Electrochimica Acta 123 (2014) 405–411

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Synthesis and Characterization of Hierarchical ZnO Structures by a Single-Step Electrodeposition under Hydrothermal Conditions

Ceren Yilmaz [a], Ugur Unal [a,b,c,*]

[a] Graduate School of Science and Engineering, Koc University, Rumelifeneri Yolu, Sariyer 34450, Istanbul, Turkey
[b] Koc University, Chemistry Department, Rumelifeneri yolu, Sariyer Istanbul,Turkey
[c] Koc University Surface Science and Technology Center (KUYTAM), Rumelifeneri yolu, Sariyer 34450 Istanbul,Turkey

ARTICLE INFO

Article history:
Received 13 August 2013
Received in revised form 8 December 2013
Accepted 8 January 2014
Available online 24 January 2014

Keywords:
hierarchical ZnO
hydrothermal
electrodeposition

ABSTRACT

We present a simple, single step process to produce hierarchical ZnO architectures which involves introduction of $Cd(CH_3COO)_2$ and electrochemical deposition under hydrothermal conditions. Effect of $Cd(CH_3COO)_2$ concentration on the morphology of ZnO films were examined. A variety of hierarchial structures were obtained including micrometer-long micro-channels, 1D twinned structures, 2D ZnO crosses and star flower-like structures by modifying [$Cd(CH_3COO)_2$/Zn(II)] ratio. Besides surface morphology, the growth mechanism giving rise to the particular structures, crystal structure, phase purity, and chemical binding characteristics of the deposits were examined.

1. Introduction

Interest in ZnO has been dramatically increased in the last decade due to its high exciton binding energy (60meV) and wide band-gap (3.3 eV) that is tunable through doping with rare earth elements, metal ions or chalcogens such as sulfur [1]. This tunability permits ZnO to possess a wide range of adjustable physical properties like conductivity, room temperature ferromagnetism, high transparency, chemical sensing, conductivity which make it possible to fabricate electronic, optoelectronic, electrochemical, and electro-mechanical nanodevices [2]. Furthermore, the morphology of ZnO particles can also be modified by adjusting growth conditions. Controllable morphology adds another charm to ZnO since effectiveness and efficiency of the fabricated product depends on the shape and size of the constituent particles. Especially, 1D ZnO nanostructures such as nanorods, nanowires, nanoribbons and nanotubes have become very attractive for optoelectronic device applications due to their high accessible area and efficient diffusion path of charge carriers [1]. In comparison to 1D nanostructures, hybrid morphologies of nanosheets and nanowires or branched structures which form hierarchical architectures are becoming more desirable for sustainable energy applications like dye-sentisized solar cells (DSSCs) and solar powered water splitters. These hierarchical assemblies combine characteristic aspects of nanometer and micrometer sized building blocks, provide higher surface area (allows higher dye loading in DSSCs) and reduced charge recombination which allows enhanced light absorption and faster charge separation, hence increase the overall efficiency of the device [3–5].

Several methodologies have been reported to obtain hierarchial ZnO nanostructures including vapor transport and condensation technique [6], sequential hydrothermal processes [5,7] and electrodeposition [3,4,8,9]. Vapor-based techniques require high vacuum and high temperatures and they might involve introduction of catalysts which might affect the physical properties of the product. On the other hand, multi-step procedures are employed to produce hierarchical ZnO nanostructures via solvothermal processes or electrodeposition. Xu *et al.* reported electrochemical deposition of ZnO nanoneedles on surfaces of ZnO nanosheets, nanorods, and nanoneedles grown a priori by electrodeposition in the presence of different additives [8]. Similarly, both C. Yao *et al.* [3] and Wang's group [9] demonstrated formation of hierarchical ZnO structures by electrodeposition of ZnO nanorods using previously electro-deposited ZnO microsheets as the working electrode. Correspondingly, hydrothermal methods involve a series of nucleation and growth sequences [7] and also might require introduction of surfactants [5]. Xu *et al.* also constructed hierarchical ZnO structures by combining a low-temperature electrodeposition process and subsequent aqueous chemical growth [4]. However, there are no reports on synthesis of hierarchical ZnO structures with a single electrodeposition step, to the best of our knowledge. In this study, we report synthesis of hierarchical ZnO architectures

* Corresponding author. Koc University, Chemistry Department, Rumelifeneri yolu, Sariyer, 34450, Istanbul, Turkey. Tel.: +90 212 338 1339; fax: +90 212 338 1559.
E-mail addresses: ugunal@ku.edu.tr, ugurunal@gmail.com (U. Unal).

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http://dx.doi.org/10.1016/j.electacta.2014.01.039

with a facile, single-pot process which combines benefits of hydrothermal conditions and electrochemistry at a single step. We shall show that introduction of $Cd(CH_3COO)_2$ into the hydrothermal deposition bath is a key factor to obtain hierarchical ZnO architectures and morphology of the films can be controlled by adjusting $[Cd(CH_3COO)_2/Zn(II)]$ ratio.

2. Materials and Methods

2.1. Materials

All the chemicals used were of analytical grade or of the highest purity commercially available. Cadmium acetate hexahydrate ($Cd(CH_3COO)_2 \bullet 6H_2O$) was obtained from Merck and zinc nitrate hexahydrate ($Zn(NO_3)_2 \bullet 6H_2O$) was purchased from Sigma-Aldrich. Indium Tin Oxide (ITO) ($\Omega < 5.0 \times 10^{-4}$ ohm.cm (Rs < 100 ohm/sq) was purchased from Teknoma Ltd. Izmir, Turkey. Double distilled, high purity water was used from Milli-Q water (Millipore) system.

2.2. Synthesis and Characterization

Cd_doped ZnO layers were grown on ITO (Indium tin oxide) coated glass electrode ($1 \times 1\ cm^2$ area) by cathodic electrodeposition in an aqueous solution of $Cd(CH_3COO)_2$ and $Zn(NO_3)_2$ mixture in different proportions. The Zn(II) concentration was fixed to 50 mM and [Cd(II)] \[Zn(II)] ratio was varied between 0.2 and 1. A conventional 3-electrode cell system in a hydrothermal glass reactor (Büchiglasuster, modified picoclave) was used for the electrochemical deposition. The volume of the reactor was 100 ml. The reference electrode was Ag/AgCl saturated with KCl (Corr Instruments, S/N P11092) whereas Pt wire served as counter electrode. The substrate was cleaned ultrasonically by ethanol, acetone and distilled water prior to depositions. Electrodepositions were carried out at constant potential of -1.1 V at 130 °C under autonomous pressure for 30 minutes with a potentiostat/galvanostat (Biologic-Science Instruments, VSP model).

The crystal structure of the samples were analyzed by X-ray diffraction (XRD) method using Bruker/D8 Advance with DaVinci with Cu Kα radiation. The surface morphology of the films was examined with ZEISS Ultra Plus Field Emission Scanning Electron Microscope (FE-SEM). The film composition was studied by X-Ray Photoelectron Spectroscopy (Thermo K-Alpha, XPS). C1s (285 eV) peak served as a reference to calibrate the binding energies. The area under the Cd 2p and Zn 2p curves was differentiated after performing a Gaussian-Lorentzian fitting to calculate the relative Cd content in the films. Both the top surface of the films and inner layers were measured after 540s of etching with Ar^+. Raman scattering experiments were carried out using a Renishaw Raman Microscope system at room temperature. 532 nm line was used for excitation.

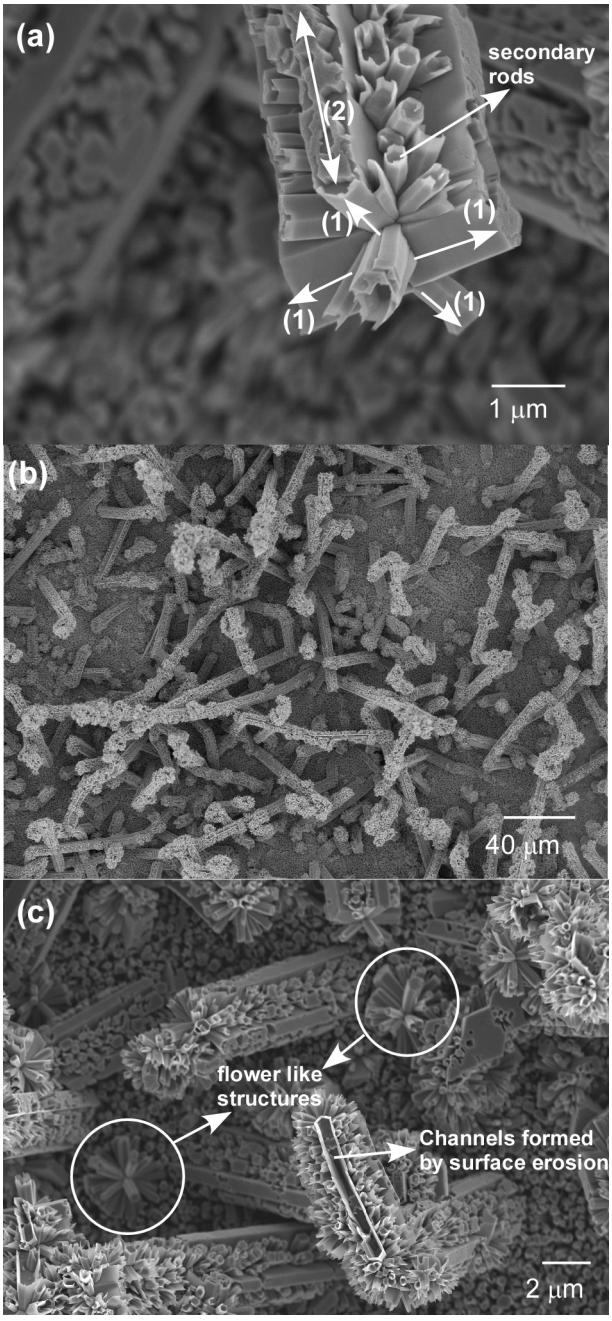

Fig. 1. FE-SEM images of the Cd_ZnO film prepared from a bath with a feed ratio [Cd(II)]/[Zn(II)] =0.2. at a) 30 K magnification, b) 1.5 K magnification, c)10 K magnification.

3. Results and Discussions

$Cd(CH_3COO)_2$ concentration was varied to provide [Cd(II)] \[Zn(II)] ratio between 0.2 and 1 to investigate the effect of introducing Cd^{2+} and CH_3COO^- to the aqueous electrodeposition bath of ZnO films. Figs. 1 and 2 show typical FE-SEM images of the as-prepared films on ITO substrates prepared by 30 minutes deposition at 130 °C, -1.1 V vs Ag/AgCl. When there is no $Cd(CH_3COO)_2$ in the precursor solution, vertically aligned ZnO rod arrays with hexagonal facets were obtained (data not shown). When $Cd(CH_3COO)_2$ was included in the deposition solution hierarchical structures with different symmetries were observed. When [Cd(II)] \[Zn(II)] ratio was 0.2, large assemblies grown on the nanorod array were observed (Fig. 1a-c). These long structures were formed by arrangement of four extensions (marked as (1) on Fig. 1a) joined together at their base perpendicular to each other. Each extension is composed of rods fused together on their lateral side. The direction of assembly is given with double arrow marked as (2) on Fig. 1a. In between these extensions, secondary rods with hexagonal tips have grown in different directions (Fig. 1a). The length of each assembly was varied between 15-20 μm. Structures that are even ~42 μm long were detected (Fig. 1b). Secondary nanorods were ~700 nm long with ~300 nm diameters. Fig. 1c shows some variations in the structure of larger assemblies. There exists a single ~5 μm long structure with secondary nanorods grown on all the 6 sides. As seen in the figure, a channel is formed on the structure as a result of the erosion. In current synthesis conditions, the surface of the rods might be eroded as explained in further paragraphs. These surface eroded rods are assembled to each other to