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A novel polysulfide hydrogel electrolyte based on low molecular mass organogelator for quasi-solid-state quantum dot-sensitized solar cells

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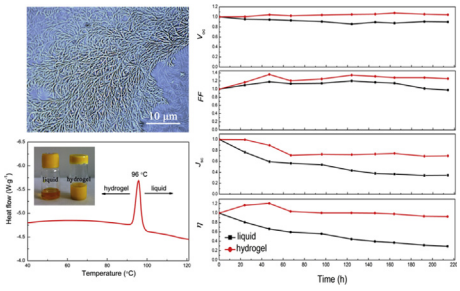
HIGHLIGHTS

- A novel and stable polysulfide hydrogel electrolyte is prepared for QS-QDSSC.
- The polysulfide hydrogel electrolyte is gelated by the 12-hydroxystearic acid.
- The influence of gelation on the electron recombination of the QDSSC is studied.
- The hydrogel electrolyte based QS-QDSSC exhibits significantly improved stability.

GRAPHICAL ABSTRACT



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ABSTRACT

A quasi-solid-state quantum dot-sensitized solar cell (QDSSC) is fabricated by using 12-hydroxystearic acid as a low molecular mass organogelator to gelate the polysulfide electrolyte. Noticeably, the gel to liquid transition temperature of this polysulfide hydrogel electrolyte is 96 °C, which contributes to the long-term stability of the quasi-solid-state QDSSC (QS-QDSSC). The influences of gelation on the charge transport, electron recombination and photovoltaic performance of the QS-QDSSC are investigated by electrochemical impedance spectroscopy. Moreover, the network of the hydrogel is investigated by the Field emission scanning electron microscopy and polarized optical light microscopy. It is found that the charge transport is influenced by the network in the hydrogel electrolyte, and the accelerated electron recombination at the photoanode/electrolyte interface leads to the decreased open-circuit voltage. The QS-QDSSC exhibits an energy conversion efficiency of 2.40% at AM 1.5 (100 mW cm^{-2}) which is slightly lower than that of liquid electrolyte based cell (2.88%). However, the QS-QDSSC exhibits significantly improved stability during the accelerated thermal test. Especially, during the accelerated aging test, the short-circuit current density (J_{sc}) of the liquid electrolyte based QDSSC sharply decreased to nearly 35% of its initial value, while there is relatively less change in the J_{sc} for the QS-QDSSC.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been considered as one of the most promising photovoltaic technologies because they are generally made from inexpensive and nontoxic components, and can be designed in a diversity of colors and transparencies [1,2]. Recently, there is a growing interest in quantum dot-sensitized solar cells (QDSSCs), which use inorganic semiconductor quantum dots (QDs) as sensitizer materials instead of conventional dyes [3–5]. The advantages of the QDs such as easy tuning of bandgap, larger extinction coefficient with wider spectral coverage, high stability and the possibility of multiple exciton generation from the absorption of a single photon makes them a very attractive and promising substitute for a future DSSC technology [3,6–10]. Although QDSSCs are promising third-generation photovoltaic devices, similar to DSSCs, the problems of leakage and volatilization of solvents caused by the liquid electrolyte are considered as the critical factors which limit the long-term performance and application of QDSSCs [11,12]. An alternate strategy to improve the stability of QDSSCs is replacing the liquid electrolyte with quasi-solid-state electrolyte, nevertheless, very few reports were published on this issue. So far, several compounds and polymers have been used as gelators to prepared the polysulfide hydrogel electrolyte, such as dextran [13], poly(propylene glycol) [14], konjac glucomannan [15] and poly(acrylamide-bis-acrylamide) [16].

In this work, a polysulfide (S^{2-}/S_x^{2-}) hydrogel electrolyte using 12-hydroxystearic acid as a low molecular mass organogelator (LMOG) is employed to assemble the CdS/CdSe co-sensitized solar cell for the first time. The thermostability of the polysulfide hydrogel electrolyte and the electron recombination behavior at the TiO_2 photoanode/electrolyte interface were investigated. Especially, the QDSSC with this hydrogel electrolyte exhibits good thermostability during the accelerated aging test.

2. Experimental methods

2.1. Preparation of CdS/CdSe QDs co-sensitized TiO_2 photoanodes

The colloidal TiO_2 mircospheres were prepared by hydrolysis of titanium tetraisopropoxide as described elsewhere [17]. The thickness of mesoporous TiO_2 film is about 10 μm which was obtained by screen-printing TiO_2 paste on FTO glass (TEC-8, LOF, USA) and sintering at 500 °C for 30 min in air. The TiO_2 photoanodes were co-sensitized by in situ growth of CdS/CdSe and SILAR process [18]. For CdS deposition, the TiO_2 photoanodes were immersed in the 0.5 mol L^{-1} Cadmium nitrate tetrahydrade ($Cd(NO_3)_2$, 98%, Aldrich) ethanol solution and 0.2 mol L^{-1} Sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$, ≥98.0%, Sinopharm Chemical Reagent Co., Ltd.) methanol solution in sequent for 5 min. And then, the TiO_2 photoanodes were rinsed with ethanol and methanol respectively, and dried with N_2. The SILAR processes of CdSe were similar to that of CdS QDs. The TiO_2/CdS photoanodes were immersed in 0.5 mol L^{-1} $Cd(NO_3)_2$ ethanol solution for 5 min at room temperature, and then in sodium seleno-sulphate (Na_2SeSO_3) aqueous solution for 1 h at 50 °C. And the preparation of Na_2SeSO_3 aqueous and SILAR cycles of CdS and CdSe, which are 7 and 4, respectively, were according to the previous report [18].

2.2. Preparation of electrolytes

The polysulfide liquid electrolyte was prepared freshly by dissolving 1.0 mol L^{-1} Na_2S, 1.0 mol L^{-1} Sulphur (S, 99.9%, Sinopharm Chemical Reagent Co., Ltd.) and 0.1 mol L^{-1} Sodium hydroxide (NaOH, ≥98.0%, Sinopharm Chemical Reagent Co., Ltd.) in deionized water.

The polysulfide hydrogel electrolyte was prepared by adding 3 wt% (vs. liquid electrolyte) 12-hydroxystearic acid into liquid electrolyte, and heated under stirring until the gelator melted. After cooling down to room temperature, the polysulfide hydrogel electrolyte was obtained.

2.3. Assembly of QDSSCs

The CdS/CdSe co-sensitized TiO_2 photoanode and Pt counter electrode were assembled into a sandwich cell by heating with a 45 μm thermal adhesive film (Surlyn 1702, Dupont, USA). The liquid electrolyte was injected into the internal space between of two electrodes through the hole on the counter electrode, which was later sealed by a cover glass and thermal adhesive films. The hydrogel electrolyte was heated to 98 °C under stirring until the gel transform to liquid completely, then the electrolyte (hot solution) was rapidly injected into the cell and the cell was sealed as the same as the liquid electrolyte. After cooling down to room temperature, a uniform motionless gel layer was formed in cell.

2.4. Field emission scanning electron microscopy (FE-SEM)

The morphologies of CdS/CdSe co-sensitized TiO_2 photoanode were characterized by field emission scanning electron microscopy (FE-SEM, FEI Sirion-200, USA).

2.5. Ultraviolet–visible absorption spectra

The absorbance of CdS/CdSe co-sensitized TiO_2 films were recorded on a UV–Vis spectrophotometer (U-3900H, Hitachi, Japan).

2.6. Polarized optical light microscopy

For optical microscopic investigations, a piece of the gel (3 wt% of LMOGs in MePN) was placed onto a glass slide and protected with a cover slip. The sample was heated to 120 °C at a rate of 10 °C min^{-1} and the micrographs were obtained during cooling between crossed polarizer using a microscope (DM2500P, Leica, Germany) equipped with a hot-stage (LTSE-420, Linkam, UK) and camera (Micropubisher 5.0 RTV, Qimaging, Canada) at a rate of 1 °C min^{-1}.

2.7. Differential scanning calorimetry

The gel to liquid transition temperature (T_{gel}) of the hydrogel electrolyte was determined by differential scanning calorimeter (DSC-Q2000, TA, USA). The sample (5–7 mg) was weighed and sealed in an aluminum pan and heated at a rate of 10 °C min^{-1} under nitrogen flow from 25 to 125 °C for differential scanning calorimeter measurement.

2.8. Conductivity measurements

The ionic conductivities of the liquid electrolyte and hydrogel electrolyte were determined by two electrodes thin-layer cells with two platinum black electrodes and ac impedance technique on electrochemical workstation (IM6e, Zahner, Germany) over a frequency range of 50 mHz–1000 kHz with voltage amplitude of 10 mV at 0 V bias.

2.9. Electrochemical impedance measurement

Electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (Autolab 320,