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Influence of seed layer treatment on ZnO growth morphology and their device performance in dye-sensitized solar cells

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ABSTRACT

The surface modification of the ZnO seed layer by ultrasonic mediated rinsing (UMR) was realized as an efficient tool for growing highly branched hierarchical ZnO nanorods through multistage approach. The hierarchical ZnO nanostructure achieved through UMR approach was performed as the photoanodes in dye-sensitized solar cells (DSSCs). The DSSC based on the novel branched network resulted in energy conversion efficiency (η) of 1.1% (J_{sc} = 4.7 mA cm^{-2}). The improved device performance was ascribed to the (a) high internal surface area for efficient dye adsorption, (b) rapid electron pathway for charge transport from ZnO to transparent conducting oxide (TCO) substrate and (c) producing random multiple scattering of the light within the hierarchical network leading to photon localization, thereby increasing the probability of the interaction between the photons and the dye molecules of the branched network. The beneficial effect of the UMR approach was distinguished by fabricating DSSCs based on randomly oriented ZnO nanorods prepared by conventional rinsing (CR), which offered lower conversion efficiency η = 0.7% (J_{sc} = 3.8 mA cm^{-2}). The exploration of novel hierarchical ZnO nanorods grown in the present work by the low temperature solution growth techniques may pave way to bring out photoanode material on flexible substrates for the fast growing DSSCs devices.

1. Introduction

Semiconductor hierarchical nanostructures have attracted much interest due to their physical properties and the potential for diverse electronic and photonic device applications [1]. In this context, ZnO became a superior candidate for optoelectronic utilizations than the other wide band gap materials such as GaN and SiC owing to wide direct band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature [2]. Recently, fabrication of ZnO nanostructures in highly oriented and ordered arrays is of crucial importance for the development of novel devices like DSSCs [3]. Generally, seeded growth methods are exploited to tailor the size, population density and spatial distributed of the crystal, where the deposition of thin layer of ZnO prior to solution growth facilitate the vertical growth of aligned ZnO nanorods/nanospines on the substrates. It is also intriguing to note that the size and shape of the ZnO seed particles on the substrate determines the resultant ZnO nanostructures [4].

To date, various methods like sputtering [5], atomic layer deposition [6], sol–gel [7], pulsed laser deposition [8] etc. have been employed to grow ZnO seed layer for obtaining hierarchical nanorods/nanospines. Nevertheless, these methods often involve complex procedures, sophisticated equipments, or rigid experimental conditions and additional high-temperature annealing step which put serious limitation to the applications. On the other hand, chemical solution method has been demonstrated to be a facile method because of the low cost equipments, lower growth temperatures, reproducibility, promising for scaling up, safe and environmentally benign processing conditions. Hence in the present work a novel two-step method was employed, by combining successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD) to achieve large scale production of hierarchical ZnO nanostructures. ZnO seed layer was first deposited on the transparent conducting substrate (TCO) using SILAR process and subsequently ZnO hierarchical growth was established through CBD method. Generally, thin film deposition by SILAR process utilizes mechanical rinsing (conventional) process for removing the excess cationic/anionic ions for further ad atom growth on substrate. However, the adverse morphology of seed layer would hinder the hierarchical growth of ZnO nanostructures during the secondary nucleation. Thus, to obtain novel hierarchical nanostructures during the subsequent CBD process, the seed layer with unique morphology is essential and it still remains a challenging

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task to engineer the suitable morphology for growing hierarchical architectures.

In this paper, we propose a simple facile treatment to synthesize hierarchical ZnO nanostructures on TCO through ultrasonic mediated SILAR method. Effect of ultrasonic treatment on structural and morphological features of seed layer was investigated. The ZnO hierarchical growth on TCO substrates explored through the UMR process will be both fundamentally interesting and technologically important for typical applications of ZnO electrodes in DSSCs.

2. Experimental procedure

2.1. Preparation of ZnO seed-coated substrate

All the chemicals used in the present work are analytic grade and used as received. ZnO seed layer was deposited on both the glass substrates and fluorinated tin oxide (FTO) (Pilkington, USA) by SILAR method using aqueous zinc–ammonia complex as the cation precursor and deionized water as anionic precursor. The aqueous zinc–ammonia complex ion ($[Zn(NH_3)_4]^{2+}$) was prepared by mixing zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and ammonia ($NH_3$), with Zn:$NH_3$ molar ratio of 1:20 and Zn^{2+} concentration of 0.1 mol/L. ZnO seed layer was deposited by alternate dipping into zinc ammonia complex kept at room temperature and hot water maintained at 85 °C. In brief, each deposition cycle consist of five steps: (1) immersion of substrate in ($[Zn(NH_3)_4]^{2+}$) solution for 12 s for complex adsorption; (2) the instant immersion of withdrawn substrates in hot water (85 °C) for 15 s to form solid ZnO layer; (3) drying of substrate in air for 10 s; (4) rinsing the substrate in deionized water under ultrasonic irradiation to remove loosely absorbed ZnO particulates; (5) drying the substrate in air for 30 s before the start of next deposition cycle. Totally 40 deposition cycles were performed. The samples derived from the key processing step (UMR process) herein named as "Sample A". For the sake of comparison, the seed layers were prepared using manual rinsing in step 4 and the sample is named as "Sample B".

2.2. Growth of ZnO by chemical bath deposition

The ZnO films were grown subsequently on seed coated substrate using the bath containing $Zn(CH_3COO)_2{\cdot}2H_2O$, NH_3 and triethanolamine ($N(C_2H_4OH)_3$) as a zinc source, a base and a stabilizer respectively. The aqueous $[Zn(NH_3)_4]^{2+}$ complex ion was prepared as mentioned above with same molar ratio and concentration. To this complex solution, 0.2 M of triethanolamine was added and the mixture was stirred for few minutes before placing in water bath. The deposition was carried at 70 °C for 2.5 h. The pH of the resultant solution was 10.5. For comparison, ZnO films grown directly on bare substrates without seed layers are named as "sample C".

2.3. DSSCs assembly

The ZnO films prepared on FTO substrates were sensitized with ruthenium based N719 dye. The ZnO electrodes (sample A, sample B and sample C) were soaked in a solution containing 0.3 mM of dye and a mixture of acetonitrile (ACN) and t-butyl alcohol (1:1, v/v) for 2 h and dried at room temperature. A sandwich-type configuration was employed to measure the performance of the DSSCs, using a Pt-coated F-doped SnO_2 film as a counter electrode and 0.5 M MPII (1-methyl-3-propylimidazolium iodide) with 0.05 M I_2 in ACN as the electrolyte solution. In order to prevent the back flow of electrons from the FTO substrate to the ZnO layer, a thin compact TiO_2 layer was formed in between the FTO electrode and the ZnO seed layer. The TiO_2 layer was deposited by spin coating 0.2 M diisopropoxy titanium bis (acetylacetonate) solution in anhydrous ethanol and subsequently calcinating at 450 °C for 30 min in air. The DSSCs prepared using sample A, sample B and sample C as photoelectrodes are herein named as DSSC-A, DSSC-B and DSSC-C respectively.

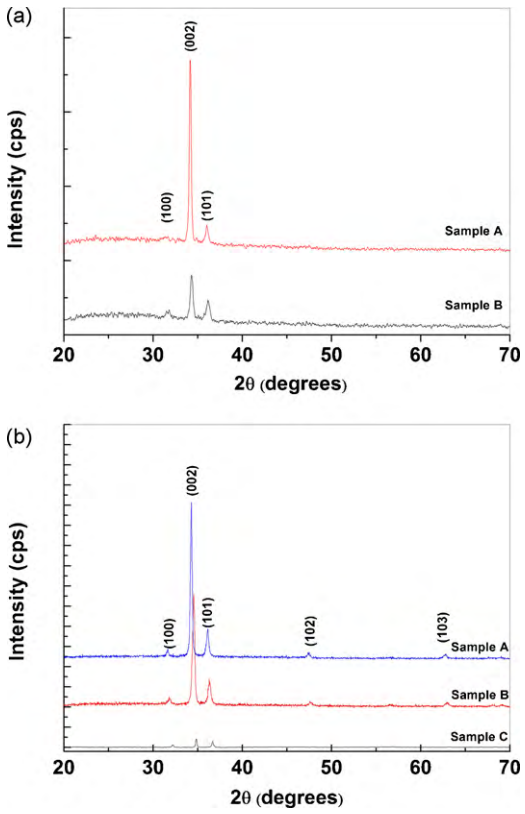

Fig. 1. XRD pattern of (a) ZnO seed layer and (b) ZnO nanostructured films.

The crystallite growth of the samples were studied by X-ray diffractometer (Bruker Axs D8) using CuKα radiation (λ = 1.5406 Å) and morphological analysis were performed by scanning electron microscopy (JEOL JSM-6330F). Optical absorption spectra were recorded using UV/VIS/NIR spectrophotometer (OPTIZEN 2010) under visible wavelength. Current–voltage characteristics of DSSCs were performed under 1 sun illumination (AM 1.5G, 100 mW cm^{-2}) with a Newport (USA) solar simulator (300 W Xe source) and a Keithley 2400 source meter (device area is 0.16 cm^2).

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1(a) shows the XRD pattern of ZnO seed layer deposited on glass substrates using SILAR method by employing UMR (Sample A) and conventional rinsing (Sample B) process. All the peaks could be indexed to hexagonal wurtize structure of ZnO, which is in close agreement with the standard card (JCPDS 36-1451). Both the samples exhibited preferential orientation along (0 0 2) plane, where intensity of (0 0 2) peak was significantly enhanced upon UMR process. No diffraction peak of impurities such as $Zn(OH)_2$ or zinc acetate was detected in both cases, indicating the high phase purity of the obtained film. The mean crystallite size of the ZnO nanostructure was determined using the (0 0 2) peaks and the Debye–Scherrer's formula. It was found to be 32 nm and 26 nm for Sample A and Sample B respectively.