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Novel counter electrodes based on NiP-plated glass and Ti plate substrate for dye-sensitized solar cells

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Abstract Novel counter electrodes based on NiP-plated glass and Ti plate substrate were prepared by thermal decomposition of H_2PtCl_6. Their properties and application in dye-sensitized solar cells were investigated. Platinized Ti plate electrode (Pt/TP electrode) and platinized NiP-plated glass electrode (Pt/NiP electrode) exhibited the same electrochemical activity for triiodide reduction as platinized fluorine-dope tin oxide (FTO) conducting glass electrode (Pt/FTO electrode). However, Pt/NiP electrode and Pt/TP electrode have the advantage over the Pt/FTO electrode in increasing the light reflectance and reducing the sheet resistance, which resulted to improve the light harvest efficiency and the fill factor of the dye-sensitized solar cells effectively. Examination of the anodic dissolution indicated the good stability of the Pt/NiP electrode and Pt/TP electrode in the electrolyte containing iodide/triiodide.

Introduction

Owing to their low production cost and high-energy conversion efficiency, dye-sensitized solar cells (DSCs) have attracted much attention and have been considered as an alternative to a conventional photovoltaic device [1–3]. Many studies have focused on the synthesis of sensitized dye [2, 4–7], the development of nanostructured semiconductor photoelectrode and the preparation of electrolyte [8–16]. However, only a few investigations have been performed on the counter electrode of DSCs [17–19].

Under illumination, a net direct current would pass from the photoelectrode to the counter electrode within DSCs and from the counter electrode to the photoelectrode in the external circuit of this device. The counter electrode of DSCs serves to transfer electrons coming from external circuit to the electrolyte containing iodide(I^-)/triiodide(I_3^-) redox couple. Hence, the counter electrode must exhibit high electrocatalytic activity for triiodide reduction and low sheet resistance in order to minimize the energy losses on the counter electrode.

Platinized fluorine-dope tin oxide (FTO) conducting glass electrode (Pt/FTO electrode) usually used as the counter electrode in DSCs shows a high electrocatalytic activity for triiodide reduction [20], but its high sheet resistance lowers the fill factor of DSCs and limits the width of DSCs to less than 1 cm [21]. The low sheet resistance of the counter electrodes is of great advantage to improve the fill factor and the conversion efficiency of DSCs, especially large-sized DSCs. In order to improve the performance of the counter electrode for DSCs applications, carbon materials based counter electrodes with high corrosion resistance and sufficient conductivity have been used as an attractive substitute [17, 18]. However, the conversion efficiencies of the DSCs based on these carbon electrodes were low.

Nickel Phosphorus (NiP) alloy layer has been widely used in various industries as protective coatings and

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function films due to the abilities of corrosion resistance, wear resistance and hardness [22]. To take the advantage of the high corrosion resistance of the NiP alloy layer and Titanium plate (TP), novel counter electrodes based on TP and NiP-plated glass substrate were prepared, its properties were investigated. The performance of DSCs with these counter electrodes was analysed. Pt/FTO electrodes were also prepared for comparison.

Experimental

Ethylene carbonate (EC) and propylene carbonate (PC) were supplied by Aldrich Corp. Titanium plate (The thickness of titanium plate is about 1 mm) and fluorine-doped tin oxide (FTO) conducting glass (sheet resistance: 20Ω per square) were purchased from Hei Longjiang Hake New Energy Corp. Potassium iodide and iodine were supplied by Beijing Chemistry Corp. FTO conducting glass and TP were degreased by sonicating in acetone, isopropanol and methanol, rinsed with deionized water and dried in a nitrogen stream.

NiP-plated glass substrate was prepared by electroless plating method [23]. The glass substrate was roughened in HF aqueous solution followed by coating with a small amount of Palladium. The electroless plating was performed by dipping the Pd coated glass into the aqueous solution containing $NiSO_4{\cdot}6H_2O$ (25 g L^{-1}), $NaPO_2{\cdot}H_2O$ (25 g L^{-1}), H_3BO_3 (15 g L^{-1}) and lactic acid (20 mL L^{-1}) at 80 °C for 20 min. The NiP-plated glass substrate was subsequent to heat-treatment at 300 °C for 60 min for enhancing the adhesion. The thickness of NiP-plated layer was about 10 μm.

The counter electrode were prepared by thermal decomposition of H_2PtCl_6 on conducting substrates (i.e., NiP-plated glass, TP and FTO glass), platinum loading was 6 μg cm^{-2}. The sheet resistance was obtained using four-point probe technique.

Electrochemical impedance spectroscopy measurements were performed in a symmetric thin-layer cell consisted of two identical counter electrodes holding at constant space by a 20 μm thick Surlyn film (supplied by Dupont). The thin-layer cell was filled with the electrolyte containing 0.5 M KI/0.05 M I_2 in the mixture of EC and PC (EC:PC = 8:2 by volume). The SOLARTRON SI 1287 electrochemical interface equipped with a SOLARTRON 1255B frequency response analyzer was used in the measurements. The UV–vis reflection spectrum was determined by U-3010 UV spectrophotometer.

Nanocrystalline TiO_2 electrode was prepared by previously described procedure [24]. Photocurrent–voltage performance of DSCs was determined under the illumination of tungsten-halogen lamp at the light intensity of 60 $mWcm^{-2}$. The active cell area was 0.20 cm^2.

Results and discussion

The performance of the counter electrode

The sheet resistance of the counter electrode

It is well known that the photovoltaic performance of DSCs are directly influenced by the sheet resistance of electrode (R_s), especially for large-sized DSCs. The sheet resistance of the counter electrode and its corresponding substrate were measured. The results were summarized in Table 1. It can be seen that no obvious difference in the R_s were observed between the three types counter electrode and their corresponding substrate. However, the R_s of the counter electrode based on TP and NiP-plated glass was low, only 0.8 Ω/square and 0.5 Ω/square, respectively. A low sheet resistance of the counter electrode is one of the key points in minimizing the energy losses on the counter electrode and improving the photovoltaic performance of DSCs, a discussion about this point would be provided in section 3.2.

The charge-transfer performance of the counter electrode

The charge-transfer performance of the counter electrode was studied by applying the electrochemical impedance spectroscopy. The charge-transfer resistance (R_{ct}) calculated from the electrochemical impedance

Table 1 R_s of counter electrodes and their corresponding substrate

The counter electrode	R_s of counter electrode (Ω/square)	R_s of corresponding substrate (Ω/square)
Pt/FTO electrode	19.5	20
Pt/TP electrode	0.8	0.7
Pt/NiP electrode	0.5	0.5

Pt/FTO electrode: Platinized FTO glass electrode; Pt/TP electrode: Platinized TP electrode; Pt/NiP electrode: Platinized NiP-plated glass electrode

Table 2 R_{ct} of the counter electrode

The counter electrode	R_{ct} (Ωcm^2)
Pt/FTO electrode	0.15
Pt/TP electrode	0.4
Pt/NiP electrode	0.15

spectra of the symmetric thin-layer cells consisted of two identical electrodes can characterize the electrocatalytic activity of the electrode for the triiodide reduction. The R_{ct} of counter electrodes were summarized in Table 2. From Table 2, it is observed that the electrocatalytic activity for triiodide reduction of the Pt/NiP electrode and Pt/TP electrode is comparable to that of Pt/FTO electrode.

The light-reflecting performance of the counter electrode

Figure 1 depicts the UV–vis reflection spectrum of Pt/NiP electrode, Pt/TP electrode and Pt/FTO electrode. As illustrated in Fig. 1, Pt/NiP electrode and Pt/TP electrode showed much higher light reflectivity than Pt/FTO electrode, especially in the region above 600 nm where the extinction coefficient of dye diminishes quickly as shown in the inset in Fig. 1. An increased light reflectivity of Pt/NiP electrode over the wavelength range of 400–800 nm is observed. In the region above 600 nm, the light reflectivity of Pt/NiP electrode is >60%, the light reflectivity of Pt/TP electrode is about 27%, while the light reflectivity is only 5% for the Pt/FTO electrode. The increased light reflectance at the red light region is of advantage to reduce the losses of the light at the longer wavelength. This result indicates that the Pt/NiP counter electrode exhibited the light-reflecting performance has the pronounced effect on increasing the light harvest efficiency leading to improving the photocurrent efficiency of DSCs. This can be observed explicitly in the section 3.2.

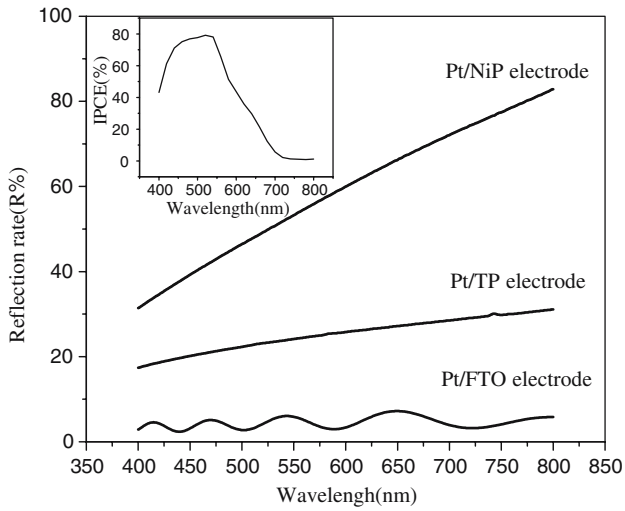

Fig. 1 The light-reflecting performance of Pt/NiP electrode, Pt/TP electrode and Pt/FTO elelctrode. The inset shows the action spectra, the action spectra (IPCE vs. <lambda>) was measured with 400 W Xenon lamp using Spectra-300i Triple Grating monochrometor

The stability of the counter electrodes

The stability of the counter electrodes was studied under anodic polarization in a thin-layer cell consisted of a counter electrode as the anode and a corresponding bare conducting substrate as the cathode. Anodic dissolution of Pt would lead to cathodic deposition at the bare conducting substrate during the cyclic voltammetric sweeps. Measuring the cathodic polarization behavior of bare conducting substrate, the anodic dissolution of Pt can be examined. The cathodic polarization behavior of bare conducting substrate were shown in Fig. 2. From Fig. 2, no observed change of the cathodic polarization curves was found in the cycles 1–10. This implied that there was no platinum dissolved from the counter electrode even under anodic polarization.

Photocurrent–voltage characteristics of DSCs with different counter electrodes

Figure 3 presents photocurrent-voltage characteristics of DSCs using different counter electrodes. They were obtained with a thin-layer sandwich-type cell under irradiance of 60 mW cm^{-2}. The short-circuit current (J_{sc}), the open-circuit voltage (V_{oc}), the overall energy conversion efficiency(η) and the fill factor (FF) were summarized in Table 3. DSCs with different counter electrodes exhibited the same value of V_{oc}. However, the DSCs with Pt/NiP electrode and Pt/TP electrode showed higher $J_{sc,}$ FF and η than the DSCs with Pt/FTO electrode. The increase in short-circuit current are attribute to the increasing the light harvesting efficiency due to the contribution of the light reflection of the Pt/NiP electrode and the Pt/TP electrode. The fill factor of DSCs is determined by the resistance of the TiO_2 porous electrode, the resistance of counter electrode and the resistance of the electrolyte. The resistance of the counter electrode consist of the charge-transfer resistance and the sheet resistance. The lower resistance of the counter electrode would improve the FF of DSCs.

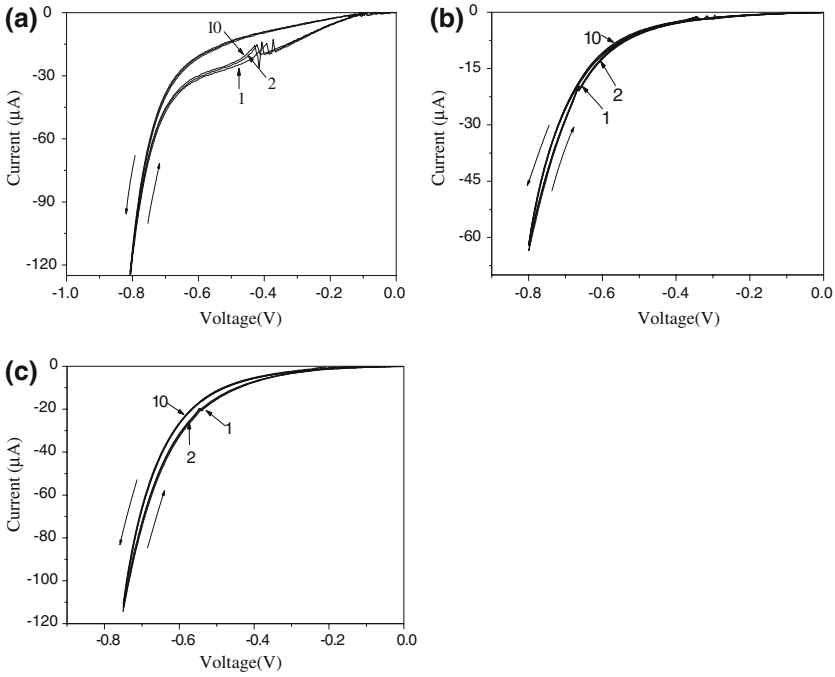

Fig. 2 Cathodic polarization behavior of a bare conducting substrate electrode measured in a thin-layer cell consisting of a counter electrode as the anode and a corresponding bare conducting substrate as the cathode, the electrolyte containing 0.5 M KI/0.05 M I_2 in the mixture of EC and PC (EC:PC = 8:2 by volume). Surface area 0.25 cm^2, scan rate 2 mVs^{-1}. Cyclic number indicated on the curves. (**a**) FTO glass; (**b**) TP; (**c**) NiP-plated glass

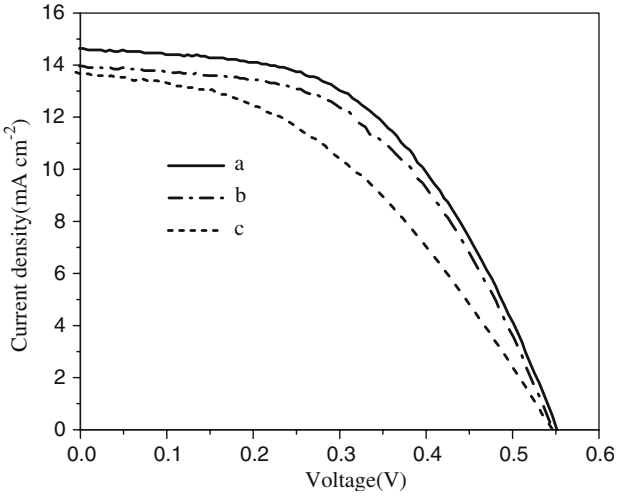

Fig. 3 Photocurrent–voltage characteristics of DSCs with different counter electrodes measured in the electrolyte as Fig. 2. Light intensity 60 $mWcm^{-2}$, active cell area 0.20 cm^2. (**a**) DSCs with Pt/NiP electrode; (**b**) DSCs with Pt/TP electrode; (**c**) DSCs with Pt/FTO electrode

Table 3 The short-circuit current, the open-circuit voltage, the overall energy conversion efficiency and the fill factor of DSCs with different counter electrode

Counter elelctrode	V_{oc} (V)	J_{sc} (mA cm^2)	FF (%)	η(%)
Pt/FTO	0.549	13.6	0.45	5.6
Pt/TP	0.549	13.9	0.61	7.7
Pt/NiP	0.551	14.8	0.6	8.3

Conclusions

Counter electrodes based on NiP-plated glass and Ti plate have been prepared, their application in DSCs have been studied. Both the Pt/NiP electrode and the Pt/TP electrode showed low sheet resistance and low charge-transfer resistance. Pt/NiP electrode exhibits an increased light reflectance especially in the red light region. As the results of the increased light reflectance and the reduced sheet resistance of the counter electrode, the photovoltaic performance of DSCs is improved effectively. The short-circuit current, the fill factor and the overall conversion efficiency of DSCs using Pt/NiP counter electrode is increased by 8%, 25% and 32% respectively, compared to that of using Pt/FTO counter electrode.

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