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Preparation of PAA-g-CTAB/PANI polymer based gel-electrolyte and the application in quasi-solid-state dye-sensitized solar cells

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ABSTRACT

A microporous hybrid polymer of poly(acrylic acid)-g-cetyltrimethylammonium bromide/polyaniline (PAA-g-CTAB/PANI) was synthesized by a two-steps solution polymerization. Using this amphipathic hybrid as host, a gel-electrolyte with a high absorbency of 17.69 (g/g) and a high conductivity of 14.29 mS cm^{-1} was prepared. The polymer hosts have been characterized by means of scanning electron microscopy (SEM), and the microporous network structure was observed. Fourier transform infrared spectroscopy (FTIR) and the electrochemical property tests of the gel-electrolytes have been carried out by means of *I–V* measurements. The quasi-solid-state dye-sensitized solar cells (QS-DSSCs) based on the hybrid gel-electrolyte reach a light-to-current efficiency of 6.68%.

1. Introduction

Since the first prototype of a dye-sensitized solar cell (DSSC) was reported in 1991 by O'Regan and Gratzel [1], it has aroused an intensive interest over the past decades due to its low cost and simple preparation procedure [1,2]. Based on liquid electrolytes, a high photoelectric conversion efficiency over 11.4% for DSSC has been achieved [3,4]. However, the potential problems caused by the liquid electrolytes, such as the leakage and volatilization of liquid, are considered as some of the critical factors limiting the long-term performance and practical use of the DSSCs [5,6]. It has been pointed by Gratzel [3] that long-term stability is a key requirement for all types of solar cells, and a vast amount of tests have therefore been carried out over the last 15 years to scrutinize the stability of the DSSCs. Recently, many efforts have been done to replace liquid electrolyte with all-solid-state electrolyte [7–10], ionic liquid electrolyte [11–13] and quasi-solid-state gel-electrolyte [5,6,14–18]. Especially, the quasi-solid-state gel-electrolyte attracts a great attention due to its higher conductivity and excellent long-term stability. For all solid-state electrolyte, though which posses the best long-term stability, it still remains an important problem such as low conversion efficiency compared to the liquid electrolyte because of the low conductivity of the solid-state electrolyte itself, imperfect wetting of the porous TiO_2 film and the high recombination rate at the TiO_2/solid-state electrolyte interface [5,17]. In contrast, quasi-solid-state gel-electrolyte exhibits an ionic conductivity as high as that of liquid electrolyte, prevents the solvent from leaking and volatilizing, and which can be nicely cast onto porous TiO_2 [17]. The enhanced conversion efficiency and improved stability of quasi-solid-state gel-electrolyte dye-sensitized solar cells (QS-DSSCs) should accelerate the practical usage of DSSC. What's more, large area quasi-solid-state DSSC also have been fabricated in the previous works by Biancardo et al. [16] and satisfactory results were reached. The usage of quasi-solid-state electrolyte in large area DSSCs shows a promising prospect to fabricate high efficient and stabile DSSCs.

The gel-electrolyte consisted of a polymer host, a solvent and an ionic conductor. In most polymer gel electrolytes, the polymer content is low, usually less than 20%, and a significant amount of organic solvent is retained. The limitation of solvent leakage and volatilization is an important issue for preparing gel-electrolyte. As we know, poly(acrylic acid) (PAA) is a superabsorbent polymer with three-dimensional (3D) network and hydrophilic groups, it can absorb large amounts of liquid and the absorbed liquid is hardly to be released even under some pressure [19–21]. However, pure PAA is not a good absorbent for conventional organic solvent used in liquid electrolytes [6], due to the hydrophilic functional group of carboxyl groups in PAA. In order to improve their absorbency of organic solvents, a modification of the carboxyl groups or an introduction of amphiphilic groups is necessary.

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In our previous work, by modifying PAA with amphiphilic poly(ethylene glycol) (PEG) [6], gelatin [20], glycerin [21], etc., we have successfully synthesized series of gel-electrolytes based on modified hybrid superabsorbents and which showed excellent stability and absorbent ability for liquid electrolyte [6]. In continuation of our studies, a microporous superabsorbent of poly(acrylic acid)-g-cetyltrimethylammonium bromide (PAA-g-CTAB) was prepared at the first stage, and followingly, aniline solution mixed with HCl was absorbed into and polymerized inside of the polymer network, and the PAA-g-CTAB/PANI hybrid polymer was obtained. Using the PAA-g-CTAB/PANI hybrid polymer as host, a gel-electrolyte with a high absorbency of 17.69 (g/g) and a high conductivity of 14.29 mS cm^{-1} was prepared. The gel-electrolyte is used to assemble QS-DSSCs, and a relatively high efficiency of 6.68% was achieved.

2. Experimental

2.1. Materials

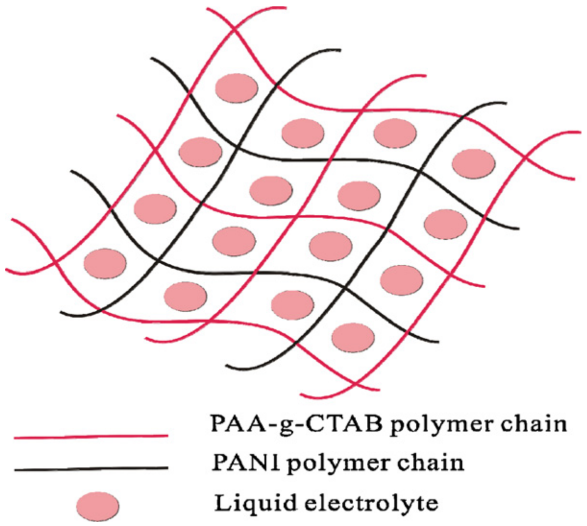
Acrylic acid monomer, purchased from Shanghai Chemical Agent Company, China, was distilled under reduced pressure prior to use. Cetyltrimethylammonium Bromide (CTAB), purchased from Shanghai Chemical Agent Company. The organometallic Sensitized dye N-719 [$RuL_2(NCS)_2$, L = 4,4′-dicarboxylate-2,2′-bipyridine] was obtained from Solaronix SA (Switzerland). Titanium(IV) isopropoxide, PEG (formula weight of 20 000), OP emulsification agent (Triton X-100) and other reagents were obtained from Shanghai Chemical Agent, P.R. China and used as received. All other chemicals were analytical pure grade and were purchased from Xilong Chemicals. Crosslink agent N,N′-(dimethyl)acrylamide was purified by recrystallization from 66 vol% ethanol/water solution before using; other chemicals and solvents were used without further purification before using.

2.2. Synthesis of PAA-g-CTAB superabsorbent polymer

PAA-g-CTAB superabsorbent polymer was synthesized by modifying the procedure from Refs. [6,22–24]. 1.0 g CTAB and 10 g acrylic acid (AA) were dispersed in 15 ml distilled water. Subsequently, initiator potassium peroxydisulfate (KPS) (weight ratio of KPS to AA was 0.8%) and N,N′-methylene bisacrylamide (NMBA) (weight ratio of NMBA to AA was 0.05%) were added to the mixed solution system. Under a nitrogen atmosphere, a polymerization reaction took place under vigorous stirring at 80 °C. After the solution became viscous, the system was cooled to room temperature. After the solution became viscous, the system was cooled to room temperature, the resultant product was filtered through Whatman filter paper No. 54 and then washed in excess distilled water to remove any impurities. Finally, the product was vacuum dried at 80 °C for more than 12 h to a constant weight.

2.3. Preparation of PAA-g-CTAB/PANI hybrid superabsorbent and gel-electrolyte

PAA-g-CTAB/PANI hybrid was prepared according to the following procedures [22,23]: 0.2 g of PAA-g-CTAB was immersed in a predetermined amount of aniline (ANI) and HCl solution (1 ml ANI, 300 ml H_2O, pH = 2.5) at ambient temperature for more than 48 h, which resulted in the absorption of ANI monomer into the PAA-g-CTAB network and leaded to the formation of a swollen sample. The swollen sample was dispersed in a KPS solution of 15 ml containing 0.0365 M KPS (act as initiator and doping agent), which caused an in situ polymerization between ANI monomers and the formation of PANI inside the network of PAA-g-CTAB. The polymerization reaction took place at 4 °C for more than 48 h in dark. When the swollen sample changed from the original pale yellow color to dark green color, the PANI was formed inside of polymer network. After the polymerization, similar to the preparation of PAA-g-CTAB, the intermediate product was filtrated, washed, dried, thus a PAA-g-CTAB/PANI hybrid superabsorbent was obtained.



Scheme 1. Structure of PAA-g-CTAB/PANI hybrid superabsorbent.

The gel-electrolyte was prepared by soaking 0.2 g dried polymer sample in liquid electrolyte for more than 96 h to reach absorption saturation. The liquid electrolyte consisted of 0.1 M tetrabutylammonium iodide (TBAI), 0.1 M tetramethylammonium iodide (TMAI), 0.1 M tetraethylammonium iodide (TEAI), 0.1 M KI, 0.1 M LiI, 0.1 M NaI, 0.06 M I_2 in mixed organic solvent of N-methyl-2-pyrrolidone (NMP) and acetonitrile (AC) (NMP/AC = 2/8). Scheme 1 shows the structure of PAA-g-CTAB/PANI polymer based gel-electrolyte.

2.4. The assembling of DSSCs

A 10-μm-thick film of TiO_2 nanocrystal anode films was prepared by using a “doctor blade method”. A QS-DSSC with PAA-g-CTAB or PAA-g-CTAB/PANI based gel-electrolyte was fabricated by sandwiching a slice of gel-electrolytes between dye-sensitized TiO_2 anode electrode and a platinum counter electrode. The detailed fabrication procedure for the nanocrystalline TiO_2 photoanodes and the assembly of DSSCs has been described by us elsewhere [6,25,26].

2.5. Characterizations

The morphology of PAA-g-CTAB and PAA-g-CTAB/PANI samples were studied by using a scanning electron microscope (SEM, Hitachi S-5200, Japan). The PAA-g-CTAB or PAA-g-CTAB/PANI sample was freeze dried by a freeze dryer (FD-1A-50, Beijing Boyikang Laboratory Instruments Co., Ltd, Beijing, China) and then cut into a slice and coated with gold, followingly its surface was observed and photographed by SEM. The groups of PAA-g-CTAB or other powdered samples were identified by Fourier transform infrared (FTIR) spectroscopy on a Nicolet Impact 410 FTIR spectrophotometer (Inspiratech 2000 Ltd, Warwickshire, UK) using KBr pellets.

2.6. Measurement

The swelling ratio (SR, g/g) of sample was measured according to the equation below [27]:

$$\text{Swelling ratio}\quad(\text{SR}) = \frac{W_2 - W_1}{W_1} \tag{1}$$