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Ionic liquid-tethered Graphene Oxide/Ionic Liquid Electrolytes for Highly Efficient Dye Sensitized Solar Cells

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ABSTRACT

Ionic liquid-tethered graphene oxide (IL-GO) are prepared by tethering 1-(3-aminopropyl)-3-methylimi-dazolium bromide to graphene oxide (GO), and followed by anion-exchange with bis(trifluoromethanesulfonyl)imide ions (TFSI$^-$). Environmental friendly ionic liquid-based composite electrolyte for dye sensitized solar cells (DSSCs) without volatile organic solvents is prepared from IL-GO and 1-propyl-3-methylimidazolium iodide (PMII). Incorporation of proper amount of IL-GO significantly increased the conductivity of the electrolyte, the open circuit voltage, the short circuit current density and the conversion efficiency of DSSCs. The dye-sensitized solar cells (DSSCs) containing 4 wt% of IL-GO composite electrolytes show an overall power conversion efficiency of 7.04% under simulated AM 1.5 solar spectrum irradiation at 100 mW cm^{-2}. These results indicate that the DSSCs based on IL-GO/IL composite electrolytes could overcome the drawbacks of volatile liquid electrolytes, and offer a feasible method to fabricate DSSCs in future practical applications.

1. Introduction

Dye-sensitized solar cells (DSSCs) are attracting both academic and industrial interests since it was first reported in 1991 by Gratzel and O'Regan [1]. Compare with the traditional silicon solar cells, DSSCs show higher efficiency, lower fabrication cost, much easier of fabrication and much more environmentally friendly operation [2–5].

A traditional DSSC is composed of a dye-sensitized TiO_2 electrode, electrolyte and a Pt counter electrode. The electrolyte which transfers charge from the counter electrode to the dye is one of the key components of DSSCs. Traditional organic solvent based electrolytes are advantages in low viscosities and high dielectric constant. However, the evaporation of the volatile organic solvent has been one of the major problems limiting the long-term applications of DSSCs. Thus, p-type inorganic semiconductor [4] and solvent-free polymer electrolytes incorporating triiodide/iodide as a redox couple [5,6] were introduced to substitute for the volatile organic electrolytes. However, cells with poor efficiency was obtained due to the imperfect filling of the dye adsorbed porous TiO_2 film by p-type semiconductors or polymers. Furthermore, the carrier diffusion lengthwas limited by the the low conductivity of polymers [7].

Ionic liquids (ILs) which are mostly room-temperature organic salts, have attracted much attention due to their negligible vapor pressure, excellent thermal stability, broad electrochemical potential window and high ionic conductivity. As ideal electrolyte materials, ionic liquids have been used for preparation of high-temperature proton exchange membrane [8,9] and alkaline anion exchange membrane [10]. Recently, ILs-based electrolytes have been developed for DSSCs as a replacement for traditional organic solvent based electrolytes [11–13]. Unfortunately, compare with the DSSCs containing conventional organic solvent-based electrolyte, the DSSCs with ILs-based electrolytes show lower conversion efficiency [14]. It has been demonstrated that a relatively high conductivity and rapid diffusion of redox couple through the electrolytes are critical to the solar cell performance [15]. The conductivity of IL-based electrolytes could be enhanced by incorporation of inorganic nanocomponents such as SiO_2, TiO_2 and carbon nanotube due to the increased number of mobile defects induced in the electrolytes [16–18]. Furthermore, the inorganic nanocomponents with high surface/volume ratio favor the conductivity of ionic liquid-based electrolyte membranes [9].

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More recently, graphene has attracted much attention due to their high thermal stability, excellent mechanical, electronic properties and high surface/volume ratio [19–21]. Brennan. et al. [22] reported that the efficiency of DSSCs has been significantly improved by the addition of small amounts (1.0 wt.%) of graphene sheets into IL-based electrolytes. In general, the uniformly dispersed nanomaterials in electrolytes could bring beneficial contributions to the short circuit current density (J_{sc}) and long stability of the devices [18,23]. However, agglomerate of the inorganic nanomaterials including graphene sheets was commonly observed [24]. Therefore, the agglomeration of graphene in the electrolytes still need to be overcome before their applications can be realized. Proper surface functionalized inorganic nanomaterials have relatively high compatibility with the ionic liquids in the preparation of the corresponding electrolyte for DSSC [24]. Compared with graphene, graphene oxide (GO) has more attractive features like simple preparation, non-toxic, environmentally friendly, low-cost, even have oxygen-containing functional groups such as hydroxyl, carboxylic acid, and can be easily chemical modification [25–27].

Here, we report the fabrication of high-performance DSSCs using IL-GO/IL composite electrolyte as a replacement for traditional organic solvent based electrolytes. IL-GO was synthesized via a nucleophilic ring-opening reaction between the epoxy groups of GO and 1-(3-aminopropyl)-3-methylimi-dazolium bromide ($IL-NH_2$), then anion-exchange with Lithiumbis (trifluoromethanesulfonyl) imide (LiTFSI). The synthesized IL-GO could be well dispersed in IL to form a homogenous electrolytes. The influence of IL-GO content on the DSSC properties was systematically investigated.

2. Experimental Section

2.1. Materials

Flaky graphite powder (45 μm, Qingdao Huatai Lubricant Sealing S&T China), sulfuric acid (98%), potassium hydroxide, ethyl acetate, 1-iodopropane, 1-methylimidazole, 3-bromopropylamine hydrobromide and 4-tert-butylpyridine (TBP) were purchased from Aladdin (Shanghai). TiO_2 nanoparticles (Titanium (IV) oxide, T-20 nm), H_2PtCl_6 (99.99%) and iodine were obtained from Sigma-Aldrich. Lithiumbis (trifluoromethanesulfonyl) imide (LiTFSI) were purchased from Alfa Aesar and used as received. N719 dye, Surlyn (ionomer films of 25-μm thick) and FTO conducting glass (resistance of 25 Ω/square, transmittance of 85%) were purchased from Dalian Rainbow Solar Technology Development Co Ltd., Dalian, China. All reagents were of analytical grade and were used as received unless otherwise stated.

2.2. Synthesis of 1-propyl-3-methylimidazolium iodide (PMII)

PMII was synthesized according to the previous report [28]. Firstly, 8.5 g (0.05 mol)1-iodopropane and 20 ml ethyl acetate were placed in a round bottom flask and using a magnet stirred in an ice water bath, 4.1 g (0.05 mol)1-methylimidazole was then added into this mixture and stirred for 2 h at 0 °C. The reaction bath was heated to room temperature and then stirred for another 48 h. The resultant viscous oil was washed with ethyl ether three times, and then dried in dynamic vacuum at 80 °C for 24 h before use. ^1H NMR (400 MHz, D_2O): δ: 8.64 (S, 1H), 7.39 (S, 1H), 7.34 (S, 1H), 4.07 (t, 2H), 3.80 (S, 1H), 1.82 (m, 2H), 0.83 (m, 3H).

2.3. Synthesis of 1-(3-aminopropyl)-3-methylimi -dazolium bromide ($IL-NH_2$)

$IL-NH_2$was synthesized as follows [29]: a mixture containing 2.70 g (0.033 mol)1-methylimidazole and7.33 g (0.033 mol) 3-bromopropylamine hydrobromide in ethanol (20 mL) was stirred at 50 °C for 24 h under an argon atmosphere. The resultant viscous oil was washed with ethyl ether three times and then dried in dynamic vacuum at room temperature for 24 h. ^1H NMR (400MHz, D_2O): δ: 8.72 (S, 1H), 7.46 (S, 1H), 7.40 (S, 1H), 4.28 (t, 2H), 3.02 (t, 2H), and 2.23 (m, 2H).

2.4. Preparation of ionic liquid-tethered graphene oxide (IL-GO)

Graphene oxide (GO) was prepared following the Hummers method [30,31]. Briefly, 2.00 g graphite powder and 2.00 g $NaNO_3$ were placed in a flask. 96 mLH_2SO_4 was added at 0 °C under vigorous stirring. Then, 12.00 g of $KMnO_4$ was gradually added into the mixture. The obtained mixture was first stirred at 0 °C for 2 h and then at 35 °C for 2 h. 80 mL Distilled water was subsequently slowly dropped into the resulting solution to dilute the mixture in 30 min. Then 200 mL distilled water was added, followed by 15 mL H_2O_2 (30%), the residual permanganate and manganese dioxide were reduced to colorless soluble manganese sulfate by H_2O_2. Finally, the GO deposit was repeatedly washed with distilled water, centrifugation, removal of the supernatant liquid, until the pH was close to neutral and then collected.

IL-GO was synthesized by an epoxide ring-opening reaction between GO and $IL-NH_2$. Firstly, 50 mg $IL-NH_2$ was added into 50 mL of GO/water (0.5 mg/mL) solution, and 50 mg KOH was added into the above turbid mixture, the mixture was stirred and ultrasonicated to obtain a homogeneous solution. The mixture solution was stirred and reflux at 80 °C for 24 h. The solid product was centrifuged and washed with ethanol to remove the unreacted$IL-NH_2$.The obtained solid product was dispersed in 50 ml water (0.5 mg/mL), and then100 mg LiTFSI was added into the solution. The mixture was stirred at 50 °C for 8 h. The solid product IL-GO was centrifuged and washed with water to remove the unreacted LiTFSI.

2.5. Preparation of IL-GO/IL electrolytes

The liquid electrolyte was composed of 1 M PMII, 0.1 M I_2, 0.2 M LITFSI, 0.5 M TBP, different amount of IL-GO was added into the mixture and stirred at 60 °C for 6 h, then the homogeneous IL-GO/IL electrolytes were obtained.

2.6. Fabrication of DSSCs

Using a conventional process to fabricate the DSSCs [22,32,33], TiO_2 working electrodes were prepared on the cleaned FTO coated glass substrates, the FTO glasses were sticky with adhesive tape on both parallel edges to control the thickness of the TiO_2 films, and were annealed at 500 °C for 30 min to ensure good electrical contact between the TiO_2 films and the FTO substrates. Dye adsorption was carried out by immersing theTiO_2 working electrodes in N719 dye solution (0.5 mM in ethanol) at room temperature for 24 h, then the TiO_2 electrodes were rinsed with ethanol and dried under nitrogen flow. The Pt counter electrode was prepared by dripping a drop of 10 mM H_2PtCl_6 ethanol solution placed onto FTO glass substrate, followed by annealed at 450 °C for 30 min. DSSCs were fabricated by sandwiching IL-GO/IL electrolytes between dye-sensitized TiO_2 working electrode and Pt counter electrode, which were using a sheet of a thermoplastic frame (25-μm thick, Surlyn) as a spacer between the two electrodes. The typical active area of the cell was 0.2025 cm^2.