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Facile electropolymerized-PANI as counter electrode for low cost dye-sensitized solar cell

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ABSTRACT

The in situ electropolymerized-polyaniline (PANI) film (thickness: $5-20 \ \mu\text{m}$) on FTO (fluorine tin oxide) glass doped by various counterions SO_4^{2-} , CIO_4^- , BF_4^- , CI^- , *p*-toluenesulfonate (TsO⁻), etc. was prepared with electropolymerized charge capacity of 50–600 mC cm⁻². Different doping counterions have great impact on the morphology, electrochemical activity of electropolymerized-PANI film. The electropolymerized-PANI doped by SO_4^{2-} anion (PANI-SO₄) film with much porous morphology and pore size diameter of several micrometers possesses higher reduction current for reduction of I_3^- and a low charge-transfer resistance of $1.3 \ \Omega \ cm^2$ in comparison with Pt as counter electrode (CE). Dye-sensitized solar cell with PANI-SO₄ as CE was assembled, and the device under full sunlight illumination (100 mW cm⁻², AM 1.5 G) shows 5.6% photovoltaic conversion efficiency, which is comparable to 6.0% of that with Pt CE under the same experimental condition.

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1. Introduction

Dye-sensitized solar cells (DSSC) have currently attracted widespread academic and commercial interests for the conversion of sunlight into electricity because of their low cost and high efficiency since reported by O'Regan and Grätzel [1–3]. In order to further improve the performance of DSSC, extensive research has been conducted on each constituent of the solar cells such as semiconductor nano-crystalline [4], dye molecules [5], electrolytes [6], and counter electrodes [7].

Counter electrode (CE), one of the indispensable components in DSSC, is usually constructed of conducting glass substrates coated with platinum films due to its excellent electrocatalytic activity for I_3^-/I^- redox couple [8]. However, platinum as noble metal is so expensive, and the cost of platinum CE is over 40% of the whole photovoltaic cell regardless of its preparation method [7]. Therefore, great effort has been made to develop low cost and more efficient cathodic materials, e.g. various carbon materials were attempted to replace Pt [9–12], but the photovoltaic conversion efficiency of the DSSC based on these carbon materials as CE was relatively low due to their poor catalytic activity. Conducting polymers are promising candidates for CE materials used in DSSC because of their low cost, high-conductivity, and excellent catalytic activity for I_3^- reduction [7,13–15]. Very recently, Li et al. used

chemically prepared PANI as CE of DSSC, achieving better conversion efficiencies than that using Pt [16].

Nevertheless, chemically prepared PANI CE mentioned above required complicated fabrication processes, moreover, the instability of catalytic activity and adhesion to glass substrate were also inevitable. On the other hand, electropolymerization method has been successfully employed to prepare polythiophene derivative polymer film as CE of DSSC [17,18], and homogeneous and well adhesive polymer film could be obtained on ITO (indium tin oxide) glass. In this work, the in situ electropolymerized-PANI film on FTO glass doped by SO_4^{2-} , CIO_4^- , BF_4^- , CI^- , TsO^- , etc. with varied electropolymerized charge capacity was prepared, and the DSSCs based on the as-prepared PANI as CEs were assembled. The influences of electropolymerized charge capacity and doping counterion on the performance of the DSSC were primarily investigated.

2. Experimental

2.1. Preparation of electropolymerized-PANI CEs

Before electropolymerization, the FTO glass (14 ohm sq⁻¹, Nippon Sheet Glass CO., Ltd., Japan) was pretreated using an ultrasonic bath in double-distilled water, acetone and ethanol for 15 min, respectively. Then the electropolymerization of aniline on FTO was conducted by constant current electrolysis (\sim 10 mA cm⁻²) for 0–60 s (typically for 40 s) in an undivided



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electrolytic cell at room temperature in 0.25 M H₂SO₄, HBF₄, HClO₄, HCl, and *p*-toluenesulfonic acid solution containing 0.25 M double-distilled aniline, respectively. After electrolysis, the electropolymerized-PANI CEs were quickly immersed in water, and then rinsed adequately with 200 ml ethanol and 200 ml two-distilled water for three times to remove residual acid and aniline monomer. Finally, the as-prepared electropolymerized-PANI CE dried at 90 °C overnight for use. The thickness of PANI film measured with a 2206 surface profile tester (China) was 5–20 μ m, depending on electropolymerized charge capacity.

2.2. Fabrication of cell assembly

The TiO₂ (P25, Degussa, Germany) film was deposited on FTO by doctor blade technique, followed by sintering at 450 °C for 30 min. The thickness and active area of the TiO₂ film were about 10 μ m and 0.15 cm². The TiO₂ film was preheated at 120 °C for 30 min and then immersed into 3.0×10^{-4} M bis(tetrabutylammonium) cis-dithio-cyanatobis-(2,2'-bipyridine-4'-COO) ruthenium(II)) (N719, Solaronix) in anhydrous ethanol overnight. For the purpose of comparison, a Pt CE was also prepared by thermal decomposition at 400 °C. Sandwich cells were assembled by sealing the TiO₂ anode together with the electropolymerized-PANI or Pt electrode using

Surlyn (1472 Dupont) at 110 °C. The liquid redox electrolyte, consisting of 0.6 M 1-propyl-3-methylimidazolium iodide (PMII, Merck), 0.05 M I₂, 0.1 M LiI and 0.5 M tertbutylpyridine in acetonitrile, was then introduced through a hole reserved in the surlyn polymer, which was sealed immediately with ultraviolet plastic (XSSS[®]) after irradiated by a sum of UV light. The active cell area was 0.15 cm².

2.3. Measurement and characterization

Surface morphology of electropolymerized-PANI film was observed using a JSM-5600LV scanning electron microscopy (JEOL, Japan). The cyclic voltammetry (CV) of PANI electrodes was conducted in acetonitrile solution containing 10 mM LiI, 1 mM I₂ and 0.1 M LiClO₄ using a CHI 660A electrochemical workstation (CH instruments, USA). The auxiliary electrode and reference electrode were platinum wire and Ag/Ag⁺ electrode. Charge-transfer resistance R_{CT} of CE was determined by electrochemical impedance spectra according to the previous report [19]. Photovoltaic performance of DSSC was determined using CHI 660A under the illumination of 500 W Xenon lamp (Beijing Changtuo technological CO., Ltd., China) equipped with infrared light filter at full sunlight of 100 mW cm⁻² (1.5 AM).



Fig. 1. SEM morphologies of (a) PANI-SO₄, (b) PANI-ClO₄, (c) PANI-BF₄, (d) PANI-Cl, (e) PANI-TsO with electropolymerized charge capacity of 400 mC cm⁻², and (f) a picture of PANI-SO₄ film.

3. Results and discussion

3.1. Morphology of electropolymerized-PANI CEs

The influence of different doping ions (PANI-ion) on morphology was investigated by SEM. Fig. 1a-f shows the surface morphologies of electropolymerized-PANI doped by various counterions with electropolymerized charge capacity of 400 mC cm^{-2} . It is noteworthy that different doping ions have great impact on the morphology of electropolymerized-PANI on FTO. See Fig. 1a, SEM micrograph of electropolymerized-PANI films doped by SO_4^{2-} ion (PANI-SO₄) exhibit porous and crude film morphology for the surface open to the environment. The pore size varies from hundreds of nanometers to several micrometers. As for PANI-ClO₄, see Fig. 1b, the SEM micrograph shows porous and incompact film morphology, moreover, the pore size of PANI-ClO₄ (ca. >10 μ m) is much larger than that of the PANI-SO₄. The SEM image of PANI-BF₄ (Fig. 1c), exhibits fibrillar morphology where the fibers are approximately 300 nm in diameter. Additionally, the PANI-Cl also displays porous film morphology with nonuniform pore distribution (Fig. 1d). Different from the above-mentioned morphology, see Fig. 1e, the PANI-TsO gives uniform particle of around 0.8 µm morphology. So, different doping counterions have great impact on the morphology of these electropolymerized-PANI films, and the porous film structures may be favorable for the high surface area porous CE (a picture of PANI-SO₄ CE was shown in Fig. 1f).

3.2. Electrochemical properties of electropolymerized-PANI CEs

The CVs of I^-/I_3^- redox on electropolymerized-PANI with 400 mC cm⁻² (10–20 µm) doped by SO₄²⁻, ClO₄⁻, BF₄⁻, Cl⁻, TsO⁻, etc. and Pt CEs are shown in Fig. 2a, and the results showed that, different from the electrochemical behavior of Pt electrode (two reduction peak) [20], the electropolymerized-PANI CEs exhibited only one reduction peak ranging from ~–0.1 V to 0.2 V (belongs to $I_3^- + 2e = 3I^-$). Different doping counterions have great impact on electrochemical activity of electropolymerized-PANI film. The reduction peak current density of the PANI-SO₄ (*ca.* 6.0 mA cm⁻²) and PANI-BF₄ (*ca.* 3.9 mA cm⁻²) CEs is significantly higher than that of Pt electrode (*ca.* 1.5 mA cm⁻²) and electropolymerized-PANI doped with other counterions. These facts confirmed that the PANI-SO₄ and PANI-BF₄ are more electrochemically active, which indicated a much faster reaction rate on PANI-SO₄ electrode. With consecutive 20 cycles test, see Fig. 2b, the CV curves did not

change and still showed stable cathodic peak currents, indicating that the PANI-SO₄ film was coated tightly and uniformly and had excellent electrochemical stability.

3.3. Photovoltaic performance of the DSSCs based on electropolymerized-PANI CEs

The photovoltaic performance of the DSSCs based on both Pt and PANI films CEs with different electrodeposited charge capacity and various doping counterions was shown in Fig. 3a. The DSSC with a PANI-SO₄ (400 mC cm⁻²) CE had the highest fill factor (FF) 0.64 and a modest short-circuit current density (I_{SC}) 10.7 mA cm⁻² and open-circuit voltage (V_{OC}) 0.81 V, resulted in a good conversion efficiency of 5.6%, which is comparable to the one using the Pt electrode (6.0%). Meanwhile, the R_{CT} of PANI- SO_4 CE had the lowest value of $1.3 \Omega \text{ cm}^2$. Although the DSSC with PANI-SO₄ (100 mC cm⁻²) and PANI-SO₄ (50 mC cm⁻²) as CE had the highest J_{SC} 11.6 mA cm⁻² and highest V_{OC} 0.82 V, however, the conversion efficiency of the DSSC is relatively low. These indicated that the best electropolymerized charge capacity was 400 mC cm⁻². The different doped counterion ion had a significant impact on the performance of DSSC using electropolymerized-PANI electrode. As seen in Fig. 3b, among the electropolymerized-PANI electrode doped with different ion, PANI-SO₄ based DSSC had the highest FF, J_{SC} , V_{OC} and η . The PANI-BF₄ and PANI-Cl with a porous and fibrillar film had modest efficiency of 3.9% and 2.6%, however, for the PANI-ClO₄ and PANI-TsO, the performance of DSSC is extremely low, *ca.* <1%, and the R_{CT} was greatly increased accordingly to over 100 Ω cm². Although the detailed mechanism is not clear at this stage, it can be conjectured that different composition and structure of PANI prepared with different electrodeposited charge capacity and doping counter ions may result in the PANI with different catalytic performance. In addition, the stability of DSSC with PANI-SO₄ as CE was primarily studied, see Fig. 3c, during the first week, a small drop in J_{SC} (ca. ~1 mA cm⁻²) and V_{OC} (ca. ~50 mV) resulted in a ~15% decrease of initial efficiency, this could be the partial volatilization of volatile electrolyte used in the device. In the following days, the parameter of DSSC trended to be stable, indicating the DSSC with PANI-SO₄ as CE had good stability. All these indicated that the electropolymerized-PANI doped with SO_4^{2-} ion with a porous and homogeneously structure were promising candidates the high performance DSSC. Further work about DSSC with PANI-SO₄ as CE in nonvolatile electrolyte was under investigation.



Fig. 2. (a): CVs of electropolymerized-PANI with 400 mC cm⁻² doped by different counterion and Pt CEs in 10 mM LiI, 1 mM I₂, and 0.1 M LiClO₄ acetonitrile solution, and (b) consecutive 20 CVs of PANI-SO₄ electrode with 400 mC cm⁻², Ag/Ag⁺ nonaqueous electrode and Pt wire as reference and auxiliary electrode, scan rate: 50 mV s⁻¹, insert: the relationship between cycle times and cathodic reduction peak current on PANI electrode.



Fig. 3. (a) The *J*–*V* curve of DSSC based Pt and PANI-SO₄ films with different electrodeposited charge capacity as CE, (b) *J*–*V* curve of DSSC based PANI films with 400 mC cm⁻² doped different ion, and (c) stability test: photovoltaic parameters (J_{SC} , V_{OC} , *FF*, and η) variations with aging time for DSSC based on PANI-SO₄ as CE, measured under illumination of 100 mW cm⁻² (AM 1.5 G).

4. Conclusions

In summary, the PANI-SO₄ film with much porous morphology and the pore size diameter of several micrometers possesses higher reduction current for reduction of I_3^- and a low charge-transfer resistance of 1.3 Ω cm² in comparison with Pt as CE. 5.6% power conversion efficiency at full sunlight and good cell stability has been achieved for DSSC based PANI-SO₄ as CE incorporating a photoanode prepared by commercial P25 TiO₂. The facile electrochemical preparation procedure, comparable photovoltaic properties and very low cost allow PANI electrode to be an alternative CE used in low cost DSSCs.

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