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Multifunctional graphene incorporated polyacrylamide conducting gel electrolytes for efficient quasi-solid-state quantum dot-sensitized solar cells

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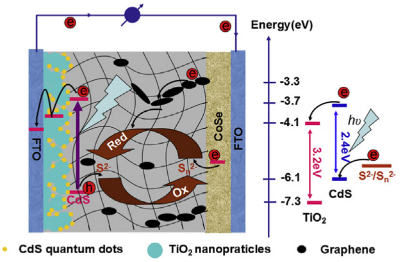
HIGHLIGHTS

- Graphene is incorporated into microporous PAAm matrix.
- The catalytic reaction of redox couples is conducted into conducting gel electrolyte.
- Liquid electrolyte is driven by osmotic pressure and capillary diffusion.
- A power conversion efficiency of 2.34% is recorded in the quasi-solid-state QDSC.

GRAPHICAL ABSTRACT



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ABSTRACT

Pursuit of a high efficiency and stability has been a persistent objective for quantum dot-sensitized solar cells (QDSCs). Here we launch a strategy of synthesizing graphene implanted polyacrylamide (PAAm-G) conducting gel electrolytes for quasi-solid-state QDSCs. With an aim of elevating the dosage of S^{2-}/S_x^{2-} redox couples and therefore charge-transfer ability, both osmotic press across the PAAm-G and capillary force within the three-dimensional micropores are utilized as driving forces. A promising power conversion efficiency of 2.34% is recorded for the QDSCs by optimizing graphene dosage in the conducting gel electrolyte. The enhanced conversion efficiency of solar cell is attributed to the expanded catalytic area from counter electrolyte/electrolyte interface to both interface and the conducting gel electrolyte.

1. Introduction

Quantum dot-sensitized solar cell (QDSC) has drawn considerable attentions as an impressive candidate for the third generation solar cells [1–3]. A typical QDSC comprises a quantum dot-sensitized photoanode, liquid electrolyte containing S^{-}/S_x^{2-} redox

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couples, and metal sulfide counter electrode. In comparison with dye-sensitized solar cells (DSSCs) [4], the QDSCs demonstrate some bewitching characteristics, such as tunable bad gap [5], high absorption coefficient [6], multiple exciton generation [7], and hot electron transfer of quantum dots (QDs) [8]. A class of narrow bandgap semiconductor QDs such as CdS [9], CdSe [10], CdTe [11], PbS [12], and In_2S_3 [13] have been successfully explored to substitute the organic dyes. In the previous studies, considerable attentions have been focused on improving the power conversion efficiencies of QDSCs by launching new strategies or techniques for synthesizing versatile QDs [14]. Recently, a power conversion efficiency as high as 7.04% has been achieved for the QDSC comprising of a liquid polysulfide (S^-/S_x^{2-}) electrolyte and ternary $CuInS_2$ QDs [15]. A remaining issue for the liquid QDSCs is the leakage of liquid electrolyte from the sandwiched solar cell [16]. By addressing this issue, significant achievements have been made by employing solid-state electrolytes [17,18]. Due to the low charge transfer kinetics and the serious photogenerated electron recombination loss and inner energy loss occurring at the electrolyte/electrode interfaces [19,20], the photovoltaic performances are still unsatisfactory. Therefore, it is a prerequisite to explore cost-effective and stable electrolytes for storing redox species.

Polymer gel electrolytes, combination of the stability of solid-state electrolytes and high charge–transfer ability of liquid electrolyte, exhibit promising performances in both quasi-solid-state DSSCs and QDSCs [21,22]. To realize these gel electrolytes, the osmotic pressure across the gel matrix is a mainly driving force for uploading the liquid electrolyte into three-dimensional (3D) gel matrix. In mechanism, the imbibition of liquid electrolyte by the gel matrix is controlled by Flory theory and the imbibed liquid electrolyte has migration kinetics similar to that in liquid system [23]. Once the gel electrolyte is sandwiched between a photoanode and a counter electrode, the reduction reaction occurs at electrolyte/counter electrode interface. Aiming at accelerating the reduction reaction of redox species in the DSSCs, conducting polymers (polyaniline, polypyrrole) [24] and carbonaceous materials (graphene, graphene oxide) [25] have been incorporated into the gel systems to fabricate conducting gel electrolytes in DSSCs, in which the electrocatalytic reaction has been expanded from electrolyte/counter electrode interface to both interface and the gel electrolyte. Moreover, the interconnected conducting channels also shorten the charge diffusion path length and yield a significantly enhanced efficiency in quasi-solid-state DSSCs. Therefore, a promising strategy of fabricating efficient QDSCs with high stability is to design conducting gel electrolytes for quasi-solid-state devices. We present here the synthesis of graphene implanted polyacrylamide (PAAm-G) conducting polymer gel electrolytes by incorporating graphene into the 3D polyacrylamide matrix under the driving force of both osmotic pressure across the gel matrix and capillary diffusion from micropores. The synergistic effect of both osmotic pressure and capillary force is believed to further elevate the dosage of liquid electrolyte in per unit volume of gel electrolyte. Moreover, CoSe alloy is utilized as a counter electrode material to substitute metal sulfides owing to its reasonable electronic conduction and electrocatalytic ability [26]. In comparison with the QDSC from pristine PAAm gel electrolyte, the photovoltaic performances of the solar cells have been markedly enhanced by employing PAAm-G conducting gel electrolytes.

2. Experimental

2.1. Synthesis of microporous PAAm-G composites

The PAM–G matrices were synthesized by an aqueous polymerization route. In details, 10 g of acrylamide monomer and stoichiometric graphene (The percentages of graphene were confined at 3, 5, 7, and 9 wt‰ of the acrylamide monomer) was thoroughly dissolved in 15 mL of deionized water. After vigorous agitation, the reactant was degassed for 10 min and heated in a water bath of 80 °C, 0.0015 g of N,N'-(methylene)bisacrylamide and 0.06 g of ammonium persulfate were successively added into the above mixture. With the proceeding of polymerization, the viscosity increased gradually. When the viscosity of the PAAm-G prepolymers reached around 180 mPa s^{-1}, the reagent was poured into a Petri dish and cooled to room temperature with the formation of an elastic black gel. After being rinsed with excess deionized water, the samples were vacuum dried at 80 °C for more than 12 h. The pristine PAAm matrix was also synthesized with the same method. The microporous PAAm-G matrices were prepared by immersing the dense PAAm-G composites into deionized water for 2 days to reach swelling equilibrium, subsequently the swollen PAAm-G hydrogels were freeze-dried under vacuum at −60 °C for 48 h. The closed 3D framework of PAAm-G matrix will open during the swelling process, whereas the freeze-dry technique can realize the elimination of water with no morphological variation.

2.2. Preparation of conducting PAAm-G gel electrolytes

To realize PAAm-G gel electrolytes, the dense or microporous PAAm and PAAm-G matrices were immersed in a liquid electrolyte consisting of 1 M S and 1 M Na_2S aqueous solution for 5 days to reach their swelling equilibriums. The imbibed liquid electrolyte having S^{2-}/S_n^{2-} redox couples will be reserved in the 3D frameworks of PAAm or PAAm-G gel matrices.

2.3. Fabrication of CdS sensitized TiO_2 anodes

FTO glass substrates (12 Ω cm^{-2}) with a size of 2 × 2 cm^2 were thoroughly rinsed by deionized water and anhydrous ethanol, and dried by N_2 gas flow. The TiO_2 colloid was prepared according to a sol-hydrothermal method [27]. The TiO_2 anode films with an average thickness of 10 μm and an active area of 0.5 × 0.5 cm^2 were fabricated by a screen printing technique. The air-dried colloids were calcined in a muffle furnace at 450 °C for 30 min. The elevation of heating temperature was controlled at a speed of 2 °C min^{-1} till 130 °C, and then at a speed of 6 °C min^{-1} until 450 °C.

To fabricate CdS sensitized TiO_2 anodes, the TiO_2 film was immersed into 0.1 M $Cd(NO_3)_2$ ethanol solution for 1.5 min, rinsed with anhydrous ethanol and dried by N_2 gas stream, then soaked in 0.1 M Na_2S methanol solution for 1.5 min, rinsed with anhydrous methanol and dried by N_2 gas. By repeating the previous procedures for 12 times, we could obtain CdS sensitized TiO_2 anodes.

2.4. Synthesis of CoSe alloy counter electrodes

The CoSe alloy counter electrode was synthesized following previous reports [18]. In details, 0.01 g of Se powers and 0.0238 g of $CoCl_2{\bullet}6H_2O$ were mixed in 27.5 mL of deionized water by vigorous agitation to obtain a homogeneous mixture. Subsequently, 7.5 mL of hydrazine hydrate (85 wt%) was dropped into the above solution. After vigorous agitating for 10 min, the reactant was transferred into a 50 ml of Teflon-lined autoclave and cleaned FTO glass substrate with FTO layer downward was immersed in. After the reaction at 120 °C for 12 h, the FTO substrate was rinsed by deionized water and vacuum dried at 50 °C.

2.5. Assembly and characterizations of quasi-solid-state QDSCs

The quasi-solid-state QDSC was fabricated by sandwiching a slice of gel electrolyte with thickness of around 500 μm between a