

Short communication

## A quasi-solid-state dye-sensitized solar cell based on the stable polymer-grafted nanoparticle composite electrolyte

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### Abstract

A novel gel electrolyte was prepared by dispersing the polymer-grafted ZnO nanoparticle into liquid electrolyte. This gel electrolyte behaves long-term stability as the poly(ethylene glycol methyl ether) molecules are strongly connected to ZnO nanoparticles with covalent bond in polymer-grafted ZnO nanoparticle. A quasi-solid-state dye-sensitized solar cell (DSC) based on this gel electrolyte yields the energy transfer efficiency of 3.1% at AM 1.5 direct irradiation of 75 mW cm<sup>-2</sup> light intensity. Addition of 4-*tert*-butylpyridine into the electrolyte results in dramatically improved short circuit current density  $I_{sc}$ , and the overall efficiency is also improved to 5.0%, while the open circuit voltage ( $V_{oc}$ ) and fill factor (ff) are insensitive to the presence of 4-*tert*-butylpyridine. DSC fabricated with this novel gel electrolyte displays better thermal stability than those solidified with the conventional nanoparticle ZnO(Ac).

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**Keywords:** Dye-sensitized solar cell; Polymer-grafted ZnO nanoparticle; Gel electrolyte

### 1. Introduction

Dye-sensitized solar cell has received considerable attention in recent years for its high energy conversion efficiency and low cost [1,2]. A new record conversion efficiency of 11% was already achieved [3]; however its practicality still remains challengeable for the volatility of electrolyte. The leakage of liquid electrolyte from DSC, possible desorption of loosely attached dyes and photo-degradation in the desorbed states as well as corrosion of the Pt counter electrode by the triiodide/iodide couple have been suggested as some of the criteria factors limiting the long-term performance of the DSC especially at elevated temperature. Great efforts have been devoted to the solidification of electrolyte. Different kinds of electrolyte such as polymer electrolytes [4–7], hole-transport materials [8–10] have been employed to substitute the liquid electrolyte; however, the efficiency of cells based on these electrolytes is not satisfying due to their low ion conductivity and poor interfacial contact.

Recently a new route was applied to fabricate gel electrolyte by dispersing nanoparticles in liquid electrolyte. This kind of nanocomposite gel electrolyte was successfully applied in dye-sensitized solar cell [11–14]. This gel electrolyte is composed of two subphases. The organic subphase serves as the mediator for ion-conducting. Inorganic nanoparticles are dispersed in organic subphase in nanoscale, and work as the holding framework. The nanoparticles can prevent the volatility and leakage of electrolyte, and improve the mechanical strength of the cell in the meantime. But these nanoparticles are apt to aggregate, and then grow to larger particles. These larger particles will deposit onto the surface of TiO<sub>2</sub> film, and retard the ion transportation on the electrode surface. As a result, the efficiency of solar cell declines dramatically after these two subphases separate.

In this article, a novel polymer-grafted ZnO nanoparticle, ZnO(PEG), was employed to solidify liquid electrolyte. A quasi-solid-state solar cell with high efficiency was assembled with this novel composite gel electrolyte. 4-*tert*-Butylpyridine was also applied as additive in the electrolyte in order to elucidate its effect on the electrochemical property of the solar cell. The thermal stability of the dye-sensitized solar cell based on the polymer-grafted ZnO nanoparticle gel electrolyte was compared

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with that based on the gel electrolyte solidified by conventional ZnO(Ac) nanoparticle.

## 2. Experimental

### 2.1. Preparation of composite gel electrolyte

Poly(ethylene glycol methyl ether) (PEGME, M.W. = 350, Fluka, normally in liquid) was grafted onto the surface of ZnO nanoparticle through covalent bond according to the method reported in our previous reference [15]. The detailed characterizations, including the high-resolution transmission electron microscopy (HRTEM) and IR spectrum, can be found in the reference [15]. The liquid electrolyte applied was composed of KI and I<sub>2</sub> in PEGME 350. A series of liquid electrolyte were prepared, in which the concentration of KI varied from 0.1 to 2.2 mol L<sup>-1</sup>. The iodine content was fixed at 10 wt% with respect to KI. The polymer-grafted nanoparticle was employed to solidify this series of liquid electrolyte. The weight percentage of the polymer-grafted nanoparticle in the composite electrolyte was adjusted to 24 wt%. As the weight ratio of ZnO in polymer-grafted nanoparticle is confirmed to be 41.4 wt% by TG analysis, the weight ratio of ZnO in the gel electrolyte is 10 wt% in our experiment. The conventional ZnO particle with acetate group on its surface (designated as ZnO(Ac)) was synthesized referring to the method described in classical literature [16] for the purpose of comparison.

### 2.2. Conductivity measurements

The conductivity measurement of electrolyte in our experiment was all conducted by placing the electrolyte between two pieces of stainless steel. The ion conductivity was measured using a Solartron Instrument Model 1287 electrochemical interface and 1255B frequency response analyzer controlled by a computer. The frequency limits were typically set between 1000 kHz and 0.01 Hz. The ac oscillation was 5 mV. The data were analyzed by Zplot software.

### 2.3. Fabrication of solar cell

Indium–tin oxide (ITO)-covered glass was used as the substrate of the electrode. TiO<sub>2</sub> paste consisting of photocatalytic TiO<sub>2</sub> power (Ishihara Sangyo Kaisha Ltd.), PEG400, acetylacetone and distilled water was spread on the glass support by doctor-blade method. After air drying, the electrode was heated to 450 °C at heating rate of 5 °C/min, and then kept at 450 °C for 30 min in air flow. Scanning electron microscopy shows that the film is composed of a three-dimensional network of particles with an average size of 35 nm. The film thickness is estimated to be 7 μm. The electrode was immersed in a 0.5 mmol/L solution of *cis*-ruthenium(II) (4,4'-COOH-2,2'-bpy)<sub>2</sub>(NCS)<sub>2</sub> (N3, solaronix) in dry ethanol for 24 h to absorb dye molecules.

The composite electrolyte was spin-coated onto the TiO<sub>2</sub> electrode. A platinum counter electrode was placed directly on the top of TiO<sub>2</sub> electrode and then applied to measurement. The cell performance was evaluated using a Keithley 2400 Source

Meter. All experiments were performed at AM 1.5 direct irradiation of 75 mW cm<sup>-2</sup> light intensity from Oriel 1000 W xenon lamp. The active area of the cell is 0.15 cm<sup>2</sup>. The thermostability of the gel electrolytes solidified by the polymer-grafted ZnO nanoparticle and ZnO(Ac) nanoparticles were compared after 1000 h storage at 55 °C. For thermal stability test of DSC, the cells were sealed with thermal plastic, and stored in the oven at 55 °C. The cell performance was measured once a week.

## 3. Results and discussion

### 3.1. Ion conductivity of the polymer-grafted ZnO nanoparticles

It is well-known that both the efficiency and the fill factor of the dye-sensitized solar cell are critically dependent on the ion conductivity of the electrolyte applied in the cell. We at first investigated the ion conductivity of the pure polymer-grafted ZnO containing the KI and I<sub>2</sub>. This was performed by dispersing homogeneously KI and I<sub>2</sub> in it. The mole ratio of ether oxygen to iodide salt was fixed at 20 (EO/K<sup>+</sup> = 20), and the iodine was fixed at 10 wt% of the KI [12]. Thermogravimetric (TG) analysis shows that the weight percentage of ZnO in polymer-grafted nanoparticle was confirmed to be 41.4 wt% [15], the viscosity of the resulting product is extremely large. Surprisingly this electrolyte base on polymer-grafted nanoparticle possesses moderate ion conductivity. At 303 K (30 °C), the ion conductivity was determined to be 2.72 × 10<sup>-5</sup> S cm<sup>-1</sup>. As is shown in Fig. 1, its conductivity–temperature behavior can be well described with the Vogel–Tammann–Fulcher (VTF) equation. The ion conductive mechanism in the polymer-grafted ZnO nanoparticle gel electrolyte might be similar to that of the pure polymer electrolyte: the increase of the temperature may facilitate the ion motion through EO chain. Moreover, the viscosity of the electrolyte becomes low when the temperature is raised. Both lead to increase of its ion conductivity. However efficiency of solar cell based on this electrolyte is not so satisfying for its low ion conductivity and high viscosity.

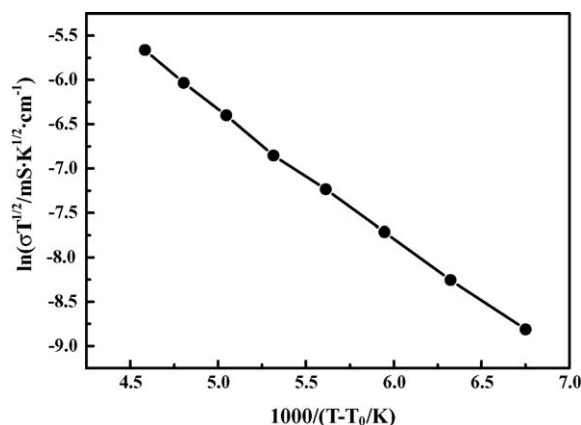


Fig. 1. Plot of conductivity–temperature data of ZnO(PEG) containing KI and I<sub>2</sub>.

### 3.2. Ion conductivity of gel electrolyte

As the electrolyte consisting of polymer-grafted ZnO, KI and  $I_2$  shows high viscosity and relative low ionic conductivity, a low-molecular-weight poly(ethylene glycol) methyl ether PEGME 350 was added into the electrolyte. The weight percentage of the polymer-grafted nanoparticle in the composite electrolyte was adjusted to 24 wt%, it means the weight ratio of ZnO in the gel electrolyte is 10 wt% that is the preferred ratio used for the inorganic particle modified gel electrolyte [12]. A series of gel electrolyte with different salt concentration were employed to select the optimum concentration value. The weight ratio between KI and iodine was also fixed to 10. The ion conductivity values of gel electrolyte with different concentration were measured at 25 °C, and the results are shown in Fig. 2. The ionic conductivity increases as the salt concentration increases, reaches a maximum value, and then decreases. As a result, its ion conductivity reaches a maximum of  $3.34 \times 10^{-4} \text{ S cm}^{-1}$  at the concentration of KI of  $0.6 \text{ mol L}^{-1}$  (ZnO(PEG):PEG:KI:I<sub>2</sub> = 19.3:73.3:6.7:0.67 in weight). After the electrolyte becomes denser, the interaction between ions becomes stronger, and then the ion transportation is restrained. So the ion electrolyte decreases after the concentration of KI exceeds  $0.6 \text{ mol L}^{-1}$ . The gel electrolyte at this concentration (denoted as gel A) was employed to fabricate solar cell in the following experiment. As is shown in Fig. 3, the gel A nearly has no fluidity at room temperature. It is suitable to serve as the electrolyte of quasi-solid-state solar cell.

### 3.3. Photovoltaic performance

Fig. 4 shows the photocurrent density–voltage curves for solar cells based on liquid electrolyte ( $0.6 \text{ mol L}^{-1}$  KI and  $I_2$  in PEGME 350,  $I_2/\text{KI} = 10 \text{ wt\%}$ , denoted as liquid A) and gel A. Their short circuit current density  $I_{sc}$ , open circuit voltage  $V_{oc}$ , fill factor  $ff$  and energy transfer efficiency  $\eta$  are summarized in Table 1. It is shown that  $V_{oc}$  increases by 0.13 V after polymer-grafted ZnO particle was added into the electrolyte, but the  $I_{sc}$  decreases probably due to the high viscosity of gel A. As a result, the energy transfer efficiency of the solar cell based on gel A decreases to 3.1% compared with the efficiency of 4.0%

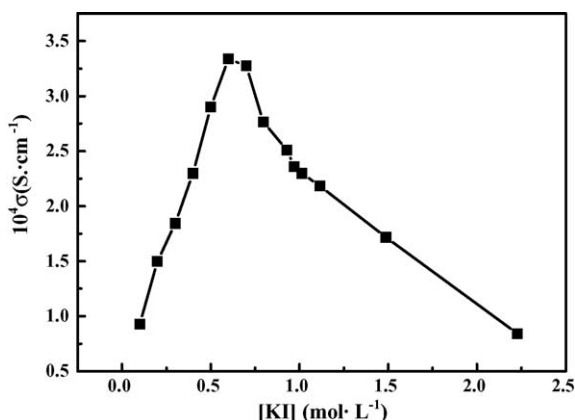


Fig. 2. Plot of conductivity of gel electrolyte with different KI salt concentration.

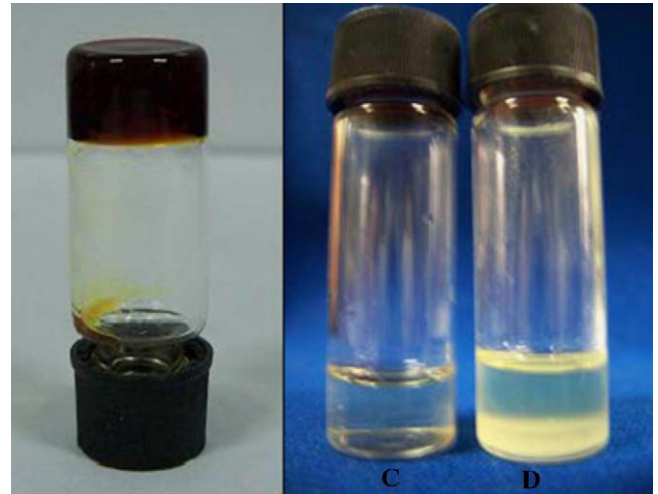


Fig. 3. Left: the photo of the gel A electrolyte. Gel A electrolyte denotes the electrolyte solidified with ZnO(PEG). Right: photos of gel C and gel D after storage at 55 °C for 1000 h.

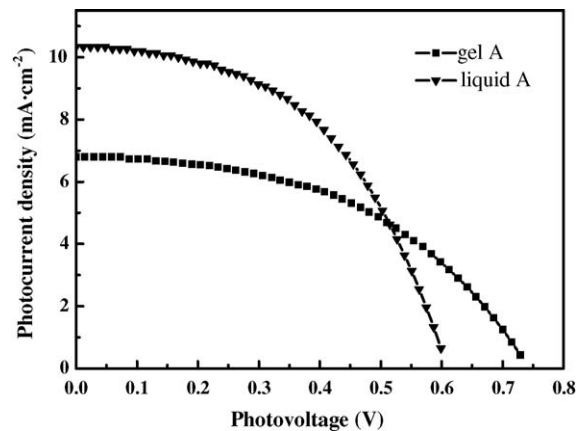


Fig. 4. Photocurrent–voltage curves for dye-sensitized solar cells containing the liquid A and gel A electrolytes.

for the liquid electrolyte. The decrease of efficiency is mainly due to the high viscosity of gel electrolyte.

It has been demonstrated in literatures that addition of 4-*tert*-butylpyridine into the solar cell may increase the voltage output  $V_{oc}$  due to its effect on charge transfer at the semiconductor electrolyte junction [17]. In our experiment, 4-*tert*-butylpyridine was employed as an additive to the electrolyte liquid A and gel A. Its concentration was fixed at  $0.5 \text{ mol L}^{-1}$ . The resulting two kinds of electrolyte were denoted as liquid B and gel B. The  $I$ – $V$  curves of solar cells employing liquid B and gel B are shown in Fig. 5. The electrochemical performance is improved

Table 1  
Electrochemical property of solar cells (under AM1.5 illumination  $75 \text{ mW cm}^{-2}$ , cell active area:  $0.15 \text{ cm}^2$ )

	$I_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	ff	$\eta$ (%)
Liquid A	10.35	0.60	0.49	4.0
Gel A	6.84	0.73	0.47	3.1
Liquid B	15.85	0.62	0.51	6.4
Gel B	9.11	0.74	0.55	5.0

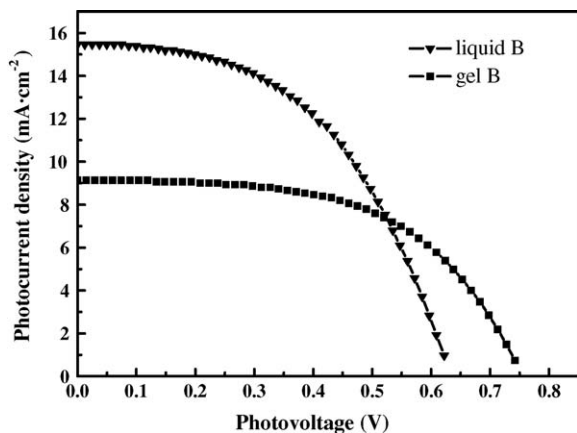


Fig. 5. Photocurrent–voltage curves for dye-sensitized solar cells based on the liquid B and gel B electrolytes.

significantly after 4-*tert*-butylpyridine was added into the electrolyte. Surprisingly the  $V_{oc}$  and  $ff$  is not improved notably in our experiment, while the  $I_{sc}$  value increases remarkably in the presence of 4-*tert*-butylpyridine. The overall conversion efficiency of solar cell based on gel B is improved from 3.1 to 5.0% due to the addition of 4-*tert*-butylpyridine. The same phenomenon was also observed in solar cell based on room temperature molten salt reported by Paulsson et al. [18]. The detailed mechanism is not clarified; it is probably due to lower viscosity and better interfacial contact of the electrolyte after addition of 4-*tert*-butylpyridine. It seems that the effect of 4-*tert*-butylpyridine on the electrode surface is not the primary factor to affect the electrochemical property of solar cells which utilize electrolyte with high viscosity.

### 3.4. Thermostability

To overcome the leakage of liquid electrolyte from the DSC, the most useful way is to solidify liquid electrolyte by dispersing nanoparticles in liquid electrolyte [11–14]; however these nanoparticles are apt to aggregate, and then grow to larger particles. As a result, the efficiency of DSC declines dramatically because the two subphases separate. The thermostability of the gel electrolyte based on the polymer-grafted nanoparticle ZnO(PEG) was evaluated compared with the gel electrolyte solidified with conventional nanoparticle ZnO(Ac). 24 wt% ZnO(PEG) and 10 wt% ZnO(Ac) were, respectively, added into PEG350 containing 0.6 mol L<sup>-1</sup> KI. Iodine was not added into the electrolyte for the convenience of observation. They were denoted as gel C and gel D. Fig. 3 shows the photos of the above gel electrolyte stored at 55 °C after 1000 h. For the conventional ZnO(Ac) nanoparticle modified gel electrolyte, phase separation was clearly observed due to the aggregation of nano-sized ZnO(Ac). The electrolyte solidified by the polymer-grafted nanoparticle still kept transparent, and no phase separation was detected. We speculate that the probability of collision between nanoparticle becomes less after the polymer molecules are modified onto their surface, so thermal stability of polymer-grafted nanoparticle is enhanced compared with the conventional nanoparticle. The excellent thermostability of the

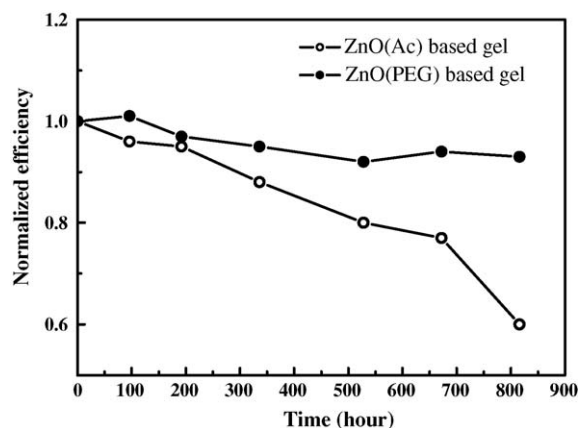


Fig. 6. Normalized device efficiency variation of the dye-sensitized solar cells based on the gel electrolytes modified by ZnO(PEG) and ZnO(Ac) nanoparticles as a function of storage time. The data was obtained once a week after the DSC was stored at 55 °C.

novel gel electrolyte is advantageous to the long-term usage of solar cell. Its transparency will also improve the light harvesting efficiency.

Two different kinds of composite electrolyte solidified, respectively, with 24 wt% polymer-grafted ZnO nanoparticle (gel A) and 10 wt% conventional ZnO(Ac) were employed to fabricate solar cell. The employed liquid electrolyte was composed of 0.6 mol L<sup>-1</sup> KI and iodine in PEGME350, in which the weight ratio between KI and I<sub>2</sub> was fixed at 10:1. These cells were sealed with thermal plastic tape for long-term test. The cells were stored at 55 °C, and the efficiency of these cells were measured once a week. Energy transfer efficiency variances of DSCs containing these two kinds of composite electrolyte are compared in Fig. 6. The DSC based on gel A maintains 93% of its initial efficiency value even under heating at 55 °C for 34 days, while the efficiency of solar cell solidified with ZnO(Ac) particle decreases to 60% of its initial value. The diminishment of quasi-solid-state solar cell based on ZnO(Ac) is most likely related to the phase separation of the gel electrolyte.

## 4. Conclusions

We prepared a stable gel electrolyte by dispersing the polymer-grafted ZnO nanoparticle into liquid electrolyte. The poly(ethylene glycol methyl ether) molecules are strongly connected to ZnO nanoparticles with covalent bond in these nanoparticles. The ion conductivity of the gel electrolyte reaches  $3.34 \times 10^{-4}$  S cm<sup>-1</sup> at 303.15 K under the optimal composition (ZnO(PEG):PEG:KI:I<sub>2</sub> = 19.3:73.3:6.7:0.67 in weight). A quasi-solid-state dye-sensitized solar cell (DSC) based on the polymer-grafted ZnO nanoparticle modified gel electrolyte yields the energy transfer efficiency of 3.1% at AM 1.5 direct irradiation of 75 mW cm<sup>-2</sup> light intensity. Addition of 4-*tert*-butylpyridine into the electrolyte results in dramatically improved  $I_{sc}$  and the overall efficiency is also improved to 5.0%. This gel electrolyte behaves long-term stability compared with the gel electrolyte solidified with conventional nanoparticle ZnO(Ac) in which the phase separation was clearly observed

after storage at 55 °C for 1000 h. The DSC fabricated with this novel gel electrolyte displays better thermal stability than those solidified with the conventional nanoparticle ZnO(Ac), it maintains 93% of its initial efficiency value after storage at 55 °C for 34 days. The technology described in the present work, in which polymer-grafted nanoparticles were used, may also be extended to other polymers to provide a high stable gel electrolyte for DSCs.

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