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General strategy for improving dye-sensitized solar cells by using sub-micrometer cavities

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ABSTRACT

In this work, photoanodes with sub-micrometer cavities of different sizes and ratios were easily fabricated by burning off the polystyrene sub-micrometer spheres (PSSs) embedded in TiO_2 paste. When the original PSS in the anode was 500 nm in diameter and the ratio was 100 µl (5 vol%) PSSs solution mixed with 0.1 g TiO_2 nanoparticles, the optimized performance of the fabricated dye-sensitized solar cells (DSSCs) was remarkably ~48% higher than that of pristine TiO_2 DSSCs without sub-micrometer cavities in control group. This great performance improvement was attributed to the ability of enhancing light scattering and maintaining low resistance with the introduction of optimized amount of sub-micrometer cavities. This general strategy should help to design and develop the future DSSCs with better performance.

1. Introduction

As one of the greatest energy sources, solar power is most likely to meet the rapid growing global demand of energy. It is stated that 10% of the solar power in 0.1% area of the earth can meet all human energy demand [1]. However, the bottlenecks for large-area applications of solar cells are high manufacture cost and low energy conversion efficiency. As a promising alternative for conventional expensive silicon-based solar cells, dye-sensitized solar cells (DSSCs) have attracted numerous attentions in the past decades because of their low cost, high power generation efficiency, and no harm to the environment. In 1991, O'Regan et al. developed the first DSSC that was based on TiO_2 nanoparticle [2], making its commercial application possible. In 2012, a high efficiency of over 12% has been achieved by high temperature annealing of nanocrystalline TiO_2 paste coated on conductive glass and using Co tris(bipyridyl)-based redox electrolyte and porphyrin dye [3].

Current research efforts on DSSCs are focusing on four areas. Firstly, new materials such as dyes and electrolytes are introduced. The dyes used in early research included N719, N3, N749 and the famous black dye [4], with which people obtained a high photoelectric efficiency. One of the common dyes people use is N719, and now it has been considered as a reference dye for designing other Ru photo sensitizers by changing some ancillary materials. The research of electrolyte mainly focuses on solid state materials in recent work [5]. For example, Chung et al. developed a new solid electrolyte of $CsSnI_{3-x}F_x$ $(0 \leqslant x \leqslant 1)$ by heating a certain proportional mixture of CsI, SnI_2 and SnF_2 in an oven at 450 °C for 30 min, and they have achieved a high conversion efficiency of 10.2% in their all solid state DSSCs [6]. Secondly, methods for enhancement of photoelectron transportation are invented. Great efforts have been made to increase the transportation of photogenerated electron and to depress the recombination of electron and hole [7]. Nanowires [8] and nanotubes [9] fabricated on the conductive glass were used as photoanodes in many articles, and these photoanodes display a higher electron transport speed due to less boundary effect. Mixed with graphene and acid treated multi-walled carbon nanotubes which have the ability to enhance electron transportation, 3-D hybrid photoanodes also achieve a high conversion efficiency about 5.8% [10] and 6.11% [11], respectively. Thirdly, newly designed counter electrode is introduced for DSSCs. Transparent conductive oxides (TCO) glass coated with platinum was used as counter electrode in many articles because this kind of electrode has a low resistance and a high electron transmission speed, but the application of noble metal significantly increases the cost of the DSSCs. Graphene nanosheet-based counter electrode was investigated by Zhang et al. in 2011 and a conversion efficiency of 6.81% was achieved [12]. Lastly, new methods are

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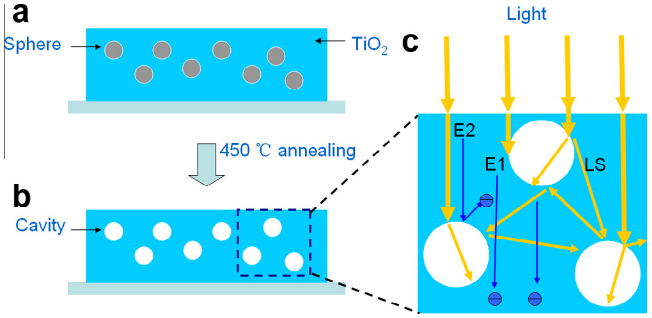

Scheme 1. (a) Schematic of a thin film made of P25 TiO_2 and PSSs mixture. After annealing, PSSs were burned off and the sub-micrometer cavities were created as illustrated in (b). (c) Schematic illustrating the light transportation process and photo-generated electron transport process.

introduced to improve photo absorption capability, which is also the focus of this work.

Usami [13], Ferber [14], Rotherenberger et al. [15] have proved that large TiO_2 particles on the top of the film would increase light absorption. Nishimura et al. [16] and Halaoui et al. [17] have succeeded in developing novel photoanodes which can enhance light-harvest capability by coupling periodic structures. Zhang et al. [18] have also demonstrated a new type of photoelectrode abundant with sub-micrometer aggregation of ZnO nanocrystallites, and the aggregation in anode could improve light harvest by changing the travel path of light through the film, and finally, a high energy conversion efficiency of 5.4% was achieved in dye-sensitized solar cells. Bohren theory [19] and Anderson localization theory [20] have provided the analytical description for the scattering of light by spherical aggregation and predicted that resonant scattering may appear when the particle size is similar to the wavelength of incident light.

Herein we demonstrated an easily fabricated TiO_2 film with sub-micrometer cavities as the photoanode in DSSCs which can improve light harvest and enhance the power conversion efficiency. These films were obtained by sintering the TiO_2 paste mixed with PSSs, and these cavities of TiO_2 films were proved to be able to enhance light scattering and absorption. Conversion efficiency of 5.43% was achieved from the film which was fabricated with a ratio of 100 μl PSS (500 nm in diameter, 5 vol%) mixing into 0.1 g TiO_2, much higher than that of 3.66% for pristine TiO_2 anode without cavities in the control group.

2. Experimental section

2.1. Preparation of photoanodes

100 μl PSSs with different diameters (200 nm, 500 nm, 2 μm) and the same volume percentages (5 vol%) were separately mixed with 0.1 g P25 TiO_2 nanoparticles in a mortar, and were continuously ground with 0.15 ml deionized water added in. The resulting colloidal dispersions were coated onto indium tin oxide (ITO) glass to form films of approximately 5 μm in thickness, as schematically shown in Scheme 1(a). Subsequently, the photoanodes with cavities were obtained by annealing at 450 °C for 20 min in air to remove residual solvents and PSSs as well as to reduce the inner resistance, as schematically shown in Scheme 1(b). Similarly, photoanodes with different ratios of cavities could also be fabricated by introducing different amounts of PSSs into the same quantity of P25 nanoparticles.

2.2. Device fabrication

Dye sensitization was continued by immersing the fabricated photoanodes in 0.5 mM N719 ruthenium dye ethanol solution for 15 min at room temperature in a sealed beaker, and then the sensitized film was placed in open air to evaporate the alcohol. The DSSC was assembled in a typical sandwich-type cell with a platinum-coated ITO as a counter anode. The electrolyte was prepared with 0.03 M I_2 (Aladdin Chemistry Co. Ltd.), 0.06 M LiI (Richjoint Chemical Co. of ShangHai), 0.6 M 1-butyl-3-methylimidazolium iodide (BMII) (Wuhan Georgi & Education & Equipment Co., Ltd.), 0.1 M guanidinium thiocyanate (Aladdin Chemistry Co. Ltd.), and 0.5 M 4-terbutylpyridine (TBP) (Aladdin Chemistry Co. Ltd.) in 3-Methoxypropionitrile (Wuhan Georgi & Education & Equipment Co., Ltd.). The electrolyte solution was injected into the assembled DSSC from the edges by capillary forces. The performance of the fabricated DSSCs was tested immediately.

2.3. Characterization methods

The morphology of the prepared photoanodes with sub-micrometer cavities was observed by scanning electron microscopy (SEM, Hitachi S-4800). UV–visible spectrophotometer (Shimazu UV-2550) was used to achieve the absorption spectra of the photoanodes over the range of 340–800 nm. Electrochemical impedance spectroscopy (EIS) measurements were taken by a computer-connected electrochemical work station (Ivium IviumStat). Current density (J)–voltage (V) curves

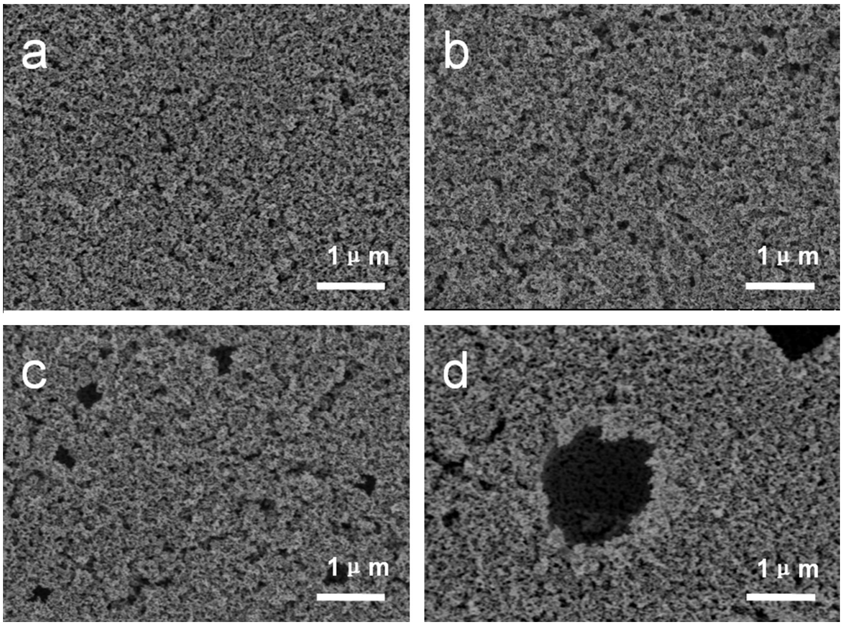

Fig. 1. (a) SEM image of photoanode film in control group which is made from pure P25 TiO_2; SEM images of photoanode films made from P25 TiO_2 (0.1 g) and PSSs (100 μl, 5 vol%) with different diameters. (b) 200 nm, (c) 500 nm and (d) 2 μm.