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Controlled synthesis of ZnO and TiO_2 nanotubes by chemical method and their application in dye-sensitized solar cells

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ABSTRACT

In this paper, the center hollow ZnO and TiO_2 nanotubes arrays were synthesized by chemical etching ZnO nanorods and sol-gel process assisted by ZnO nanorods templates, respectively. And the process concerning the formation of nanotubes was analyzed. Furthermore, as an application of the ZnO and TiO_2 nanotubes, dye-sensitized solar cells (DSSCs) based on them were successfully fabricated and the cell performances were characterized. The efficiency of DSSCs based on ZnO and TiO_2 nanotubes was 1.2% and 2.1%, respectively.

1. Introduction

Dye-sensitized solar cell (DSSC) is currently the most efficient and stable photocell and is one of the promising alternatives for silicon solar cell, as it possesses advantages such as low cost, simple process, and large-scale production [1]. Nowadays, considerable efforts of DSSC have been invested in morphology control of photoanode film and synthesis of stable optical sensitizers [2]. Besides, due to the encapsulation problem posed by the use of the liquid electrolyte in conventional liquid electrolyte based DSSC, solvent leakage and evaporation are two main challenges; therefore, much work is being done to make a solid-state DSSC. Moreover, the use of quasi-solid-state or solid-state electrolytes in the DSSC is expected to offer stable performance for the device [2–5].

DSSC with TiO_2 nanoparticle photoanode films have been demonstrated with a power conversion efficiency of 11% in which a thick layer of nanoporous film provides a large surface area of anchoring the light harvesting dye molecules [1,2,6]. However, slow electron percolation through the interconnected nanoparticles and the charge recombination between injected electrons and electron acceptors in the electrolyte hinder the DSSC performance [7,8]. A desirable morphology of the film should have the channels parallel to each other and vertically with respect to the substrate such as nanorods arrays. Superior photo-to-electric performance of such oriented film is promising. Then a version of nanorods/nanowires dye-sensitized cells was introduced and got good score [9–11]. Moreover, in order to anchor more dye and improve charge transfer, an electrode comprised of an oriented architecture with high surface area, such as a highly ordered nanotubes arrays aligned perpendicularly to the surface, was proposed to increase cell efficiency of energy conversion [12–19].

In this paper, the center hollow ZnO nanotubes arrays with high surface area were synthesized by chemical etching ZnO nanorods using alkaline solution at low temperature. And the aligned TiO_2 nanotubes arrays were fabricated by using an aqueous solution synthesized ZnO nanorods as a template. Furthermore, as an application of the ZnO and TiO_2 nanotubes, dye-sensitized solar cells based on them (nanotubes DSSCs) were successfully fabricated and the cell performances were characterized.

2. Experimental

2.1. Growth of ZnO nanorods arrays

Large-scale arrays of oriented single-crystal ZnO nanorods were successfully fabricated on electrodeposited ZnO seed layer by aqueous solution method from zinc nitrate and hexamethylenetetramine at low temperature (typically 95 °C) [20].

2.2. Preparation of ZnO nanotubes arrays

The center hollow ZnO nanotubes arrays were obtained by chemical etching as-prepared nanorod arrays using 0.1 M alkaline

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solution (KOH) at 85 °C for 1 h, which were thoroughly rinsed in distilled water in order to remove any residual salt or amino complex, and then were dried in air at room temperature.

2.3. Preparation of TiO_2 nanotubes arrays

The aligned TiO_2 nanotubes arrays were fabricated by sol-gel process assisted by ZnO nanorods templates [21].

Firstly, 8.68 ml of tetrabutylorthotitanate was dissolved in the mixture solution of 35 ml of ethanol and 2.82 ml diethanolamine. After magnetic stirring for 2 h, the obtained solution was hydrolyzed by the addition of a mixture of 0.45 ml deionized water and 4.5 ml ethanol dropwise under magnetic stirring for 2 h until a transparent TiO_2 sol was obtained. Secondly, the TiO_2 sol was deposited on ZnO nanorods templates by dip-coating with a withdrawing speed about 3 cm/min. The deposited films were dried at 100 °C for 20 min, and heated up to 550 °C for 1 h at 2 °C/min to obtain ZnO/TiO_2 core-shell arrays. The process above was repeated several times so as to obtain the required thickness of TiO_2. Thirdly, the ZnO/TiO_2 core-shell arrays were immersed 3% (vol) diluted hydrochloric acid aqueous solution at room temperature for 3–4 s, subsequently were thoroughly washed with deionized water to remove any residual solution and dried in air at room temperature.

2.4. Assembly of nanotubes dye-sensitized solar cells

The ZnO and TiO_2 nanotubes arrays films were used as photoanodes in DSSCs with a 2-μm thickness, sensitized in a 0.05 mM ethanol solution of Ruthenium(II)cis-di(thiocyano) bis(2,2′-bypyridyl-4,4′dicarboxylic acid) (N3) dyes for at least 12 h at 60 °C. The excess unanchored dyes were rinsed off using absolute ethanol and dried in air, then covered with platinum sheet as counter electrodes. The internal space of the cell was filled with liquid electrolyte (0.5 M LiI, 0.05 M I_2) dissolved in acetonitrile by capillary action.

2.5. Characterization

Morphology of the films was observed using a PHILIPS XL-30 environment scanning electron microscopy (ESEM). X-ray diffraction (XRD) patterns of the ZnO nanorods were examined with a Rigaku D/max-2500 using Cu Kα radiation ($\lambda = 0.154059$ nm). Photocurrent of the nanotubes DSSCs was measured under irradiation of a xenon lamp (80 mW cm^{-2}) with global AM1.5 condition, and photocurrent-voltage curves of the nanotubes DSSCs were obtained using a potentiostat (TD3691, Tianjin Zhonghuan CO., LTD, China).

3. Results and discussion

3.1. ZnO nanorods

As we all know, wet chemical approaches to well-aligned ZnO nanorods arrays on substrates are attracting considerable research activities because of their low growth temperatures and good potential for scale-up. In this regard, Boyle et al developed a two-step approach, which involves a pre-coating step of ZnO seed layer and a subsequent solution deposition process, to produce perpendicularly oriented ZnO nanorods [22]. In the two-step approach, the ZnO seed layers were usually synthesized by sol-gel method due to its particularly attractive advantages: good homogeneity, ease of composition control, low processing temperature, large area coatings, low equipment cost and good optical properties. However, the film prepared by sol-gel method needs to be fired in order to form crystallization, which usually causes some structure defects and wastes a long time. Recently, cathodic electrodeposition technique emerged as a competitive technique for the fabrication of semiconducting films. The main advantage is the easy control of film thickness, morphology, composition etc. through electrical quantities such as deposition current and applied potential. Especially, the deposition leads to direct formation of crystalline thin films under near-room temperatures [23,24]. As mentioned in reference [20], we presented a novel seed growth process for fabrication of highly oriented ZnO nanorods arrays in aqueous solution at low temperature. We first deposited a ZnO thin film on ITO substrate by electrochemical deposition technique. This thin film serves as a seed layer for the subsequent growth of nanorods in aqueous solutions of zinc nitrate and hexamethylenetetramine at low temperature. The results indicate that well-aligned ZnO nanorods arrays in large scale can be successfully fabricated on electrodeposited ZnO seed layer, and the well-defined crystallographic planes of the hexagonal nanorods can be clearly identified, providing strong evidence that the nanorods grow along the [001] direction (as shown in Fig. 1). Meanwhile, the morphology of ZnO nanorods can be easily controlled by changing the technology parameters [20].

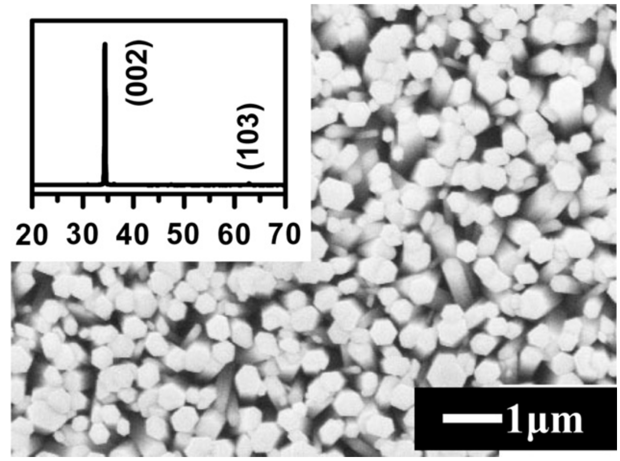

Fig. 1. SEM image of ZnO nanorods arrays (the inset is XRD).

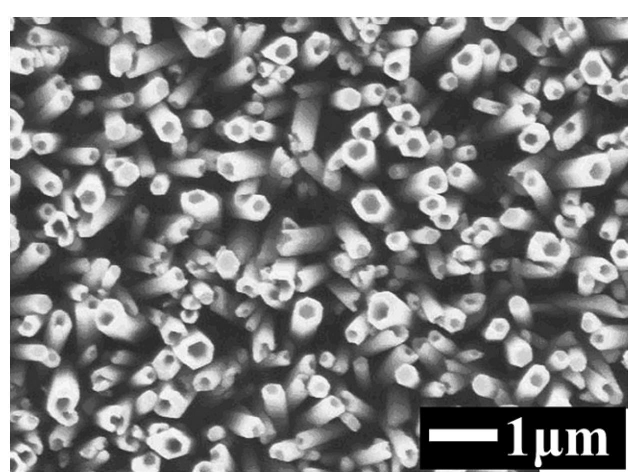

Fig. 2. SEM image of ZnO nanotubes arrays.