Ionic gel electrolytes composite with SiO$_2$ nanoparticles for quasi-solid-state dye-sensitized solar cells

Liguo Jin[1] · Taiyang Liu[1] · Chao Wang[1]

Abstract Composite ionic gel electrolytes were facilely prepared by mixing ionic gel electrolytes with SiO$_2$ nanoparticles. The dye-sensitized solar cells (DSSCs) assembled with the composite ionic gel electrolytes exhibit the higher photovoltaic performance and better durability compared to the original DSSCs based on pure ionic gel electrolytes. In particular, the DSSC assembled with the electrolytes containing 0.15 g of SiO$_2$ shows superior J_{SC} (14.4 mA cm^{-2}), V_{OC} (0.67 V), fill factor (0.69) and power conversion efficiency (6.71 %) (measured at AM 1.5, light intensity of 100 mW/cm^2). The electrochemical impedance spectra, SEM and conductivity were used to characterize the composite ionic gel electrolytes.

1 Introduction

Since its invention by O'regan and Grätzel [1], dye-sensitized solar cells have attracted considerable interests due to its low cost and high efficiency [2–4]. DSSCs are composed of a dye-sensitized TiO$_2$ anode electrode, a counter electrode and an electrolyte of I^-/I_3^- redox couple which was sandwiched between the anode and counter electrode. The main working mechanisms of the DSSCs are that dye molecules absorb incident light, which excites electrons in the HOMO to the LUMO. The excited electrons rapidly inject into the matching conduction band of the TiO$_2$. The moving electrons collected on the substrate facilitate the

formation of photocurrent, which reaches the counter electrode through an external circuit simultaneously. Short-circuit current depends on the number of excited dye, the number of electrons injecting TiO$_2$ conduction band, and the transmission loss of charge in the mesoporous film and electrolyte. Open-circuit voltage is the difference between the Fermi level and the Nernst potential of redox couple in the electrolyte of the semiconductor at light irradiation [5].

The electrolyte serves as an important part of DSCCs, not only because of its important role in the regeneration of the oxidized dye but also in the acceleration of the charge transport from the counter electrode to the TiO$_2$ electrode [6]. In short, the property of electrolyte largely determines the performance of DSSCs [7]. Though the liquid electrolyte presents relatively high power conversion efficiency, the problems such as instability at high temperature and the difficulty in sealing of liquid electrolyte prevent it from meeting the requirements for practical application. Recent investigations have focused on quasi-solid electrolytes due to their good thermostability and simple preparation process. Furthermore, employing SiO$_2$ nanoparticles as the gelling agent to prepare quasi-solid electrolytes shows promising photovoltaic performances.

The propyl-methyl-imidazolium iodide (PMII) ionic liquid (IL) with the addition of SiO$_2$ nanoparticles improved the charge transport of I^-/I_3^- redox couple in the electrolyte and consequently increased the efficiency of DSSC up to 20 %, relatively [8]. Moreover, the incorporation of SiO$_2$ in all-solid-state polymer-blend electrolytes may enhance the photocurrent generation of DSSCs. This improvement could be explained by the fact that modification of the polar polymer chains on SiO$_2$ surface can greatly promote the transport of electrolytes and ionic diffusion by improving salt dissociation and inhibiting phase separation [9]. The hybrid polymer electrolytes

✉ Liguo Jin
jinliguo@hrbust.edu.cn

1 The School of Material Science and Engineering, Harbin University of Science and Technology, Harbin 150040, People's Republic of China

comprised of the SiO$_2$ nanofiber were prepared for DSSCs. The results exposed that appropriate SiO$_2$ nanofiber contributed to increasing the ionic conductivity and boosting the interface contact between the electrolytes and TiO$_2$ layer. Moreover, it greatly prolonged the electron lifetime and exhibited minor interfacial impedance [10].

Herein, The quasi-solid-state composite ionic gel electrolytes with SiO$_2$ nanoparticles we prepared could reduce leakage of the liquid electrolyte and provide with better interface bonding between the electrolyte and TiO$_2$ layer. The quasi-solid-state dye-sensitized solar cells assembled with the composite ionic gel electrolytes yielded a maximum PCE of 6.71 % under AM 1.5 conditions.

2 Experimental procedure

2.1 Materials

3-Methoxy propionitrile (98 %, Sinopharm Chemical Reagent Co. Ltd), 1-methylbenzimidazole (99 %, Aldrich), anhydrous iodine (99.8 %, Solaronix S.A), lithium Iodide (99.9 %, Solaronix S.A), N3 dye (cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II), Solaronix S.A) and 1-propyl-3-methylimidazolium iodide (99 %, Aldrich) were all used without further purification. Moreover, titanium(IV) isopropoxide, SiO$_2$ nanoparticles (15 nm) and tetrabutyl titanate were obtained from Sinopharm Chemical Reagent Co. Ltd. Dodecylbenzenesulfonic acid (98 %), P25 (TiO$_2$) and polyvinylalcohol (PVA, $M = 20,000$, 99 %) were purchased from Aladdin.

2.2 Preparation of the ionic gel electrolytes composite with SiO$_2$ nanoparticles

0.1 M lithium iodide, 0.05 M anhydrous iodine and 0.45 M 1-methylbenzimidazole were dissolved in the solution of mixed volume ratio (1:2) of 1-propyl-3-methylimidazolium iodide and 3-methoxy propionitrile as the precursor electrolyte. The electrolyte precursor was dispersed by ultrasonic method at room temperature for 1 h to obtain a red-brown, uniform solution. Then, 0.05, 0.15 and 0.30 g of SiO$_2$ nanoparticles were dispersed in 5 ml of absolute ethanol, respectively. Subsequently, 1.5 ml of the ionic liquid was added to the above mixed ethanol solution. Stirring, ultrasonic, rotary evaporation were performed sequentially until a red-brown composite ionic gel electrolyte was obtained.

2.3 Assembly of the dye-sensitized solar cells

The cleansed transparent conducting substrate was coated by spin-coating tetrabutyl titanate sol on a TiO$_2$ compact layer (400 nm). After drying at 125 °C for 30 min, a mesoporous TiO$_2$ layer of 9–11 μm in thickness was deposited by the high-voltage electrohydrodynamic equipment (EHD) using the nanocrystalline TiO$_2$ paste. The detailed preparation process of TiO$_2$ paste can be found elsewhere [11]. In short, 1 g of PVA solution (33.3 %) and 4 ml of ethanol were dissolved in 5 ml of the deionized water. Subsequently, 0.04 g of dodecylbenzenesulfonic acid and 0.6 g of P-25 TiO$_2$ powder were dispersed in the above solution by ultrasonic method for 20 min. After the mesoporous TiO$_2$ layer was annealed at 450 °C for 60 min and cooled down to the room temperature, the prepared TiO$_2$ layer was immersed in the absolute ethanol solution of dye N3 (0.3 mM) for 24 h. Finally, the sensitized photoanode was infiltrated with the prepared electrolytes and the platinum was deposited on top of the device to form the counter electrode.

2.4 Characterization

In order to characterize the performance of the DSCC, a field emission scanning electron microscopy (FE-SEM, FEI Sirion200, Philips, Dutch) was taken to present surface and cross-sectional images of the electrolytes on dye-sensitized TiO$_2$ film. Ionic conductivity, photocurrent density–voltage (I–V curve) and electrochemical impedance spectroscopy (EIS) were measured by an electrochemical station (RST5000, Zhengzhou) equipped with simulated solar illumination (NBET, Solar-500, Beijing) from a 0.2 cm^2 active area under the light intensity of 100 mW/cm^2. The data of photoelectrical parameters were averaged from eight devices. The ionic conductivity was estimated by the equation $\sigma = L/(AR_b)$, where R_b is obtained from the intercept of the Nyquist plot with the real axis in high frequency, A is the area of electrode layer, and L is the thickness of electrode layer [12].

3 Results and discussion

3.1 Mobility and distribution of the composite ionic gel electrolytes on dye-sensitized TiO$_2$ film

Figure 1 shows the photos of the composite ionic gel electrolytes in the states of gel (Fig. 1a) and solution (Fig. 1b). The electrolytes present a certain viscosity in the state of gel. However, the electrolytes with liquid characteristics show a certain viscous flow along the glass tube after stirring for 2 min. Liquid electrolyte helps to improve the physical diffusion of I^-/I_3^- ions, reduce electron recombination and enhance the short-circuit current [9].

Meanwhile, the flow capacity of the electrolyte also affects its penetrating and filling behavior in the mesoporous TiO$_2$ layer and thereby impacts on the contact
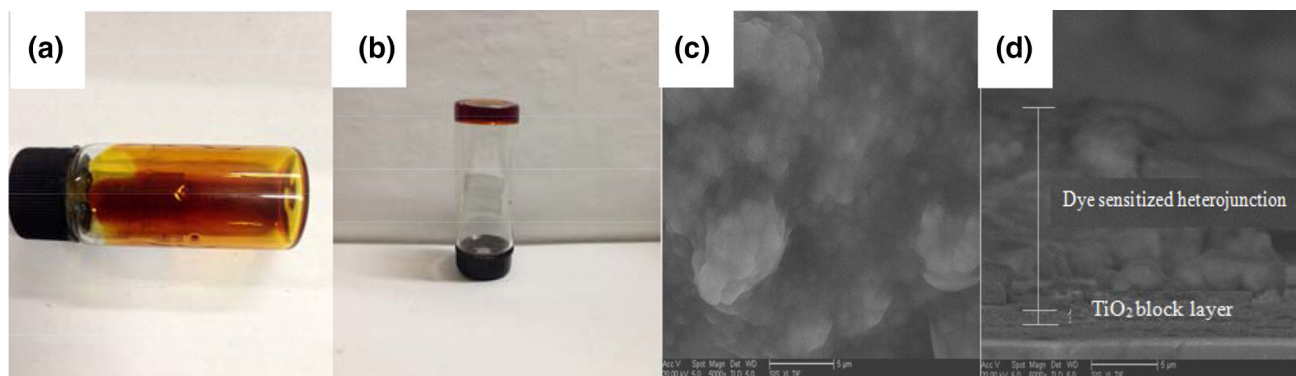
Fig. 1 Morphologies of the composite ionic gel electrolytes before (**a**) and after (**b**) stirring. Distribution of electrolytes on dye-sensitized TiO$_2$ film: surface (**c**) and cross-sectional (**d**) SEM images
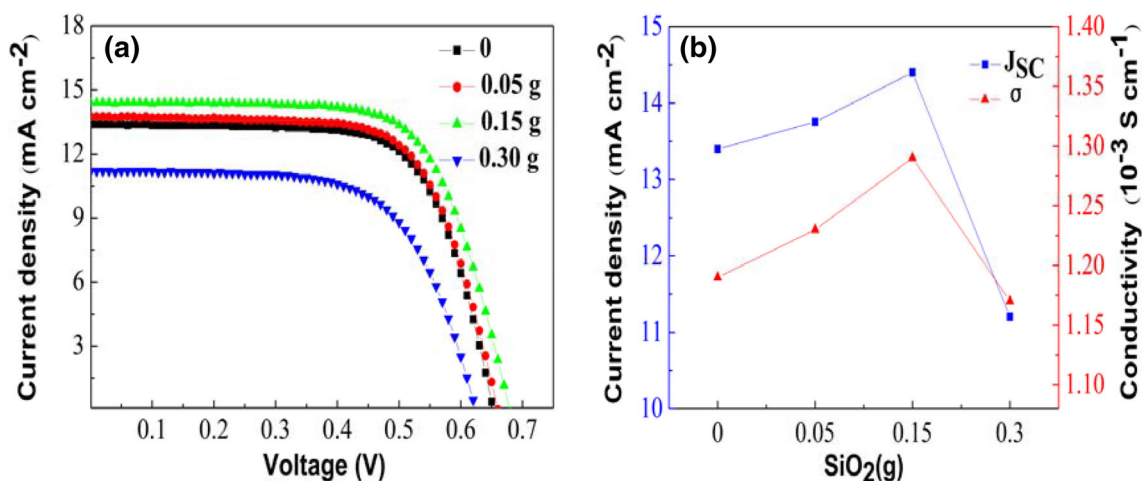

Fig. 2 a Photocurrent density–voltage characteristics of DSCCs with electrolytes containing 0, 0.05, 0.15 and 0.30 g of SiO$_2$ nanoparticles. **b** Dependence of J_{SC} and conductivity on the SiO$_2$ loading amount

interface between electrolytes and mesoporous TiO$_2$ layer [13]. Figure 2c clearly shows a smoother surface morphology of electrolytes containing 0.15 g of SiO$_2$ nanoparticles on dye-sensitized TiO$_2$ film. The homogeneous and continuous inner structure of TiO$_2$ layer can be seen from the cross-sectional SEM images (Fig. 2d). It turned out that the electrolyte after stirring is beneficial for filling into the nanoporous TiO$_2$ layer. Meanwhile, the electrolytes are self-assembled into the nanopores existing in the interface between the TiO$_2$ layer and the counter electrode, and the electrolytes filled and perfused in the nanopores facilitate the transfer of the redox couple I^-/I_3^- in the network path among the nanopores [14, 15].

3.2 Influence of SiO$_2$ nanoparticles on photoelectrical parameters

Figure 2a shows the voltage–current curve of DSSCs with electrolytes containing different qualities of SiO$_2$ nanoparticles. The corresponding photoelectrical parameters of

DSSCs are listed in Table 1. It is clearly indicated that the electrolyte containing 0.15 g SiO$_2$ exhibits the highest η (6.71 %) upon an irradiation of AM 1.5 (100 mW/cm^2) among the four types of electrolytes. It was proposed that short-circuit current depends on the efficiency of electron generated by dye molecules injecting to TiO$_2$ films and reverse recombination efficiency among the electronics after injecting to TiO$_2$ films, electrolyte and the oxidized dye molecule. The reason may be that the addition of the SiO$_2$ nanoparticles contributes to improving interface bonding between the electrolytes and the dye/TiO$_2$.

The outstanding interface bonding can enhance the charge transfer and decrease the electron recombination as a feedback, which would prompt electron injection into the TiO$_2$ films and consequently improve the J_{SC} [10]. Furthermore, the J_{SC} and ion conductivity of the electrolytes are proportional to the amount of SiO$_2$ nanoparticles as shown in Fig. 2b. The explanation is that imidazolium cations are adsorbed on the surface of the nanoparticles, while the adsorbed imidazolium cations are encircled with

Table 1 Photoelectrical parameters and simulated EIS data of DSSC based on composite ionic gel electrolytes with various qualities of SiO_2 nanoparticles

SiO_2 (g)	J_{SC} (mA cm^{-2})	V_{OC} (V)	ff	η (%)	R_{ct1} (Ω)	R_{ct2} (Ω)	R_w (Ω)	τ (ms)
0	13.4	0.65	0.697	6.08	3.072	18.75	1.22	71.4
0.05	13.75	0.66	0.685	6.22	3.10	15.34	1.34	82.3
0.15	14.4	0.67	0.695	6.71	3.16	14.49	3.58	98.4
0.30	11.2	0.62	0.653	4.54	3.022	18.96	6.25	46.6

continuous chains of I^- and I_3^- anions by electrostatic interaction according to the ion-exchange mechanism and electron transport path [8]. Thus, the structure of such a composite ionic gel electrolytes is in favor of enhancing the ionic conductivity which generates efficient electron transfer to increase the J_{SC} [16].

When the quantity of SiO_2 nanoparticles increased to 0.30 g, the excessive content of SiO_2 resulted in significantly increased viscosity of the electrolytes. The aggregation of SiO_2 nanoparticles hampered physical diffusion of I^-/I_3^- ions and consequently resulted in higher recombination and lower electron collection efficiency.

The slight rise of the V_{OC} values by increasing SiO_2 with the absorbed amount of liquid electrolyte is correlated. The reason is that the SiO_2 nanoparticles can decrease the extent of direct contact between the TiO_2 layer/electrolytes. A high interfacial potential barrier between TiO_2 and SiO_2 can hinder the interface reaction between TiO_2 and I_3^- ions, which can result in the suppression of back electron transfer from the conduction band of TiO_2 to I_3^- ions in the electrolyte to reduce electron recombination. Quasi-Fermi level of conduction band electrons in TiO_2 layer (($E_{fermi})_{TiO2}$) was increased [17, 18]. As a result, the open-circuit voltage of DSSC is increased due to the difference between the quasi-Fermi level of conduction band electrons in TiO_2 layer, and Nernst potential ($E_{R/R}^-$) of I^-/I_3^- in electrolyte is improved [19]. The V_{OC} can be obtained via the equation: $V_{OC} = [(E_{fermi})_{TiO2} - E_{R/R}^-]/q$.

3.3 Electrochemical impedance spectroscopy analyses

Figure 3a, b shows the Nyquist and Bode plots of DSSCs equipped with various quantities of SiO_2 in the ionic liquid electrolyte measured under the light intensity (100 mW/cm^2) [20, 21]. The equivalent circuit model fitted for the impedance spectra of the DSSCs is shown in the insert of Fig. 3a. The Nyquist plots usually exhibit three semicircles which are attributed to charge transfer at the counter electrode (R_{ct1}), the electron transfer at the interface between the electrolytes and TiO_2 layer (R_{ct2}) and the Warburg diffusion of I^-/I_3^- in the electrolyte (W_s) [22]. The R_{ct2} of DSSCs decreases after the introduction of 0.05–0.15 g of SiO_2 nanoparticles into ionic liquid electrolyte. The decrease is related to the addition of SiO_2

nanoparticles in ionic liquid electrolyte, which improves the integration in the interface between TiO_2/electrolyte/counter electrode [23, 24]. An excellent interface contact facilitates electron transfer from counter electrode to electrolyte and thus decreases electron recombination and increases J_{SC}.

The medium-frequency semicircle (100–1 Hz) is associated with charge transport at the interface between electrolytes and TiO_2 film, corresponding to the Bode phase plots as shown in Fig. 3b. The middle characteristic frequencies are inversely proportional to the electron lifetime ($\omega = \tau^{-1}$) in Table 1 [25]. The middle-frequency feature shifted to a lower frequency, indicating that the electron lifetime increased after the addition of SiO_2. This red shift of features indicates that SiO_2 nanoparticles not only reduce the electron recombination and prolong the electron lifetime but also promote the charge transfer in the electrolyte and suppress the dark reaction [12, 17].

3.4 The durability test of the DSSCs employed composite ionic gel electrolytes

The photoelectrical parameters of DSSC employed ionic gel electrolyte with or without the SiO_2 after 10 days of testing are shown in Fig. 4. The DSSCs were not sealed or otherwise protected. Photoelectric conversion efficiencies (η) of DSSCs using ionic liquid electrolyte decreased to 26 % while the η of cells containing 0.15 g SiO_2 only decreased by 12 %, which indicates that the addition of SiO_2 nanoparticles is beneficial to improving cell stability.

4 Conclusions

Composite ionic gel electrolytes were fabricated by mixing ionic gel electrolytes with SiO_2 nanoparticles. The DSSCs assembled with the composite ionic gel electrolytes containing 0.15 g SiO_2 showed a power conversion efficiency of 6.71 % ($J_{SC} = 14.4$ mA cm^{-2}, $V_{OC} = 0.67$ V, $ff = 0.695$), superior to that of the pure ionic liquid electrolyte of only 6.08 % ($J_{SC} = 13.4$ mA cm^{-2}, $V_{OC} = 0.65$ V, $ff = 0.697$). Another significant merit of our DSSCs is that composite ionic gel electrolytes have a superior capacity of penetrating and filling in mesoporous TiO_2 layer and provide with better interface bonding between the electrolyte and TiO_2 layer.
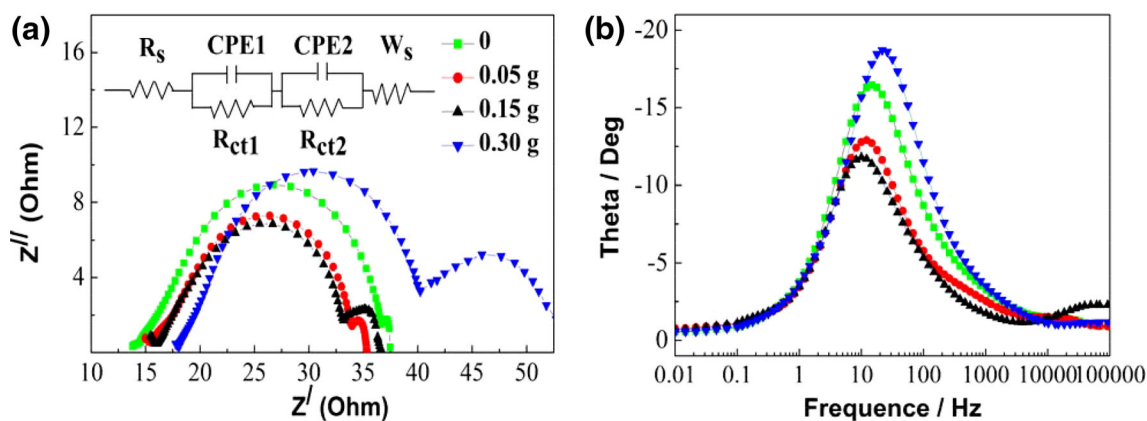
Fig. 3 Impedance spectra of DSSCs employed various quantities of SiO₂ in the ionic liquid electrolyte. **a** Nyquist plots and **b** Bode phase plots
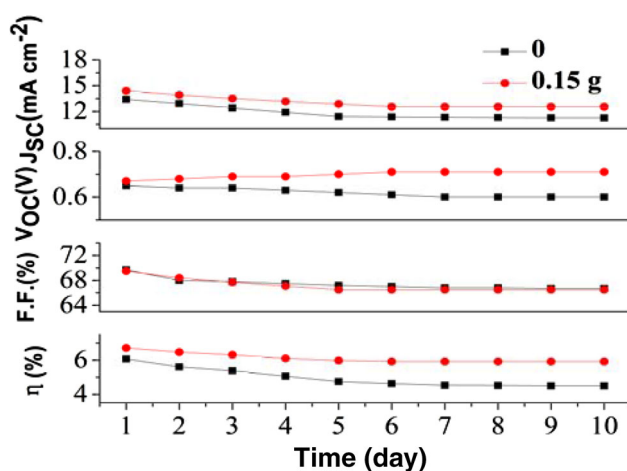

Fig. 4 Durability data of the DSSCs employed composite ionic gel electrolytes

The addition of SiO_2 is also beneficial to the increase in short-circuit photocurrent by building good contacts in the interfaces of TiO_2/electrolyte/counter electrode. At the same time, the addition of SiO_2 has little influence on the open-circuit voltage and fill factor. The efficiency of DSSCs using composite ionic gel electrolytes declines by about 12 %, superior to that of the pure ionic liquid electrolyte by 26 % under the same condition. The durability test indicates that the addition of SiO_2 in electrolytes could improve the stability of the DSSCs.

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