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Preparation and Characterization of Polyaniline Film on Conductive Glass for Dye-Sensitized Solar Cell Counter Electrodes by Chemical Deposition

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Abstract

The objective of this research is to fabricate dye-sensitized solar cells (DSSCs) by chemical deposition method. Polyaniline films were coated on conductive glass for four different deposition times (30, 60, 120 and 180 min). They were then used as the dye-sensitized solar cell counter electrodes. The results found that scanning electron microscopy reveals the polyaniline-island forming on the FTO conductive glass for all four deposition times. The polymer-island size and film thickness increase with the deposition duration. The performance of polyaniline based dye-sensitized solar cells is dependent upon polymer thickness. The highest energy conversion efficiency of the polyaniline based dye-sensitized solar cells was ~6.02%, obtained from the 60-min polyaniline electrode and the lowest efficiency is ~ 5.34 % was found to be in the case of 180-min electrode. The polymer deposition duration above 60 min degrades the solar cell efficiency because of the decreasing of film catalytic activity as observed by cyclic voltammogram measurement. Taking all the results together, 60-min polyaniline electrode has the best potentials for dye-sensitized solar cells application.

Keywords: *Dye-sensitized solar cell; polyaniline; chemical deposition*

1. Introduction

Since the first report of a dye-sensitized solar cell (DSSC) by O'Regan and Grätzel in 1991 (O'Regan), this system has attracted worldwide attention because of its low fabrication costs, high efficiency, and simple preparation procedure (Grätzel, 2001; Smestad, Bignozzi & Argazzi, 1994; Wu et al., 2007). Generally, a dye-sensitized solar cell consists of three main components: 1) a dye covered nanocrystalline TiO_2 layer on the transparent conductive glass substrate as a working electrode, 2) an iodide/triiodide redox couple in an organic solvent as an electrolyte and 3) a platinum film as a counter electrode. Platinized counter electrode is an expensive component in DSSC. To reduce DSSC production cost, low cost catalysts should be used to substitute platinum such as carbon black (Murakami et al., 2006), carbon nanotube (Nam et al., 2010) and conductive polymers (Keothongkham et al., 2012; Li et al., 2009; Qin et al., 2011; Saito et al., 2002).

Conducting polymers have received highly interest for counter electrode materials because of their unique properties, such as inexpensive, high conductivity, good stability and high catalytic activity for I3- reduction (Saito et al., 2004; Wei et al., 2006). Polyaniline (PANI) is one of the most intensively studied polymers because of its widely applications: rechargeable battery, sensor, indicator, membrane, electrochemical capacitor and dye-sensitized solar cell (Blinova et al., 2007; Drelinkiewicz et al., 2007; Dutta et al., 2005; Q. Li et al., 2008; MacDiarmid et al., 1987; Sun et al., 2008). There are many techniques in preparing PANI film such as electrodeposition, chemical vapor deposition and chemical deposition. The chemical deposition is a simple process of coating polymer film on both non-conductive and conductive substrates. Ameen et al. (2010) synthesized PANI films by chemical polymerization process, and obtained the highest efficiency ~ 5.5 % (Ameen et al., 2010). Qin et al. (2011) synthesized polyaniline by oxidative polymerization on ITO substrate, and the promising efficiency of ~ 2.64% was gained. However, the effect of the deposition duration of PANI films on the film structure and the DSSC performance has not yet been fully characterized.

In this present work, polyaniline films were prepared via chemical deposition for four different deposition durations (30, 60, 120 and 180 min). The polymer surface morphology was imaged by scanning electron microscope (SEM). The influence upon solar cell performance was analyzed by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV).

2. Materials and Methods

2.1 Polyaniline (PANI) films

A Fluoride-doped Tin Oxide (FTO, sheet resistance 8Ω/sq, Solaronix, SA) glass was used as the conducting substrate for both working and counter electrodes. An insulating tape was taped on the conducting glass with an open area of 0.4 cm x 1.1 cm for a specific polymerization. An aniline solution consists of 100 µl aniline monomer in 20 ml of 0.5 M sulfuric acid (H_2SO_4), was used for depositing polymer films. A 0.2 M Ammonium persulfate ($(NH_4)_2S_2O_8$) solution was mixed with the aniline solution at volume ratio 1:1. This solution was stirring continuously for one minute. After that, the clean FTO glass was immersed into the solution and kept at 10-15˚C for 30, 60, 120 and 180 minutes. The polymer films were then washed with DI water and ethyl ethanol for several times to remove oligomers, sulfuric acid and water residuals. For a comparison, the Pt thermally deposited films were prepared by a spin coating of Pt solution, composing of 2 mM tetraammine platinum (II) chloride hydrate ($Pt(NH_3)_4Cl_2{\cdot}H_2O$, Aldrich Company) and 0.2 g ethyl cellulose in 5 ml DI water and 15 ml isoproponal. It was then annealed at 500 °C for 1 h.

2.2 TiO_2 films

The nanoporous TiO_2 film was prepared by a screen printing method. In briefly, the blocking layer was prepared by spin coating technique of the platinum solution, consisting of 1 ml titanium diisoproxide bis(acetylacetonate) ($C_{16}H_{28}O_6Ti$) in 20 ml isopropanol ($(CH_3)_2CHOH$). The transparent and scattering TiO_2 films were coated on blocking layer using commercial TiO_2 pastes. The compounds used were PST-18NR and PST-400 (JGC Catalysts and Chemicals Company, Japan) as transparent and scattering layers, respectively. The TiO_2 films were dried at 80 °C for 10 min, and then sintered at temperature 500 °C for 1 h. TiO_2 thickness was ~10 µm as observed by cross-section scanning electron microscopy. TiO_2 film was treated with UV for 10 min, and then immersed in 0.3 mM *cis*-bis-(isothiocy-anato)bis(2,2-bipyridyl-4,4-dicarboxylato)-ruthenium(II)-bis-tetrabutylam-monium (N-719, Solaronix) in acetonitrile/tert-butanol (1:1 v/v) solution under the dark conditions for 24 h. Finally, dye residuals were removed by washing in ethanol.

2.3 Cell assembly

A dye-sensitized nanocrystallized solar cell (active area of 0.25 cm^2) was assembled by using a dye-coated TiO_2 film as the working electrodes and PANI or Pt films as the counter electrodes. The electrodes were assembled together with a plastic film (Surlyn, thickness ~60 µm). The electrolyte solution, a mixture of 0.05 M iodine (I_2), 0.1 M lithium iodide (LiI), 0.0025 M lithium carbonate (Li_2CO_3), 0.5 M of 4-tert-butylpyridine (TBP) and 0.6 M of 1-methyl-3-propylimidazolium iodide (MPI) in acetonitrile, was injected into a drilled hole on the counter electrode. Then, the small hole was sealed with plastic film to prevent electrolyte the leaking.

2.4 Film and cell characteristics

The characteristics of dye-sensitized solar cells were analyzed by a solar simulator (PEC-L11, Japan) under air mass 1.5 and light intensity of 100 mW/cm^2. The film surface morphology and thickness were characterized by scanning electron microscopy (SEM, 1450VP. LEO Company, England). Catalytic activities of PANI and Pt films were analyzed by cyclic voltammetry with a three-component electrode: Pt plate as the counter electrode, Ag/AgCl electrode as the reference electrode and PANI or Pt films as the working electrode at a scan rate of 20 mV/s. The DSSC impedance was measured by electrochemical impedance spectroscopy (Gamry REF 3000, USA) under a light intensity 100 mW/cm^2, frequency ranging from 0.1 Hz to 100,000 Hz under the AC amplitude 10 mV.

3. Results

3.1 PANI films

Figure 1 shows the optical images of chemically deposited PANI films at four different deposition durations. It is seen that the longer deposition time results in the bluer polymer films. This implies that the longer soaking time induces more PANI polymerized on the conductive glass. To deeply view the PANI surface morphologies, scanning electron microscope (SEM) was used to image the polymer structures. Figure 2 shows the top view of PANI surfaces, and it clearly sees the polymer island formed on the FTO surface. The polymer thickness was estimated from the cross-section SEM images (Fig. 3), which is about 600 nm, 700 nm, 900 nm and 1µm for the 30-min, 60-min, 120-min and 180 min PANI films, respectively. The PANI polymerization on conductive glass can be explained as following. First, aniline cations get absorbed on the substrate due to the attractive force such as van der Waals force or chemical attractive force. Next, ammonium persulfate activates the oxidation process of aniline monomers resulting in a growing polymer chain (Amou et al., 1999). PANI oxidative polymerization reaction is proposed as diagram bellow (Kulkarni et al., 2011).

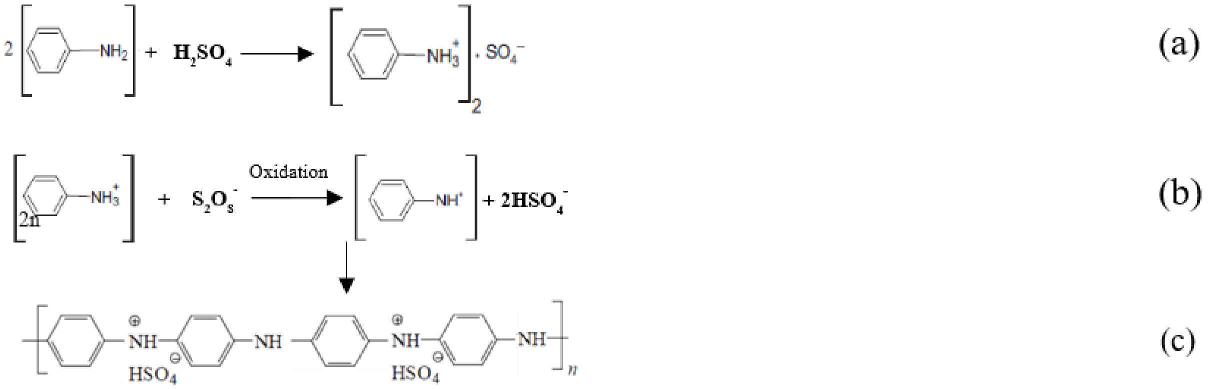

Diagram 1: Polymerization reaction of PANI. (a) The reaction of aniline with sulfuric acid gives anilinium cations in the form of anilinium persulfate. (b) The oxidative chemical reaction of anilinium cations by persulfate anions of ammonium persulfate leads to the generation of aniline nitrenium cations. (c) Aniline nitrenium cations react with hydrogen sulfate anions to form PANI (emeraldine) hydrogen sulfate.

The catalytic activity of PANI films was characterized by the cyclic voltammogram (CV) measurement, and CV result is shown in Fig. 4. For a comparison, Pt film was also scanned. It is observed in Fig. 4 that Pt film consists of two oxidation peaks (~0.36 and ~0.7 V) and two reduction peaks (~0.55 and ~0.05 V). PANI films also generate two oxidation peaks (~0.38 and ~0.8 V) and two reduction peaks (~0.60 and ~0.04 V). The presence of oxidation and reduction peaks of PANI films indicates its potential use as DSSC counter electrodes. However, the current density of PANI films is lower than those of Pt film. This may be due to the discontinuity polymer film (as seen in Fig. 2) and the low polymer electrical conductivities.

3.2 DSSC performance

The performance of DSSCs was measured under light irradiation of 100 mW/cm^2. Photocurrent density (J) vs. photovoltage (V) curves are shown in Fig. 5. Photoelectric parameters such as short circuit-current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and energy conversion efficiency (η) are extracted from J-V curves and listed in Table.1. It is observed that the 60-min PANI DSSC delivers the highest energy conversion efficiency (~6.02%) among polymer solar cells. The efficiency of PANI DSSCs in this study is higher than Ameen et al. work (5.5%).

4. Discussion

In these results, the increase of the deposition duration from 30 min to 60 min improves the solar cell performance, but the further deposition duration (120 and 180 min) degrades the solar cell efficiency. As observed from J-V curves, PANI DSSCs exhibit less squareness and lower FF values than Pt DSSC. The curve squareness and FF are primarily governed by the solar cell impedance, i.e. charge-transfer resistance at the working electrode/electrolyte, charge-transfer resistance at the counter electrode/electrolyte, Nernst diffusion and series resistance. The change of DSSC impedances was measured by the electrochemical impedance spectroscopy (EIS), and Nyquist curves are plotted. It is seen that the impedance of Pt cell (~18 Ω) is smaller than those of PANI cells (~25-30 Ω). This means that Pt cell has a lower charge-transfer resistance than polymer cells. The low Pt DSSC impedance is well agreed with its high solar cell performance. Since all DSSC devices are constructed of the same FTO glass, TiO_2 films and electrolyte. Thus, the charge-transfer resistance at working electrode/ electrolyte, Nernst diffusion and series resistance would be approximately the same. Electrochemical impedance spectroscopy is an important method to investigate the internal resistances of the DSSCs (Yi et al., 2013). Therefore, the major cause on the cell impedance differences should be from the counter electrodes, lower impedance of the composite solar cell is responsible for its higher cell efficiency (Thiangkaew et al., 2014). Figure 6 shows that the 30-min PANI DSSC has the highest impedance, but the 60-min, 120-min and 180-min PANI DSSCs have about the same impedance values. As mention earlier that the performance of dye-sensitized solar cells is dependent on properties of counter electrodes such as film catalytic activity and/or film resistivity. Although there is no significant difference on cell impedances among the 60-min, 120-min and 180-min DSSCs, there are greatly differences on the CV curves. Especially, the reduction of the CV curve of the 180-min film, compared to the three other polymer cells. Thus, the reduction of CV peak (i.e. the reduction of film catalytic activity) of the 180-min film is a main cause of its inferior cell performance. The current peak of the positive potential is assigned to oxidation reaction and the current peak of the negative potential is assigned to reduction reaction (Qin et al., 2011). In addition, high electrochemical stability in the electrolyte system, low charge transfer resistance, high electrical conductivity, and high electro-catalytic activity are all necessary for an effective counter electrode (Abdulelah et al., 2017; Xue et al., 2015). Hence, it can be inferred of this study that the preferred polymer counter electrode should be a high conductivity and catalytic activity in order to generate high dye-sensitized solar cell efficiency.

5. Conclusions

PANI films were coated on conductive glass by chemical deposition method and used as DSSC counter electrodes. Scanning electron microscopy images show the PANI-island formation on the FTO conductive substrate for all four deposition times. The highest energy conversion efficiency of the polyaniline based

DSSCs is ~ 6.02%, obtained from the 60-min polyaniline electrode and the lowest efficiency is ~ 5.43% was found to be in the case of 180-min electrode. The polymer deposition duration above 60 min degrades the solar cell efficiency, which is due to the reduction of polyaniline film catalytic activity. The inferior performance of polymer DSSCs compared to Pt DSSC is because of the lower polymer catalytic activity and conductivity than those of Pt film. Therefore, the chemical deposition method of preparing polyaniline film is appropriate for use in dye-sensitized solar cells.

6. Conflict of Interest

We certify that there is no conflict of interest with any financial organization regarding the material discussed in the manuscript.

7. Acknowledgements

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Table 1. Summary of open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF) and solar cell efficiency (η) of PANI and Pt DSSCs.

Electrodes	J_{sc} (mA/cm^{-2})	V_{oc} (V)	FF	η (%)
PANI-30min	11.80	0.76	0.62	5.57
PANI-60min	12.34	0.76	0.63	6.02
PANI-120min	12.33	0.75	0.62	5.86
PANI-180min	11.42	0.75	0.62	5.34
Thermal Pt	13.25	0.78	0.67	7.05

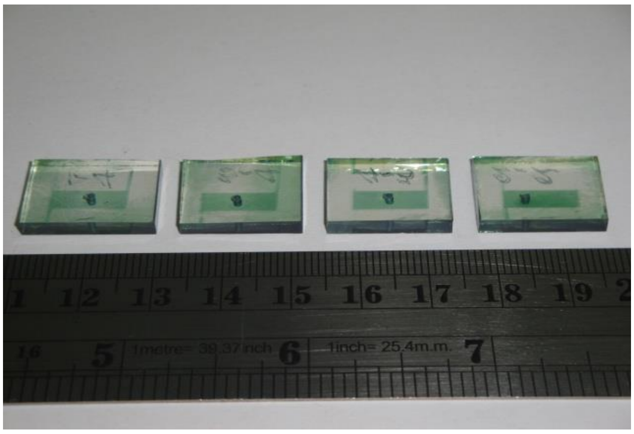

Figure 1. The optical image of polyaniline films deposited for 30 min, 60 min, 120 min and 180 min.

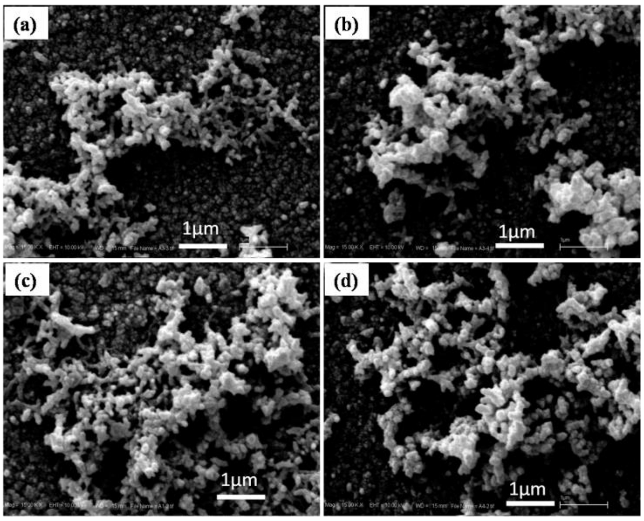

Figure 2. Top views SEM images of PANI films deposited (a) for 30 min, (b) 60min, (c) 120 min and (d) 180 min.

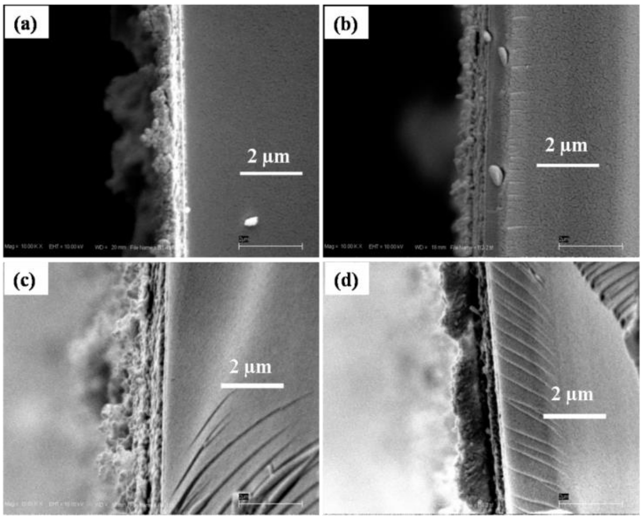

Figure 3. Cross-section SEM images of polyanilne films deposited for a) 30 min, b) 60 min, c) 120 min and d) 180 min.

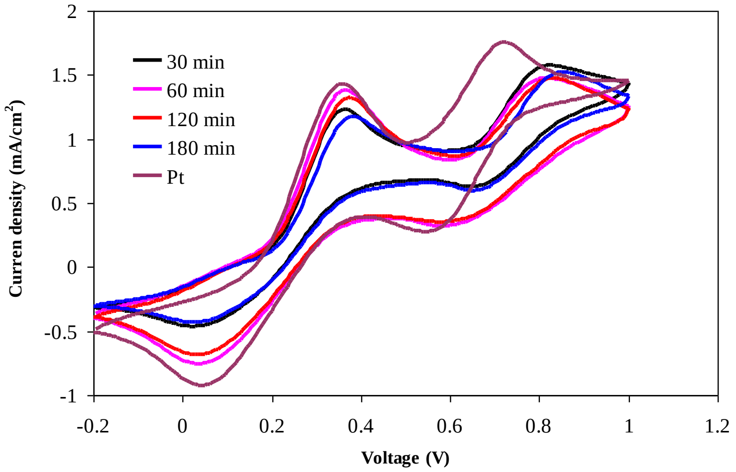

Figure 4. Cyclic voltammogram (CV) curves of PANI and Pt films at a scan rate of 20 mV/s in 10 mM LiI, 1 mM I_2, and 0.1 M $LiClO_4$ in acetonitrile solution.

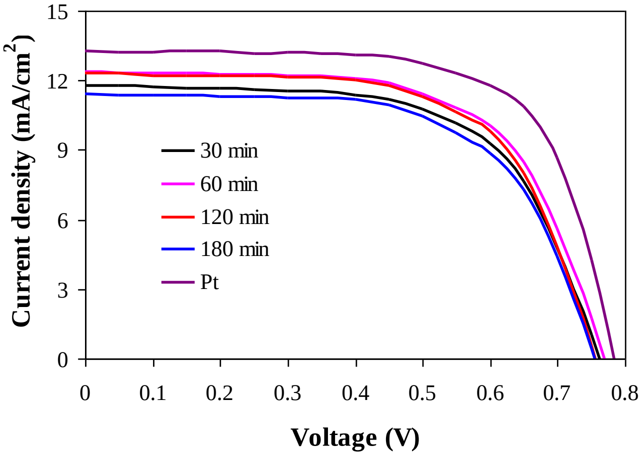

Figure 5. Photocurrent density (J) vs. photovoltage (V) curves of PANI and Pt DSSCs.

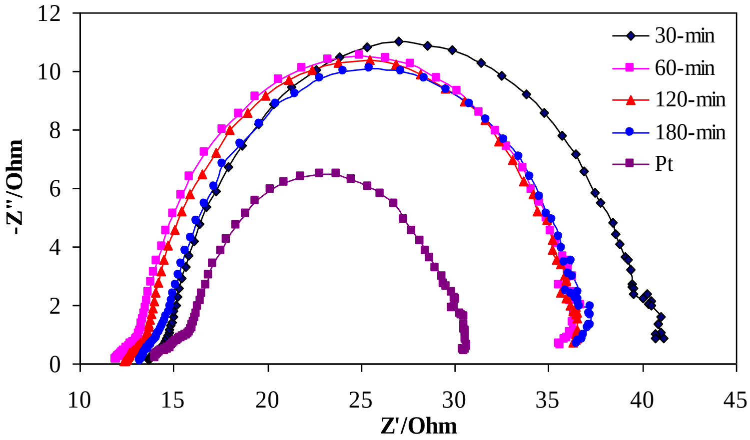

Figure 6. Nyquist plots of Pt and PANIs DSSCs from 0.1 Hz to 100.000 Hz.