g of P25 TiO₂ powder in 8mL butanol, 4mL isopropanol and 2mL ethanol. The suspension was ultrasonicated for 30min before electrophoretic deposition. In the electrophoretic deposition procedure, a 48Vcm⁻¹ DC field was applied. The deposition was carried out for 30 s at room temperature. The double-layer nanocrystalline TiO₂ films, composed of a light-scattering layer and a transparent layer, were prepared by electrophoretic deposition of a light-scattering TiO₂ layer on the Ti substrate using a suspension containing 0.5 g of 25nm TiO₂ particles (P25) and 0.04 g of 100 nm TiO₂ particles in 8mL butanol, 4mL isopropanol and 2mL ethanol.

Preparation of TNAs and TNAP. Pieces of Ti foil were used for the anodic growth of titanium dioxide nanotube arrays (TNAs). The cleaned pieces of Ti foils were anodized in a solution of 0.5 wt% NH₄F, 1 wt% deionized water, and 98.5 wt% ethylene glycol. Anodization was performed under constant voltage. The voltage was held at 60 V for 40 h. TiO₂ nanoparticles (TNPs) of 12 nm diameter was used in our experiments. One gram of the prepared colloidal TiO₂ was added to 49 g ethanol, and the suspension was stirred for 30 min before use. Electrophoretic deposition was performed at 20 V for 30 s, with platinum foil as the counter electrode. The prepared nanoparticles coated nanotube arrays (TNAP) were washed with deionized water. All TNAs and TNAP were sintered in a furnace at 500 °C for 2 h in air and cooled to room temperature.

Results and Discussion

Less attention has been paid to study the platinized counter electrodes based on flexible substrates, in particular concerning both the electrocatalytic performance and the optical transmittance which are more important for developing the highly efficient flexible cells under a back illumination.

Table 1. The Relationship Between The Concentration Of H₂PtCl₆ And Behavior Of Pt/ITO-PEN CEs

Concentration of H ₂ PtCl ₆ (mM)	Pt-loading (μg/cm ²)	transmittance	Rct (Ωcm ²)
0.4	2.4	84.0%	1.38
0.6	3.5	80.8%	0.53
0.8	5.8	78.9%	0.30
1.0	7.7	75.9%	0.26

Table 1 shows the Pt loading, transmission, and charge transfer resistance of Pt/ITO-PEN CEs prepared with different concentrations of H₂PtCl₆ solutions. As a result, the CEs prepared by the paste with higher concentration of H₂PtCl₆ usually have lower Rct and lower light transmittance. Low Rct is beneficial to high performance of CEs, however, low light transmittance of the CEs will decrease the performance of DSCs in the back illumination model. Therefore, it is necessary to balance between Rct and light transmittance. Further experiments showed that the optimal concentration of H₂PtCl₆ for high performance Pt CEs was about 0.6mM.

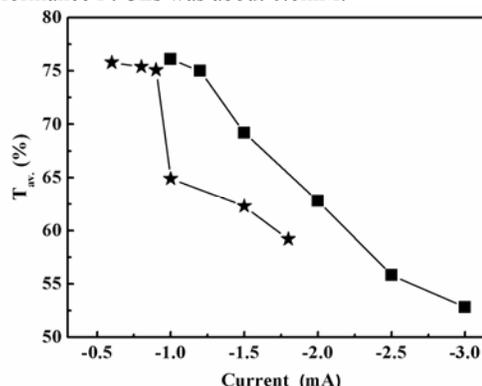


Figure 1. The influence of deposition currents of the I₁ (■) and the I₂ (★) on the average optical transmittance T_{av}

The influence of deposition current to the optical transmittance and electrochemical catalytic behavior of electrodeposited Pt/ITO-PEN CEs was studied. The average optical transmittance T_{av} as function of the deposition currents of the first step I₁ and the second step I₂ were further examined and shown in Fig.1. To obtain the plot of T_{av} vs I₁, I₂ was kept at -0.9 mA, and the plot of T_{av} vs I₂, I₁ was kept at -1.2 mA. In both cases, t₁ was 5 S, and

the total charge amount was 38 mC. The decreases of T_{av} with the increases of the cathodic currents of I_1 and I_2 can be seen. The decreases of T_{av} shown in both plots were slower at $I_1 \leq -1.2$ mA and $I_2 \leq -0.9$ mA and became faster at $I_1 > -1.2$ mA and $I_2 > -0.9$ mA. This observation demonstrates that the increases of the cathodic currents of I_1 and I_2 resulted in the higher packing number density and surface coverage of the Pt particles leading to reduction of the optical transmittance of platinized electrodes significantly.

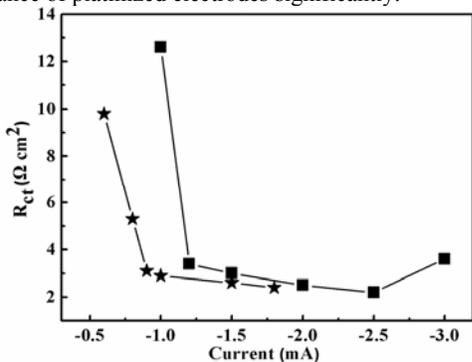


Figure 2. The influence of deposition currents of the I_1 (■) and the I_2 (★) on the charge transfer resistance R_{ct}

The influence of the deposition currents of the first step I_1 and the second step I_2 on the R_{ct} were studied and shown in Fig.2, where the plots of R_{ct} vs I_1 and I_2 were obtained under the same conditions as that mentioned in Fig.1. The R_{ct} which has a higher value at smaller cathodic currents of I_1 and I_2 decreased steeply to a lower value at $I_1 \geq -1.2$ mA and $I_2 \geq -0.9$ mA in both plots. The decreases of R_{ct} imply the improvement of electrocatalytic activity due to the increases of packing number density and surface coverage of Pt clusters at larger cathodic current depositions.

Fig.2 manifests that the electrocatalytic activity of the platinized electrodes can be improved under the larger cathodic current depositions due to the decrease of R_{ct} . However, the average optical transmittance shown in Fig.1 may decrease in the larger cathodic current depositions. Based on the comprehensive analysis, the deposition conditions of the first and second step were optimized reasonably at $I_1 = -1.2$ mA, $t_1 = 5$ S and $I_2 = -0.9$ mA, $t_2 = 35$ S

Recently, an enhancement in light absorption via application of light scattering has been studied for dye-sensitized nanocrystalline TiO₂ films, theoretically and experimentally. In order to obtain high photoelectric conversion efficiency in flexible DSCs prepared on Ti substrates, a double-layer nanocrystalline TiO₂ film was designed composed of a light-scattering layer and a transparent layer (referred to as double-layer film). Due to the illumination of the nanocrystalline TiO₂ film on the Ti substrate through the Pt counter electrode, the double-layer film was prepared by deposition of a light-scattering layer on the Ti substrate and a transparent layer on top of the light-scattering layer. The thickness of the double-layer film was about 11 μm. The enhanced diffuse reflectance between 400 nm and 750 nm is observed in the spectrum of the double-layer film, indicating efficient light scattering. The diffuse reflectance of the double-transparent-layer film is weak compared to that of the double-layer film. An improvement in the IPCE is observed in the visible wavelength range of 400 - 700 nm for devices incorporating the double-layer film. This is due to enhanced solar adsorption resulting from light scattering. These results suggest that double-layer film can be used as an efficient photoelectrode in flexible DSCs to enhance light absorption by light scattering and improve the IPCE.

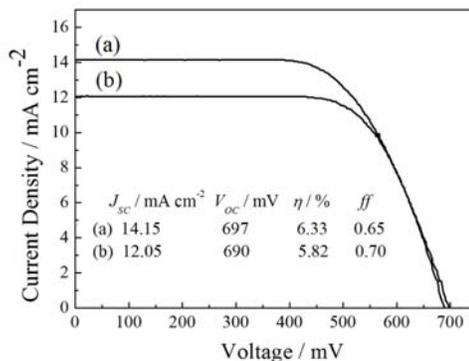


Figure 3. Photocurrent-voltage characteristics for DSCs using double-layer nanocrystalline TiO₂ films comprised of a scattering layer and a transparent layer (a) and comprised of two transparent layers (b)

Photocurrent-voltage characteristics of the DSCs that incorporate the double-layer film are shown in Fig. 3. It is observed that the incorporation of the double-layer film improves the short-circuit photocurrent (J_{sc}) of the cell, resulting in a high conversion efficiency of 6.33%.

The highly ordered architecture of TNAs allows fast electron transport due to the suppression of random walk phenomena, and their structure influences the absorption and propagation of light. The reported efficiencies of pure TNA-based DSCs are between 0.61% and 3.4%, generally lower than those of DSCs based on TiO₂ nanoparticles (TNPs) when illuminated from the counter electrode. One of the shortcomings is that the surface area of TNAs is smaller than that of TNP.

The morphology of the TNAs and TNAP was characterized by field emission SEM. The hexagonal packing had an inner diameter of 90 nm and a wall thickness of 10 nm. The surface smooth nanotube had a length of 26 μm. After deposition of TNP, the surface of the nanotube was covered with TNP. The measured dye loading for TNAP were 1.56×10^{-7} mol cm⁻² larger than that of TNAs' 1.06×10^{-7} .

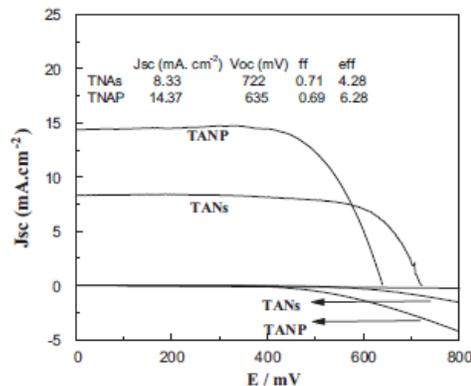


Figure 4. Current - voltage characteristics of the DSCs based on TNAs (A) and TNAP(B)

DSC performance of TNAs and TNPs was measured with illumination from the counter electrode. The photovoltaic performance parameters of the DSCs based on TNAs and TNAP are shown in Fig. 4. TNAP improved the short-circuit photocurrent (J_{sc}) of the cell. The TNA-based DSC exhibited a J_{sc} of 8.33 mA cm^{-2} ,

and the TNAP-based DSC had a J_{sc} of 14.37 mA cm^{-2} . The higher J_{sc} of TNAP can be attributed to the larger dye loading. Thus, more electrons were generated when DSCs were illuminated.

Conclusions

The Pt CE was prepared on ITO-PEN using screen printing technology followed by NaBH_4 reduction combining with hydrothermal method and electrochemical deposition method. The influence of the concentration of H_2PtCl_6 in the paste and deposition conditions of the two step processes on the optical transmittance and interfacial charge transfer resistance was examined. The platinized electrodes with high electrochemical activity and good optical transmittance were obtained.

A double-layer film composed of a light-scattering layer and a transparent layer was designed to enhance light absorption by increased light scattering. And TNP were electrophoretically deposited inside nanotubes to increase the surface area for dye loading. The dye loading increased 47.2% after depositing TNP. Both methods can improve IPCE and conversion efficiency of flexible DSCs with Ti based photoanode.

The maximal light to electricity conversion efficiency of 6.3% was achieved in all flexible DSCs composed of flexible photoanode and flexible counter electrode.

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References

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