



Bilayer ZnO nanostructure fabricated by chemical bath and its application in quantum dot sensitized solar cell

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ABSTRACT

Chemical bath method was used to synthesize bilayer ZnO nanostructure on ITO glass in the alkaline solution. As revealed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), the product consists of a layered structure of ZnO nanorods at the bottom and nanoflower atop. The as-prepared sample was assembled in quantum dot sensitized solar cell (QDSSC), which obtained the incident photon to current conversion efficiency (IPCE) of 15% at 400 nm and power conversion efficiency (PCE) of 0.45%. Therefore, this novel bilayer ZnO nanostructure has the potential for application in solar cell device as the photoelectrode.

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1. Introduction

Recently, dye-sensitized solar cell (DSSC) has attracted much of attention due to their efficiency and low-cost fabrication procedure. And overall conversion efficiency of DSSC up to 11% can be achieved by using ruthenium complex as the sensitizer [1]. In addition to organic dyes, semiconductor quantum dots (QDs), for example CdSe, which absorb light in the visible spectrum are good candidates to be a sensitizer in the so-called QD-sensitized solar cell (QDSSC) [2]. Due to the larger extinction coefficient and proper energy level of QDs, electrons can be efficiently transferred to the conduction band of TiO₂ or ZnO [3]. Meanwhile, the multiple exciton generation effect exists in QDs, leading to high quantum efficiency [4]. However, the overall conversion efficiency (PCE) of QDSSC is still very low, one of the main reasons is that lots of electrons loss during the charge transport across the TiO₂ film in QDSSC [5].

Zinc oxide (ZnO) is a multifunctional material with a wide direct band gap (3.37 eV) and large exciton binding energy (60 meV) [6]. Recently, Vayssieres has reported a simple solution approach to synthesis ZnO nanostructure at low-temperature [7]. It provides a low-cost, simple, and large-scale route for growing ZnO nanostructure directly on the transparent substrate. Thus, it has the great potential of application ZnO based photoelectrode in QD- or dye-sensitized solar cell, for example, Leschies et al. have reported 0.4% of PCE value of QDSSC based on single layer ZnO nanowire [8]. And Guo et al. have reported 2.1% of PCE based on ZnO nanorod for DSSC [9]. It has been demonstrated that the morphology of ZnO nanowires can help to improve electron transport by avoiding the particle-to-particle hopping that occurs in the TiO₂ network [8]. And the shape of ZnO nanoflower can increase the adsorption intensity of sensitizers to improve the overall power conversion efficiency of solar cell. For example, Jiang et al. have reported 90% improvement of PCE value based on ZnO nanoflower compared with nanorod photoelectrode in DSSC [10].

In this paper, we shall report the bilayer ZnO architecture synthesized with nanoflower on the upper layer and nanorod array at the bottom layer by chemical bath growth process. We synthesize CdSe quantum dot as the sensitizer. And we shall also report the photovoltaic property of bilayer ZnO architecture assembled in QDSSC as the photoelectrode.

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2. Experiment details

In our experiment, indium–tin–oxide (ITO) glass ($20 \Omega/\square$) was used as substrate. All the chemicals used in experiment were purchased from Aldrich. Generally, two samples were fabricated in a single run for process split and comparison. Firstly, ITO glass substrates were ultrasonically soaked in de-ionized water, acetone, and iso-propanol alcohol subsequently, and then dried at 100°C in a laboratory oven. Afterwards, a 10 nm ZnO seed layer was deposited on the ITO glass substrates by sputtering method. ITO substrates were then put into a solution of 0.05 M zinc acetate, one substrate was faced downwards (sample A) and another one was faced upwards (sample B) immersed in the solution. Then ammonia was dropped into the solution until pH value was 10.35. The growth was carried out at 95°C . After 2.5 h of growth, as one circle growth, the solution was refreshed and the circle was repeated three times. Both two samples were taken out, washed clean and dried. After plasma processing, samples A and B immersed into 3 nm MPA capped CdSe quantum dot aqueous solution which was prepared as the literature for 2 days [8]. After that, samples A and B took out, rinsed with alcohol, and tried. Separated by a $60 \mu\text{m}$ thermal-plastic spacer, samples A and B were assembled separately with 200 \AA platinum-coated indium–tin–oxide (ITO) glass counter electrode, and bonded by epoxy to form cells. The devices fabricated for testing IPCE, PCE values and polysulfide acted as the electrolyte.

Crystal property and morphology of the samples were examined by X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ nm}$), scanning electron microscopy (JSM-5910LV), PCE values of solar cells were measured by a Keithley model 3260 digital source meter using Sun 2000 solar simulator light source (Abet-technologies, U.S.A.) with an irradiance of 100 mW cm^{-2} (the equivalent of one sun at air mass, AM 1.5) at the surface of solar cells. Newport monochromator was introduced

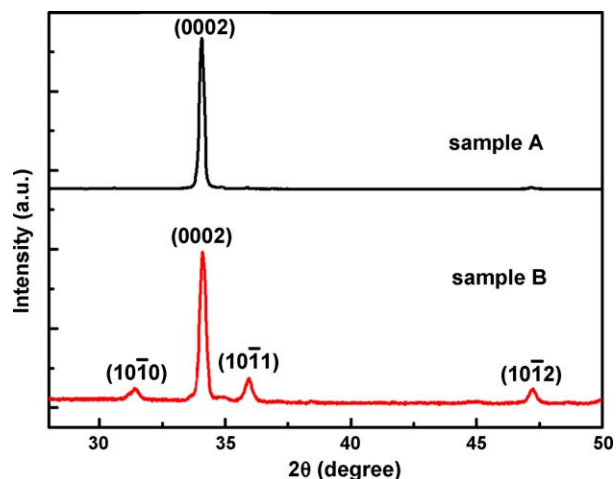


Fig. 1. XRD data for samples A and B.

into the light path to select the excitation wavelength during IPCE measurements.

3. Results and discussion

Fig. 1 shows XRD patterns of samples A and B. It can be seen that only the (0 0 0 2) peak is present for sample A, indicating a highly *c*-axis oriented structure. For sample B, peaks other than (0 0 0 2) are present, all of which can be indexed to the hexagonal wurtzite phase of ZnO. Thus, sample B is less oriented compared to sample A.

Fig. 2 shows the SEM images of sample A. Fig. 2a and b presents the cross-section images of sample A. It can be seen that the length of sample A is $3\text{--}4 \mu\text{m}$, and nanorods growth vertically on the substrate, which is consistent with the results of XRD. Thus, the

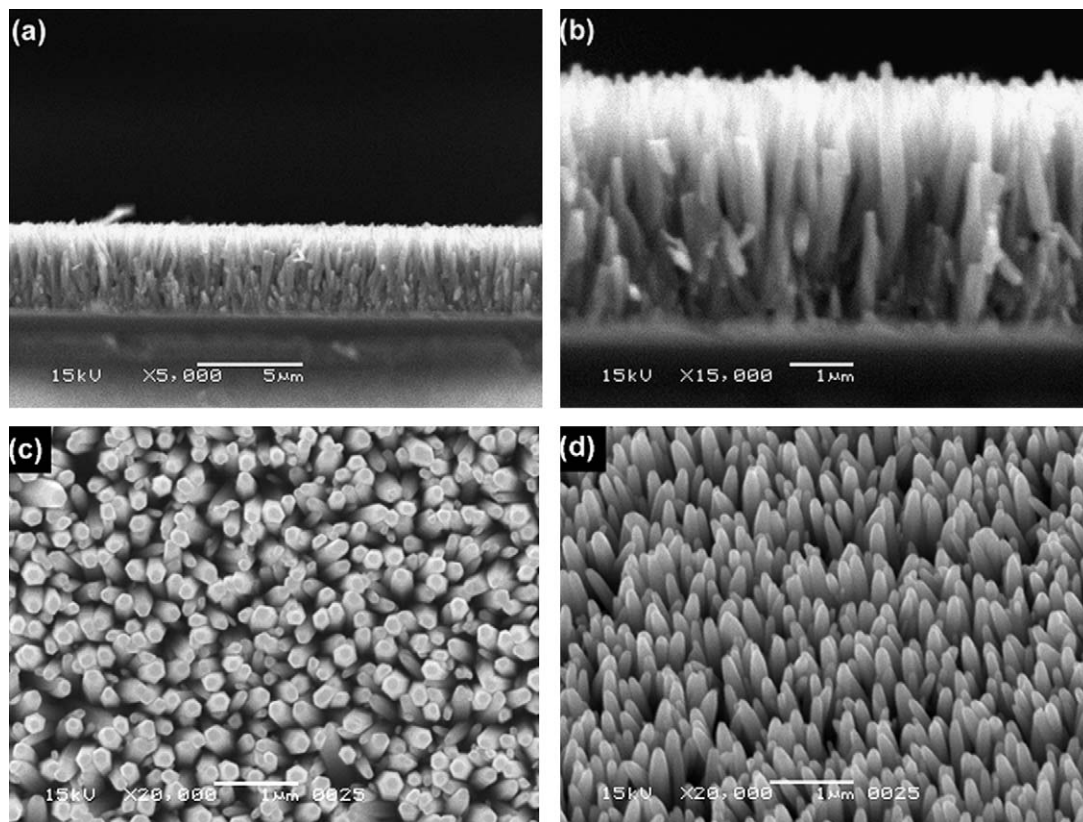


Fig. 2. SEM images of sample A (a) cross-section, (b) magnified cross-section, (c) over-view and (d) with 30° tilt.

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