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Optimized photonic crystal structure for DSSC

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Abstract

Different to isotropic materials, photonic crystals (PCs) exhibit extraordinary optical properties, which are quite helpful for enhancing light absorption and boosting solar cells' photovoltaic conversion efficiency. In our work, the advantages of applying PCs on DSSC were systemically analyzed with theoretical calculations and experimental verifications, a series of formula were also proposed accordingly, to predict PCs' optical properties and select the most suitable PC for DSSC. Based on these work, a double-layer DSSC (a nanocrystalline layer ahead of a PC layer) with an optimized PC geometric structure was fabricated, *I–V* tests showed that its photovoltaic conversion efficiency was 30% higher than the traditional DSSC.

Keywords: Photonic crystal; Light-harvesting; Dye-sensitized solar cell; Optimized structure

1. Introduction

Since the first proposition by John (1987) and Yablonovitch (1987) in 1987, photonic crystal (PC) has attracted wide-spread attention around the world, as a new type of nonlinear optical material manipulating light propagation in nontraditional ways (John, 1987; Yablonovitch, 1987; Joannopoulos et al., 1997; López, 2003; Park and Xia, 1999). Many applications have been put forward based on PCs, such as low threshold lasers (Yamamoto and Slusher, 1993), waveguide structures that cause light to curve at acute angles (Mekis et al., 1996) and optical wave plates (Li, 2001). Especially, fabricating working electrodes of dye-sensitized solar cells (DSSC) (Nazeeruddin et al., 2011) with PC structures has been proven efficient in boosting the photovoltaic conversion efficiency by enhancing light absorption on the working electrodes, and Mallouk et al. have achieved 26% enhancement of photogenerated current with respect to a conventional (i.e., nonperiodically structured) photoelectrode (Nishimura et al., 2003).

In several past reports of PC DSSC, two important mechanisms for photonic crystal's potential in boosting light absorption have been proposed: slow photon effect and back scattering effect. The slow photon effect was systemically discussed in the literatures (Imhof et al., 1999; Tocci et al., 1996; Scalora et al., 1994; Vlasov et al., 1999): the group velocity of propagating light in PCs becomes anomalously small (close to zero) at the edges of PCs' band gap. Therefore, light absorption can be significantly enhanced, especially at the red edge. And back scattering effects were talked about in other works (Halaoui et al., 2005; Mihi and Míguez, 2005): the enhancement of light absorption in the materials ahead of photonic crystals resulted from the strong prevention of light transportation at the photonic band gaps. To date, although it has not yet been concluded which mechanism plays a more significant effect, such a viewpoint has been widely accepted that both of these phenomena contribute to the final light harvesting, and the boosted photovoltaic conversion efficiency.

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However, nearly all the previous works just stopped at the proposition of these mechanisms based on theoretical simulations or experiments individually, and did not explore further to optimize the photovoltaic conversion efficiency of PC DSSC considering both of these two mechanisms and the impact of dye's intrinsic absorption spectra, either (Tao et al., 2010; Liu et al., 2011). The optical properties of PCs are closely related to their geometric structures, it is of great importance to analyze the PCs' geometric parameters' impact on the DSSC's behavior and choose the most suitable PC for DSSC's fabrication before promoting it into production on a large scale. Therefore, in our work, considering both of the enhancement mechanisms, we systemically analyzed the dependence of the most generally applied PC-fcc inverse opals' optical properties on their geometric parameters, with systematic theoretical simulations and experiment tests. The optimized fcc inverse opal for DSSC was found and the fabricated DSSC has 30% enhancement of photovoltaic conversion efficiency than the traditional DSSC, based on the simple formula we had proposed during the theoretical and experimental analysis.

2. Experimental section

2.1. Materials

Methacrylic acid, styene monomer and potassium persulfate (Sinopharm Chemicals) were used for the preparation of monodispersed polystyrene (PS) particles. Titanium isopropoxide, acetic acid and nitric acid (Sinopharm Chemicals) were used for the fabrication of titanium dioxide inverse opals. TiO_2 slurry ($d = 9$ nm, Solaronix), cis-bis-(isothiocyanato)-bis-(2,2′-bipyridyl-4,4′-dicarboxylato)-tuthenium (II) complex ($RuL_2(NCS)_2$, $L = 2,2'$-bipydyl-4,4′-dicaroxylate, also known as N3, Solaronix) and electrolyte solution consisted of iodide/triiodide (Iodolyte TG50, Solaronix) were used for fabricating DSSC working electrode. Electrodes were fluorine-doped tin oxide coated glass substrates (FTO, NGS). All reagents in this experiment were directly used as-received without further treatment or modification unless special notification.

2.2. Fabrication of photonic crystals

The fabrication process of photonic crystals is presented in Fig. 1a. Different monodispersed PS particles with diameters of 195, 220 and 262 nm were synthesized with the standard emulsion polymerization method (Kawai et al., 2006) as the first step. Photonic crystal opals were fabricated by immersing acetone rinsed transparent glasses vertically into 10 ml vials filled with 0.05 wt.% monodisperse PS particle aqueous solution, at an ambient environment for several days. After the evaporation completed, a colloidal crystal film was left on the surface of transparent glass. And the photonic crystals assembled with different PS particles were labeled as PS-195, PS-220, and PS-262, respectively.

The preparation of TiO_2 inverse opal films were carried on with a similar method mentioned in literature (Barbé et al., 1997). Briefly, TiO_2 sol was synthesized by hydrolyzing tetraisopropyl titanate in deionized water: 0.5 ml of tetraisopropyl titanate modified with 1 ml acetic acid was rapidly added to 50 ml 0.1 M nitric acid aqueous solution. The solution was left stirring for about 10 h to complete the hydrolysis process, with the flask capped. The fabricated PS colloidal crystals were annealed at 80 °C for 2–3 h to achieve a stronger structure before the subsequent infiltration of TiO_2 sol. The interstitial of the PS opal was infiltrated with TiO_2 sol by repeating dip coating (the second step in Fig. 1a). After each dip coating, the PS opal was left to dry vertically in air and then heated to 80 °C for 10 min. The dip coating cycle was not completed until an 8% shift of the reflection peak was observed with a spectrometer (Yip et al., 2008). This signifies a nearly full filling of TiO_2 precursors in the PS opal. After the infiltration, the samples were kept in an electric oven at 450 °C for 30 min (the last step in Fig. 1a). And the diameters of the duplicated air particles in the inverse opals are 167 nm for PS-195, 196 nm for PS-220, and 223 nm for PS-262 (labeled as inv-167, inv-196, and inv-223, respectively).

2.3. Fabrication of double-layer DSSC

The double-layer DSSC is composed of a microporous nanocrystalline TiO_2 layer and an interconnected macroporous inverse opal TiO_2 (pc-TiO_2) layer on a FTO glass substrate (2.2 mm thick and 14 ohm/sq, NGS Japan). The nanocrystalline TiO_2 layer was controlled at about 7 μm thick and made from a commercial TiO_2 nanoparticle slurry with 9 nm particle size with doctor blade method, while the pc-TiO_2 layer was controlled at about 4 μm thick and prepared by a PS opal template growing on the nc-TiO_2 layer penetrated with sol–gel TiO_2 solution, according to Mallouk's report (Halaoui et al., 2005). After sintering, the obtained double-layer photoelectrode was controlled around 10 μm thick. Afterward, the dye sensitization was fulfilled in 0.5 mM N3 anhydrous alcohol solution under darkness for 24 h at 40 °C. The commercial electrolyte solution was injected into an assembled new cell for *I–V* test illuminated under a Xenon lamp with 100 mW cm^{-2}, calibrated by a standard silicon solar cell. A traditional DSSC made from the nanocrystalline TiO_2 (9 μm) was also assembled under the same conditions for control tests.

2.4. Characterization

Scanning electron microscope was used to evaluate the quality of the self-assembled photonic crystals. The reflection spectra were measured by a MAYA-2000 spectrometer. The absorption spectra were tested by UV spectrometer (Cary 500). X-ray diffraction (XRD) was used to analyze the crystal form of the synthesized TiO_2. IPCE