



Low-Dose Imidazolium Cation Grafted Polymeric Nanotubes for Quasi-solid-state Dye-sensitized Solar Cells



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ABSTRACT

Poly(divinylbenzene-co-chloromethylstyrene) (poly(DVB-co-VBC)) nanotubes (PDVBVBC-NT) and imidazolium surface functionalized poly(DVB-co-VBC) (Im-PDVBVBC-NT) are synthesized by cationic polymerization and utilized as the gelators for ionic liquid based gel electrolytes. Compared with the synthesized pristine PDVBVBC-NT, Im-PDVBVBC-NT (a gelator dose as low as 1 wt%) based gel electrolytes show higher ionic conductivity and diffusion coefficient. The fabricated DSSCs based on Im-PDVBVBC-NT gel electrolyte show a power conversion efficiency of 4.9% and 5.5% under a simulated air mass 1.5 solar spectrum illumination at 100 mW cm⁻² and 50 mW cm⁻², respectively. Furthermore, Im-PDVBVBC-NT based DSSCs show better long-term stability than that with ionic liquid electrolyte, which indicated that Im-PDVBVBC-NT based gel electrolytes could overcome the leakage problems of the cells with pure ionic liquid electrolytes.

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1. Introduction

Dye-sensitized solar cell (DSSCs) have been considered as a new type of solar cells which could replace traditional silicon-based solar cells with their charming traits of high-efficiency, easy-handling fabrication and low production cost [1]. Recently, photoelectric conversion efficiency as high as 13% has been obtained with organic solvent liquid electrolyte [2]. However, the leakage and the evaporation of liquid electrolyte may lead to the decay in the cell performance during the long-term operation. To overcome these drawbacks, several attempts, including p-type semiconductors [3], organic and inorganic hole conductors [4,5], gel and polymer electrolytes [6–16], have been applied as the alternatives to liquid electrolytes. Among the studies reported, quasi-solid-state polymer electrolytes have attracted extensive attentions due to their good contact with the electrodes [17–19]. However, in most cases, volatile organic solvents were used as the plasticizer for the preparation of polymer gel electrolytes, which still gives rise to potential problems, such as flammability and high-temperature instability [20–24].

Polymeric ionic liquids (poly(ILs), polymers formed from IL monomers) are a type of polymers that combine both the novel

properties of ionic liquids and improved mechanical durability and dimensional control after polymerization. A series of poly(ILs) have been recently synthesized and applied as the gelators for gel electrolytes. In general, good long-term stability of the devices could be obtained [25–28].

On the other hand, one-dimensional nanomaterials have attracted growing interest in recent years for both fundamental research and practical applications [29,30]. Among the nanomaterials studied, carbon nanotubes (CNTs) were considered as one of the most promising materials for electrochemistry applications due to their high thermal stability, mechanical strength and excellent electronic properties. Synthesis of CNT-based gel electrolytes for quasi-solid-state DSSCs have been recently studied by several groups [18,31–33]. Though impressive device performances were achieved, several drawbacks, such as high CNT amount (as high as 40 wt%) [33] and (or) complex gelation process still need to be overcome [18]. Therefore, polymeric nanofibers (or nanotubes) have been attracting growing interest due to their easy control in microstructures and compositions [34,35].

The aim of this work is to fabricate polymeric nanofiber (or nanotube) based gel electrolyte for quasi-solid-state DSSCs. Here, poly(divinylbenzene-co-chloromethylstyrene) (poly(DVB-co-VBC)) nanotubes (PDVBVBC-NT) and imidazolium cations functionalized poly(DVB-co-VBC) (Im-PDVBVBC-NT) were synthesized. The synthesized PDVBVBC-NT and Im-PDVBVBC-NT were dispersed in room temperature ionic liquid (IL) to form

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quasi-solid-state gel electrolytes. Gelator dose as low as 1 wt% of Im-PDVBVBC-NT could form stable ionic liquid gel electrolytes, which displayed better long-term stability than those with conventional ionic liquid electrolytes, indicating that IL/Im-PDVBVBC-NT gel electrolytes are promising candidates for solar cells with good durability.

2. Experimental

2.1. Materials

Iodoethane, 1-iodopropane, 1-methylimidazole, Lithium iodide, n-heptane, 4-tert-butylpyridine (TBP), divinylbenzene (DVB), chloromethylstyrene (VBC), boron trifluoride-ether complex (BFEE) were purchased from Alfa Aesar and used as received. H_2PtCl_6 was purchased from Aldrich. 1-Propyl-3-methylimidazolium iodide (PMII), and 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide (EMITFSI) were synthesized according to the previous report [36]. Cis-Bis(isothiocyanato) bis(2,20-bipyridyl-4,40-dicarboxylato) ruthenium (II) ($[\text{RuL}_2(\text{NCS})_2]$) was purchased from Solarnix SA (Switzerland) and used without further purification.

2.2. Synthesis of pristine polymer nanotube (PDVBVBC-NT)

The poly(DVB-co-VBC) nanotubes were synthesized according to the literature [37]. Typically, a given amount (for example 15 mg) of BFEE was added into 120 g of n-heptane containing 1.2 g (9.2 mmol) DVB and 1.2 g VBC (7.9 mmol) under stirring to initiate the cationic polymerization at 25 °C for 15 min. The polymerization was terminated by pouring into ethanol. The samples were filtered and washed with ethanol to remove residual initiator and monomer. The obtained nanotubes were finally dried under vacuum at 60 °C for 24 h. Elemental analysis Found: C, 84.15%; H 7.06%; N 0%.

2.3. Synthesis of Im-PDVBVBC-NT

A mixture containing poly(DVB-co-VBC) (1 g) and N-methylimidazole (1 g) in 25 ml DMF was sonicated for 5 min and then stirred at 80 °C for 24 h. The product was concentrated and washed with ethanol several times to thoroughly remove physically absorbed N-methylimidazole. Then the precipitate denoted as Im-PDVBVBC-NT was dried in a vacuum oven at 60 °C overnight to remove the residual solvent. Elemental analysis Found: C, 68.64%; H 7.19%; N 5.67%.

2.4. Preparation of electrolytes

Ionic liquid electrolyte composed of 0.1 M I_2 , 0.5 M TBP, 0.1 M LiI, PMII/EMITFSI (13:7, v/v) was stirred at room temperature before the device fabrication. Then 1 wt% PDVBVBC-NT or Im-PDVBVBC-NT was added into the liquid electrolyte and stirred at 70 °C to form a quasi-solid-state gel electrolyte. The devices based on the ionic liquid electrolyte, PDVBVBC-NT gel electrolyte and Im-PDVBVBC-NT gel electrolyte were denoted as cell A, cell B and cell C, respectively.

2.5. Device fabrication

The cleaned FTO glass was covered at perforated adhesive tape to control the thickness and the area of mesoporous TiO_2 film (about 0.283 cm^2). A 10- μm -thick film of 20-nm-sized TiO_2 particles was deposited onto the FTO glass electrode by the doctor-blade technique. The film was dried at 125 °C for 5 min. Then, a second 5- μm -thick layer of 200-nm light scattering anatase particles

was coated on the top of the first TiO_2 layer. The resulting TiO_2 films were annealed at 500 °C for 30 min. After cooling to 80 °C, the obtained TiO_2 electrode was immersed in 0.3 mM solution of $[\text{RuL}_2(\text{NCS})_2]$ in acetonitrile and tertbutyl alcohol (v/v = 1:1) at room temperature for 24 h. Afterward, the dye-coated TiO_2 electrode was washed with anhydrous ethanol and dried with nitrogen stream and used as photoelectrode. To prepare the Pt counter electrode, two drops of 5 mM H_2PtCl_6 in ethanol were placed onto the cleaned FTO glass substrate, followed by drying and annealing at 400 °C for 15 min.

DSSCs were fabricated by sandwiching gel electrolytes between a dye-coated TiO_2 photoelectrode and a Pt counter electrode, which were separated by a 25 μm thick hot melt ring (Surlyn, Dupont) and sealed by heating.

2.6. Characterization and Photoelectrochemical Measurements

Fourier-transform infrared (FT-IR) spectra were recorded on a ProStar LC240 spectrometer in the range of 4000–400 cm^{-1} . The viscosity measurements were carried out on a viscometer (Haake® Rheo Stress 6000 Rotational Rheometer, Germany) using a cone-plate geometry. Tests at constant shear rate were performed in strain-controlled mode. All experiments were performed at $T = 25$ °C. A TecnaiG 220 transmission electron microscopy (TEM) and a FEI-quanta 200F scanning electron microscope (SEM) were used to determine the microstructure of samples. The conductivity of the electrolytes was characterized in an ordinary cell composed of Teflon tube and two identical stainless steel electrodes (diameter of 1 cm) on a CHI660c electrochemical workstation at room temperature, using the AC impedance method over the frequency range 1 Hz – 1 MHz. The conductivity was calculated using the following equation:

$$\sigma = \frac{1}{RS} \quad (1)$$

where σ is the conductivity in S cm^{-1} , R is the ohmic resistance of the electrolyte, l is the distance between two electrodes, and S is the area of the electrodes [18].

Steady-state voltammetry was tested in a conventional photoelectrochemical cell equipped with a radius of 5.0 μm platinum ultramicroelectrode (CHI107) as the working electrode, and a platinum foil as a counter electrode and reference electrode, respectively. The apparent diffusion coefficient of triiodide ($\text{D}_{\text{app}}(\text{I}_3^-)$) was calculated from the anodic and cathodic steady-state I_{ss} by using the following equation:

$$I_{\text{ss}} = 4nrFCD_{\text{app}} \quad (2)$$

where n is the number of electrons per molecule, F is the Faraday constant, r is the radius of the ultramicroelectrode, and C is the bulk concentration of the electroactive species [38].

Electrochemical impedance spectra (EIS) of the devices were carried out on a CHI660c electrochemical workstation using the AC impedance method at the forward bias voltage for the impedance measurement was -0.70 V and the frequency ranged from 0.01– 10^5 Hz under dark condition and the amplitude is 5 mV.

The photocurrent density-voltage ($J - V$) curves of the assembled DSSCs shielded by an aluminum foil mask with an aperture area of ~ 0.1 cm^2 were measured with a digital source meter (Keithley, model 2612) under simulated air mass (AM) 1.5 solar spectrum illumination at 15, 50, and 100 mW cm^{-2} , respectively. Incident photo-to-current conversion efficiency (IPCE) plotted as a function of excitation wavelength was recorded on a Keithley 2612 source meter under the irradiation of a Xenon lamp with a monochromator (Oriel Cornerstone™ 260 1/4). Hermetically sealed cells were used for long-term stability tests. For thermal stress the cells were covered with UV cutoff filter, put on the magnetic heater at 60 °C and

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