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A polymer gel electrolyte with an inverse opal structure and its effects on the performance of quasi-solid-state dye-sensitized solar cells

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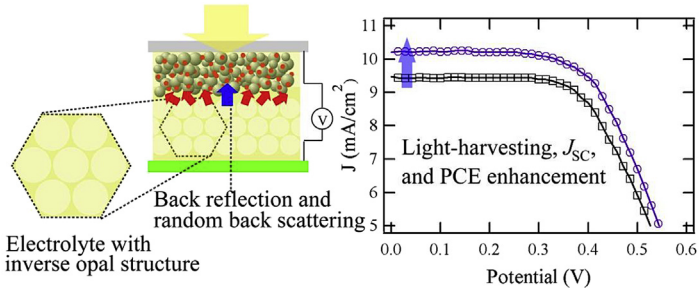
HIGHLIGHTS

- Inverse opal structures were incorporated into polymer gel electrolytes.
- It is the first report of gel electrolytes with ordered nanostructures.
- The gel electrolytes can tailor light propagation in dye-sensitized solar cells.
- Light-harvesting and PCEs of the cells are enhanced by the electrolytes.
- We report a new and promising approach for light-harvesting enhancement.

GRAPHICAL ABSTRACT



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ABSTRACT

To make the use of dye-sensitized solar cells (DSCs) practical, improvements in their light harvesting and power conversion efficiencies (PCEs) are needed. Hybrid polymer gels with an inverse opal structure (IOS) are prepared using various SiO_2 opal films as templates and subsequent template etching. The polymer gel is further used as a host to prepare gel electrolytes with a photonic band gap (PBG), based on which quasi-solid-state DSCs are fabricated. The current–voltage curves indicate higher PCEs for the gel electrolytes with IOS than for reference gel electrolytes. A maximum average PCE of 3.85% is achieved for the gel electrolytes with a PBG around 690 nm, which is *ca.* 10% higher than the value for the reference gel electrolyte (3.48%). The action spectra reveal increases in the incident photo-to-current conversion efficiencies in and/or away the PBG region, indicating the significance of IOS for light-harvesting and PCE enhancement by back scattering and reflection of light. The electrochemical impedance spectra further demonstrate that the gel electrolytes with IOS have a lower Warburg impedance value than the reference gel electrolyte, which may also have contributed to the observed PCE enhancement. Besides, the IOS is found to give more stable performance of DSCs.

1. Introduction

Since the pioneering work of O'Regan and Grätzel [1], dye-sensitized solar cells (DSCs) have been considered to be one of the most promising solutions to the decline in the earth's natural energy resources because of their simple structure with relatively

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high power conversion efficiencies (PCEs) and inexpensive fabrication procedures. However, to put DSCs into practical use, major breakthroughs are necessary to obtain higher PCEs and better long-term performance.

The PCE of a DSC is determined by the open circuit voltage (V_{OC}), the short circuit current (J_{SC}), and the fill factor (FF). The value of J_{SC} is mainly governed by the amount of sunlight harvested in the visible portion of the solar spectrum by a sensitizer [2]. Recently, the coupling of 3D titania inverse opals or 1D photonic crystals in the form of porous Bragg stacks to nanocrystalline titania layers has been proposed to improve light reflection and scattering. This method has become a novel approach to enhance light harvesting in DSCs [3–7], distinct from the development of new porphyrin and organic D–π–A sensitizers with high extinction coefficients [8–10]. However, this method tends to result in thickened photoanode layers containing more grain boundaries. In the titania 3D inverse opal structure (IOS), [3–6] there is no energy level gradient for the conduction band of the inorganic semiconductor layer, and photoelectron transport is therefore nondirectional (*e.g.*, toward the counter electrode). The increased thickness of the photoanode and greater number of grain boundaries should give rise to a relatively long and difficult path for photoelectron collection, during which the photoelectrons may be intercepted and undergo recombination. [3,11] Although the PCEs were indeed improved by this method in many reports, [4–6] the adverse effects on charge transport and recombination, as described above, are non-negligible. These effects may sometimes become dominant, which results in a penalty in the PCE, as reported by Guldin et al. [3] In the 1D photonic crystal structure, [7] the photoelectron transport problems may be avoided owing to the sandwiched SiO_2 and TiO_2 layers in the structure; however, electrolyte diffusion resistance significantly decreases the FF and limits the usefulness of these structures for solid-state or quasi-solid-state electrolytes [2]. Therefore, to further improve the PCEs of DSCs, it is essential to develop innovative approaches to achieve light-harvesting enhancement without disrupting photoelectron transport or increasing the diffusion resistance of electrolytes.

An electrolyte acting as a hole conducting material is one of the major components of DSCs. Traditional organic solvent-based electrolytes have the advantage of low viscosities and high dielectric constants, and a number of studies have shown that DSCs with the I^-/I_3^- redox couple in an organic solvent as a liquid electrolyte are able to attain PCEs as high as ~11% [12]. However, such DSCs suffer from leakage and volatilization of the organic solvent, which greatly limits the long-term performance of liquid electrolyte-based DSCs. Therefore, numerous materials, such as p-type semiconductors [13,14], organic hole conductors [15,16], ionic liquids [17–22], and polymer gel electrolytes, [23–25] have been used to replace liquid electrolytes. Among the possible candidates, solid-state or quasi-solid-state electrolytes offer electrolyte stability and the additional opportunity to incorporate ordered nanostructures to tailor light propagation in DSCs; such an approach could achieve light-harvesting enhancement, as mentioned above.

Herein, we report the preparation of quasi-solid-state polymer gel electrolytes with IOS using SiO_2 opal films as templates and subsequent template etching. The effects of the IOS on the DSC performance were systematically investigated, and the results indicated the significance of IOS for light-harvesting, PCE, and stability enhancement. To the best of our knowledge, this is the first report of quasi-solid-state electrolytes with ordered nanostructures and their exploitation as a new approach for light-harvesting enhancement.

2. Experimental

2.1. Materials

Acrylic acid monomer (AA), purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China, was distilled under reduced pressure prior before use. *N*,*N*′-methylene bisacrylamide (NMBA) and ammonium peroxydisulfate (APS), as a crosslinker and a radical initiator, respectively, were also obtained from Sinopharm Chemical Reagent Co., Ltd. and used as received. The organometallic sensitizer N-719 [*cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) bis(tetrabutylammonium)] and a fluorine-doped tin oxide (FTO)-coated glass plate (resistance of 25 Ω/square, 85% transmittance) were both obtained from Dalian Rainbow Solar Technology Development Co., Ltd., Dalian, China. TiO_2 nanoparticles (20 nm) were purchased from Sigma–Aldrich. All other solvents and chemicals were obtained from commercial supplies and used without further purification.

2.2. Preparation of SiO_2 opal films

SiO_2 seeds were synthesized according to the reported method [26]. Subsequently, monodisperse samples of SiO_2 spheres with different diameters were prepared by regrowth of the seeds according to the Stöber method. The obtained spheres were further purified by centrifugation and redispersed in ethanol at a concentration of about 5 wt%. These suspensions were used to fabricate SiO_2 opal films by the vertical deposition method [27]; in which a slide glass after hydrophilic treatment [28], was partially immersed in a suspension and SiO_2 colloidal crystals deposited on the glass during the evaporation of the solvent. The thickness of prepared opal films ranged from 4 to 5 μm.

2.3. Preparation of gel electrolytes with IOS

AA (10 g), gelatin (1 g), NMBA (1 g), and APS (0.08 g) were dissolved in deionized water (15 mL) under a nitrogen atmosphere and used as the pre-gel solution. This solution was used to fill the interspace between two slide glasses, one of which had a SiO_2 opal film deposited on it for use as a template. Polymerization of the pre-gel solution was carried out at 80 °C, and the thickness of the gel film (*e.g.*, 0.2 mm) was controlled by two stainless steel spacers between the slide glasses. After the polymerization, the gel film was carefully separated from the glasses and immersed in an HF aqueous solution (4 wt%) to remove the SiO_2 spheres. The film was then gently washed with pure water to remove excess HF, and a hydrogel with IOS was obtained. The hydrogel underwent a solvent exchange treatment, in which water in the film was gradually replaced by ethanol. Finally, a gel electrolyte with IOS was prepared by soaking the film for 6 h in a liquid electrolyte containing 0.5 M LiI and 0.05 M I_2 in ethanol. The procedure for preparation of a gel electrolyte without IOS was similar to the above, except for the use of the template.

2.4. Assembly of DSCs

The photoanodes, consisting of a TiO_2 nanoparticle film on FTO-coated glass, were prepared according to our previous report with some modification [18]. The TiO_2 electrodes were sensitized by immersion in an N719 dye solution (0.5 mM in ethanol) at 60 °C for 24 h. The Pt counter electrodes were prepared by drip-coating an H_2PtCl_6 solution (10 mM in ethanol) onto FTO-coated glass and sintering at 450 °C for 30 min. A quasi-solid-state DSC was assembled by sandwiching a gel electrolyte between a dye-sensitized TiO_2 electrode and a Pt counter electrode. The typical