Enhanced Charge Transfer of Liquid and Gel Electrolytes Using Nano Platinum in Dye-sensitized Solar Cells

Thi-Thao Hoang[1], Phuoc-Hiep Nguyen[1], Tan-Phat Huynh[2], The-Vinh Nguyen[3]
[1]*Faculty of Materials Technology, Hochiminh City University of Technology, Hochiminh City, Vietnam.*
[2]*Department of Physical Chemistry of Supramolecular Complexes, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland.*
[3]*Faculty of Environment, Hochiminh City University of Technology, Hochiminh City, Vietnam.*

ABSTRACT

One of the key components of dye-sensitized solar cell (DSSC) is electrolyte that strongly affects its stability and overall conversion efficiency. In order to improve charge transfer of the electrolyte, lab-made platinum nanoparticles (nano Pt) were employed in this present work as catalysts in both conventional and flexible DSSC. The presence of nano Pt in a commercial electrolyte (R50, Solaronix) was found to significantly improve the photovoltaic performance of the resulting DSSC at AM 1.5: V_{OC} of 0.74 V, J_{SC} of 19.7 mA/cm^2, FF of 43.2% and η of 6.33 %, which were much better than those of a corresponding DSSC fabricated with the R50 electrolyte alone (η of 5.0%). Addition of nano Pt as catalysts for charge transfer in gel electrolyte was also found to substantially enhance the efficiency of the derived flexible-DSSC at AM 1.5: V_{OC} of 0.69 V, J_{SC} of 5.22 mA/cm^2, FF of 51.0% and η of 1.84 %, compared with η of 1.20 % in the case of using the gel electrolyte without nano Pt. The effect of anti-electron-hole-recombination layer on the overall conversion efficiency of the obtained DSSC was also studied and discussed.

INTRODUCTION

DSSC is among the most extensively investigated device that provides a high light-to electric energy conversion yield. Although the efficiency of DSSC is currently improved to over 12% [1], full commercialization and popularity of this novel solar cell definitely require further study related to its efficiency, stability and flexibility. For the purpose of improving efficiency, many investigations have focused on the redox couples with the aim of enhancement of the open circuit photovoltage and the short-circuit current density via suppressing the recombination reaction between the injected electrons and oxidized moiety of the redox electrolyte which occurs at the nanostructured TiO_2/redox electrolyte interface [2]. In addition to the catalytic role of platinum coating on the counter electrode, nano Pt were employed in this present work as additives in liquid/gel electrolytes to improve charge transfer between these redox couples and the counter electrodes/the oxidized dyes in both conventional DSSC (using FTO glass) and flexible-DSSC (using ITO PET). In order to prevent the combination of electron-hole, an amorphous layer of TiO_2 was coated on FTO/ITO-PET photoelectrodes by using titanium tetraisopropoxide (TTIP) solution in propanol [3]. The effect of this layer on photovoltaic performance of the flexible-DSSC was also investigated in this study.

EXPERIMENTAL

A. Materials

Commercial titanium dioxide powder (P25**,** Degussa) and TTIP (Merck) were used as TiO_2 sources. Ruthenium 535 bis-TEA dye or N-719 (Solaronix) as a sensitizer, polyethylene oxide (PEO) (M=1,000,000, Sigma Aldrich) and other chemicals were analytical grade and used as received. Iodolyte R50 (Solaronix) was used as electrolyte. Lab-made platinum nanoparticles were prepared by using $H_2PtCl_6.5H2O$ (Sigma Aldrich). The transparent conducting oxide glass substrate (FTO glass) was supplied by Solaronix (8Ω/sq, 80% transmittance in visible light). ITO-PET (Indium Tin Oxide coated polyethylene terephthalate)) was generously supplied by KINTEC (10 ohm/sq, 80% transmittance in visible light).

B. Preparation of photo-electrode

In conventional DSSC, preparation of dense TiO_2 paste was illustrated in our previous study [4]. The resulting TiO_2-based paste was coated on TCO glass to make a thin film by using a modified doctor-blade method [4].

For fabrication of flexible-DSSC, a dense TiO_2 paste was prepared as following: TiO_2 powder (1 g) was mixed with ethanol (10 ml) by using an ultrasonicator for 15 min, then TTIP was dropped gradually into this solution at different TiO_2:TTIP weight ratios. After that, the resulting TiO_2 paste was coated on ITO PET to make a thin film using a doctor-blade method. Finally, this film was covered with a flat glass and compressed at pressure of 49 MPa for 5 s. The derived TiO_2 thin film was finally irradiated in a 300 W microwave for 1 min.

To prepare the working electrodes for both kinds of DSSCs, TiO_2 thin film was dipped in N719 dye solution of 0.5mM in ethanol for 20 h to achieve a monolayer-dye absorbed on the TiO_2 layer. The thin film was then rinsed thoroughly with ethanol and dried at 80^{o}C in air for 30 min.

C. Preparation of nano Pt

Lab-made nano Pt were prepared by thermolysis method using $H_2PtCl_6.5H2O$ 5mmol in ethanol solution. Schematic diagram of nano Pt preparation process was shown in our previous study [4].

D. Preparation of electrolytes

In this study, we used Iodolyle R50 as a standard electrolyte for both conventional and flexible-DSSCs to compare with the modified-R50 electrolyte that was added with the lab-made nano Pt. Besides, PEO-based

gel electrolytes were prepared as follows: LiI (0.102 g), I_2 (0.071 g), PEO (0.264 g) and nano Pt (0.01mg) or nano Pt (0.1wt%)-TiO_2 (10 mg) as catalyst were added into 50 ml acetonitrile under ultrasonic condition to make a gel electrolyte with the molar ratio of PEO : LiI : I_2 of 3 : 3 : 1. The obtained solution was put in a sealed vessel and stirred vigorously at 40°C for 3 h. The vessel was finally opened for natural evaporation of solvent in air to obtain 10 ml of gel electrolyte.

E. Fabrication of DSSC

The details of DSSC fabrication were illustrated in our previous studies [3,4]. Briefly, the 2-electrode sandwich cell for photovoltaic measurement consisted of a dye adsorbed TiO_2 electrode, a Pt counter electrode, a spacer and an organic electrolyte.

In conventional DSSC, Pt counter electrode was prepared on FTO coated glass substrate. A few droplets of platinum solution ($PtCl_4$) were spread on the substrate and heated at 450°C for 30 min in air. For fabrication of flexible DSSC, the Pt counter electrode was prepared by electron beam deposition of Pt (20 nm thickness) on ITO-PET substrate.

In the case of using liquid electrolyte, the electrolyte was injected in the cell through one of two holes on the counter electrode. Meanwhile, in the case of using a gel electrolyte for flexible DSSC, the dye adsorbed TiO_2 working electrode was casted with the gel electrolyte before the two electrodes were sandwiched with a spacer. The resulting cells had active areas of 0.25 cm^2.

RESULTS AND DISCUSSION

A. Optimization of anti-electron-hole-recombination layer using different TTIP solutions

Anti-electron-hole-recombination layer was prepared by spin-coating a few droplets of TTIP solution (0-10% TTIP in propanol) to obtain a thin layer of amorphous TiO_2 right on the top of ITO PET substrate (Fig. 1). This amorphous TiO_2 layer separates conductive electrodes from the electrolyte in the cell and therefore, reduces the chance of electron-hole recombination. Thanks to this dense amorphous TiO_2 layer, short circuit current density, I_{SC} of the derived DSSC was observed to increase and reach the peak as the TTIP solution of 3% was used (Table 1). Therefore, this rate will be applied for all of the photoelectrodes based on ITO PET substrate.

Table 1: Photovoltaic performances of flexible DSSC fabricated with different TTIP solutions

Anti-electron-hole recombination layer	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	η (%)
TTIP 0%	0.72	3.24	67.3	1.57
TTIP 3%	0.71	6.30	50.0	2.24
TTIP 5%	0.72	3.69	62.4	1.66
TTIP 10%	0.71	1.25	59.4	0.53

As presented in Table 1, when the concentration of TTIP solution increases from 3% to 10%, the thickness of the resulting amorphous TiO_2 layer consequently increases. The thicker the amorphous TiO_2 layer, the higher the opportunity of electron-hole recombination. This in turn decreases the short circuit current density, I_{SC} of the corresponding DSSC.

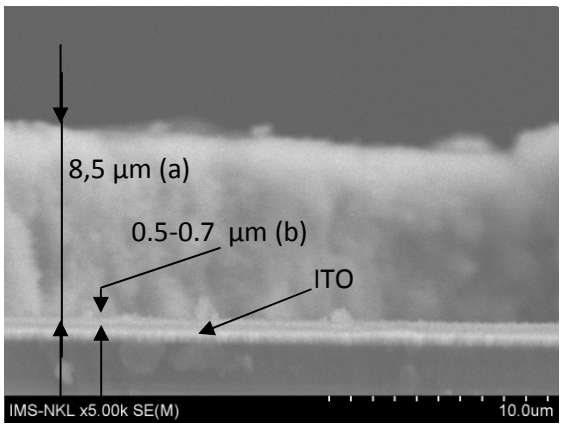

Fig. 1. Cross-section FE-SEM image of photo-electrode. (a) TiO_2 nanoparticle thin film and (b) anti-electron-hole-recombination layer.

B. Microstructure of gel electrolyte

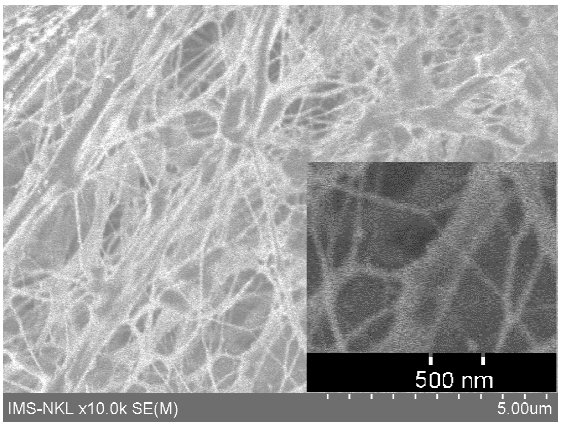

Fig. 2. FE-SEM image of Pt-PEO-TiO_2 gel.

Microstructure of gel electrolyte investigated using FE-SEM is presented in Fig. 2. PEO in the gel electrolyte exists as a nano-web that allows solvent in the gel not to be disconnected. This also implies that the derived gel electrolyte still has characteristics of a conventional liquid counterpart to some extent. Such microstructure is some how called quasi-solid electrolyte that can significantly improve stability of the corresponding DSSC.

C. Effect of nano Pt catalyst on photovoltaic performance of DSSC

Pt catalyst coated on counter electrode plays a significant role in DSSC to accelerate reduction-oxidation of I^-/I_3^- couple, which provides electron to regenerate oxidized dye.

$I_3^- + 2e \rightarrow 3I^-$ at counter electrode

$3I^- - 2e \rightarrow I_3^-$ at photo electrode.

In this study, owing to low solubility of gel electrolyte, nano Pt or nano Pt impregnated on the nano-substrates was also employed as catalyst in the electrolyte to further enhance charge transfer between the redox couples and the counter electrodes/the oxidized dyes in both conventional and flexible DSSCs. The detailed compositions are displayed in Table 2. I^-/I_3^- oxidation-reduction potential of gel electrolyte were measured using cyclic voltammetry with Ag/AgCl as a reference electrode that was converted into Normal Hydrogen Electrode Potential, E_{redox} (NHE).

Table 2: Gel electrolyte prepared with different catalysts

Gel electrolyte	Gel PEO 10% (ml)	Catalyst
Gel PEO	10	NONE
Gel Pt-PEO	10	0.01 mg Pt
Gel PEO-TiO_2	10	10 mg TiO_2
Gel Pt-PEO-TiO_2	10	10 mg Pt/TiO_2

Table 3: I^-/I_3^- oxidation-reduction potential E_{redox} of gel electrolytes with different catalysts

Gel electrolyte	E_{redox} (mV) Ag/AgCl	E_{redox} (mV) NHE
Gel PEO	578	388
Gel Pt-PEO	495	302
Gel PEO-TiO_2	554	364
Gel Pt-PEO-TiO_2	511	321

It was found in Table 3 that the presence of nano Pt in the gel electrolyte was observed to substantially decline its reduction-oxidation potential. Although overall conversion efficiency of DSSC depends on many factors, decrease of reduction-oxidation potential of I^-/I_3^- in gel electrolytes is expected to enhance charge transfer between two electrodes. This accordingly might increase the I_{SC} and therefore, improve overall conversion efficiency of the DSSC.

Photovoltaic performance of conventional DSSC fabricated with R50 and R50 added with nano Pt are shown in Table 4. The data in this table reveal that the presence of nano Pt in the electrolyte dramatically increases both open-circuit potential (from 0.69 to 0.74 V) and short-circuit current density (from 14.42 to 19.79 mA/cm^2). This in turn enhances the efficiency of the conventional DSSC from 5.04 to 6.33 %.

Table 4: Effect of nano Pt in electrolyte on the performance of conventional DSSC

Electrolyte	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	η [%]
R50	0.69	14.42	50.7	5.04
Pt-R50	0.74	19.79	43.2	6.33

Table 5 presents the electrochemical behavior of flexible DSSC fabricated with different gel electrolytes. The overall conversion efficiency of flexible DSSC is also well consistent with the reduction-oxidation potential of the electrolytes as depicted in Table 3.

Table 5: Performance of flexible DSSC fabricated with different electrolytes

Electrolyte	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	η [%]
R50	0.71	6.30	50.0	2.24
Pt-R50	0.73	8.35	39.4	2.40
Gel PEO	0.67	2.57	67.8	1.20
Gel Pt-PEO	0.69	5.22	51.0	1.84
Gel PEO-TiO_2	0.68	1.96	68.6	0.91
Gel Pt-PEO-TiO_2	0.71	2.35	66.7	1.11

CONCLUSIONS

An amorphous TiO_2 layer prepared with a solution of 3% TTIP in propanol as an anti-electron-hole recombination agent is found to substantially increase the overall conversion efficiency of the resulting flexible DSSC. Meanwhile, addition of nano Pt as a catalyst to the gel electrolyte was observed to significantly declined its oxidation-reduction potential, which could result from the enhanced charge transfer between the redox couples and the counter electrodes/the oxidized dyes in the flexible DSSC. This, in turn, could explain the superior open-circuit potential, short-circuit current density and overall conversion efficiency of the both conventional and flexible DSSCs that were fabricated with the nano Pt-based electrolytes.

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