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Hybrid structure of polyaniline/ZnO nanograss and its application in dye-sensitized solar cell with performance improvement

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ABSTRACT

Polyaniline (PANI) hybridized ZnO photoanode for dye-sensitized solar cell (DSSC) was primarily prepared via a two-step process which involved hydrothermal growth of ZnO nanograss on the fluorine-doped tin oxide (FTO) substrate and subsequently chemisorption of PANI on the surfaces of the ZnO nanorods. The PANI hybridized ZnO nanograss films were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectra (FT-IR), and the results indicated that there were chemical interactions between PANI and ZnO. Both pure ZnO nanograss and PANI hybridized ZnO nanograss were applied to DSSC. The results of photoelectrochemical measurement showed that the photocurrent density of PANI (100 mg/L) hybridized ZnO nanograss photoanode was significantly enhanced, and the overall light-conversion efficiency increased by 60%. The electrochemical impedance spectra (EIS) displayed that the electron densities in photoanodes of PANI hybridized ZnO nanograss were larger than that in pure ZnO nanograss. This is ascribed to more effective charge separation and faster interfacial charge transferring occurred in the hybrid photoanode.

1. Introduction

In sight of rising energy demand and depleting fossil fuels, alternative energy resources are attractively sought. In order to maintain the development of society and economy, more efforts need to be made on finding high effective and renewable energy resources. The primary source of clean abundant energy is the sun. To date, most successful photovoltaic devices are fabricated by semiconductor such as silicon [1]. In recent years, several alternatives to silica-based solar cells have become attractive and considerable research to reduce the cost of electric generation. Dye-sensitized solar cells based on oxide semiconductor and organic dye or metallorganic-complex dye, first reported by Grätzel in 1991 [2], have recently emerged as they are potential to be inexpensive, light weight, portable, flexible and easier manufacture than silica-based solar cells [3,4]. DSSC is a photochemical system fabricated by porous structured film of wide-band oxide semiconductor as a photoanode offering large surface area for dye loading. A photo-to-electric conversion efficiency of more than 11% has been achieved by TiO_2 nanoparticles film sensitized by ruthenium based dye systems [5,6]. However, electron multiple trapping/detrapping events occurring among grains boundaries during electron diffusion through the nanoparticles film decrease the electron transportation rate with the NP film [7,8].

To solve the problem, ZnO nanowire alternative to TiO_2 nanoparticles is considered as one of the most promising materials for photoanode. ZnO is a versatile and wide-band-gap semiconductor that possesses energy-band structure and physical properties similar to those of TiO_2, while electronic mobility of ZnO is about 2–3 orders of magnitude faster than that in TiO_2 nanoparticles film [3]. In addition, ZnO can also be tailored to various nanostructures compared to TiO_2. Therefore, ZnO nanowire was first used as a photoanode of DSSC by Yang et al. (2005) with the purpose of taking place of traditional NP film [9]. Based on the consideration of providing a direct conduction transport path way for photoexcited electron and increasing the electron diffusion length, the overall conversion efficiency of ZnO nanowire was up to 1.2–1.5% [10]. From then on, more and more attempts have been made to improve photo-to-electric conversion efficiency [11–13]. One of the effective approaches is to enhance the aspect ratio of ZnO nanowire/nanorod, thus increasing the density of array. Cao et al. [14] reported a simple method of preparing high aspect ratio of 100–200, a length of 14 μm and a diameter of 120–150 nm. The conversion efficiency of the DSSC using this film was measured to be 1.7%, which meant an increase of almost there times as compared to that using ZnO nanorod with low aspect ratios. The other attention is focused on increasing the

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surface area of ZnO nanowire film, such as fabricating hierarchical nanostructure. Hsieh et al. [15] and Ko et al. [16] reported that the tree-like and nanoforest of high density multigeneration hierarchical ZnO nanostructure photoanodes could significantly increase the power conversion efficiency (up to 2.63% for ZnO nanoforest). Interfacial charge recombination and electron back transferring are the problems that exist in DSSC and cause loss of the photogenerated electrons [17]. That core-shell nanostructured electrode consists of ZnO or TiO_2 covered with a shell of another metal oxide were developed and applied to DSSC with a consideration of reducing electron back transferring [18]. Recently, researchers reported that polyaniline (PANI) hybridized metal oxide semiconductor enhanced the efficiency of electron separation and suppressed the photocorrosion [19,20].

Herein, we first present the photoanode of PANI hybridized ZnO nanograss for DSSC. The results demonstrated that there was hybrid effect existing between PANI and ZnO. This hybrid effect, resulting in increasing the photocurrent density and accelerating the electron separation, was investigated in detail. The overall photovoltaic conversion efficiency of the DSSC based on ZnO nanograss photoanode was enhanced by 60% after it was hybridized by PANI. The possible mechanism is suggested and discussed. It is anticipated that this type of hybrid materials will enable us to design high-efficiency and high-stability photoanodes for solar cell devices in the future.

2. Experiment

2.1. Synthesis of zinc oxide nanograss

Zinc oxide nanograss was grown on the ZnO seeded fluorinated tin oxide (FTO, 15 Ω/cm^2, Nippon Sheet Glass, Japan) by hydrothermal method. Prior to seeding, FTO substrates were first rinsed ultrasonically in acetone, ethanol and distilled water for 15 min, respectively. The cleaned FTO substrates were slowly dipped into 5 mmol/L ethanolic solutions of zinc acetate and then withdrawn at 3 cm/min. Subsequently they were preheated at 300 °C for 15 min in the air to form a ZnO gel seed layer. ZnO nanograss were grown by immersing the ZnO-seeded FTO substrates vertically in solutions with 25 mmol/L $Zn(NO_3)_2$, 25 mmol/L hexamethylenetetramine (HMTA) and 5 mmol/L polyethyleneimine (branched, low molecular weight, Aldrich) at 90 °C in a sealed vessel. In order to obtain longer ZnO nanograss, the solutions were refreshed every 6 h during the reaction period, and the total reaction time was up to 48 h. Subsequently, the arrays were then rinsed with ethanol and deionized water, respectively, and baked in air at 450 °C for 30 min to remove any residual organics and to optimize cell performance.

2.2. Preparation of PANI hybridized ZnO nanograss

PANI-CSA ((1S)-(+)-10-camphorsulfonic acid, CSA) m-cresol solutions were prepared by a doped-dedoped-redoped process as described by Cao et al. [21] to obtain concentrations of 50, 100 and 200 mg/L, respectively. The typical procedure for PANI hybridizing ZnO nanograss film was as follows: ZnO nanograss films were dipped into the PANI solution for 24 h, and then washed with deionized water and ethanol, respectively. All samples were dried in a vacuum oven at 60 °C for 24 h.

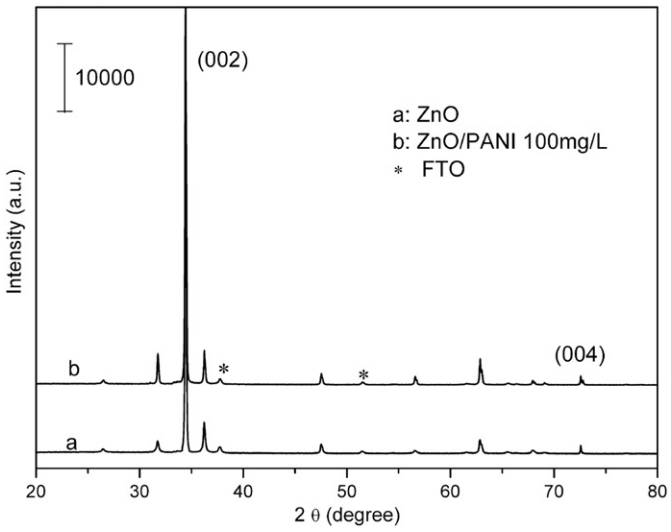

Fig. 2. The XRD patterns of ZnO nanograss and PANI hybridized ZnO nanograss (100 mg/L).

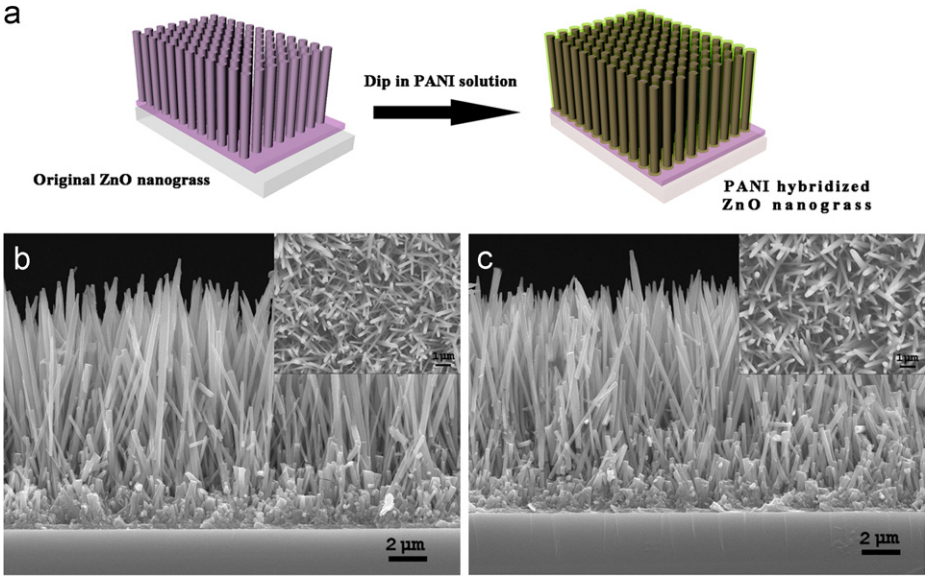

Fig. 1. (a) The schematic procedure of PANI hybridizing ZnO nanograss, (b) side view FE-SEM images of ZnO nanograss obtained by hydrothermal methods, and (c) hybridized sample with 100 mg/L PANI. The insert images show top views.