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Synthesis of ZnO Hierarchical Structure by Thermal Oxidation of Zinc Foil

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ABSTRACT

Zinc oxide (ZnO) nanorods, as well as nanotowers were successfully synthesized by thermal oxidation of gold coated zinc foil substrate in air. To reveal effect of oxidation temperature and time on structure and morphology properties, the samples were oxidized at 400°C and 450°C for 2 hours and 4 hours using tube furnace. A combination of X-ray diffraction and field emission scanning electron microscope (FESEM) was employed to study the structure and morphology of the ZnO nanostructures. X-ray diffraction revealed that the synthesized ZnOwas in hexagonal wurtzite phase. FESEM results showed that the formation of ZnOnanorods with diameter of (28nm) and length up to (1.5μm) occurred at 400°C while nanotowres formation occured at 450°C. These ZnO nanostructures have promising potential application in photocatalytic and gas sensors.

INTRODUCTION

Zinc oxide (ZnO) is a direct, wide band gap (3.37 eV) semiconductor material anda large exciton binding energy of(60 meV) at room temperature. It has many potential applications in the field of electronics, optoelectronics, sensors, spintronics and photocatalysis especially in the form of nanostructures. (S.N. Cha*et al*.,2006),(Jong-Yeob Kim*et al*.,2011),(Zhizhong Han*et al*.,2012) and (BhagabanBehera and Sudhir Chandra,2015).Nanostructured materials have attracted much attention due to their novel physical and chemical properties in comparison with their bulk or thin films counterpart.(D. Yuvarajand K. Narasimha,2009).Where shrinking itsgrean size to nanoscale cause the large specific surfaces and size _induced quantum effect's(ChuanFeiGuo*et al*.,2010).ZnO nanostructure have been synthesized using different fabrication methods. These fabrication methods include thermal evaporation (K.M.K. Srivatsa*et al*.,2011), hydrothermal (Ping Wang*et al*.,2012), chemical deposition (Xiaojinj Yu*et al*.,2011), chemical vapor deposition (J,-J,Wu and S,-C,Liu,2002), Chemical Bath Deposition(Zhaolin Yuan,2015)and sol-gel (M.Kashif*et al*.,2012).There are some limitations in these processes in terms of high thermal budget, requirement of a catalyst or the high cost involved. Thermal oxidation is a batter candidate for synthesizing nanostructures, This method is becoming an increasingly attractive method because it's simply, low cost, convent and fast to produce different morphologies of nanostructure like nanowire (Lu Yuan and Guangwen Zhou,2012),nanoneedles (I. Mihailova*et al*.,2013),nanosheets (WaiKian Tan*et al*.,2014),nanobelts (A. Umar*et al*.,2005), nanorods (W. K. Tan*et al*.,2011) andnanotowers (Da Deng*et al*.,2010).Many studies on preparation of ZnOnanostructures by thermal oxidation have been reported up to now with or without catalyst layer, the commonly used catalyst for ZnO is Au(PungSwee-Yong*et al*.,2012).ZnO nanostructures have thus been synthesized successfully by directly heating zinc foil (C. Florica *et al*.,2016), Zn thin film on top of different substrates (Mohammad Reza Khanlary*et*

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al.,2012),brass foil($Cu_{0.7}$ – $Zn_{0.3}$ alloy)(Xuebin Wang*et al*.,2009)and metallic Zn powder(NurulIzniRusli,2012).The temperatures reported for ZnO nanostructure formation during oxidation vary typically from (400 to1000 °C), which cover the melting temperature (420° C) and boiling temperature (907 °C) of Zn (Lu Yuan*et al*.,2014).

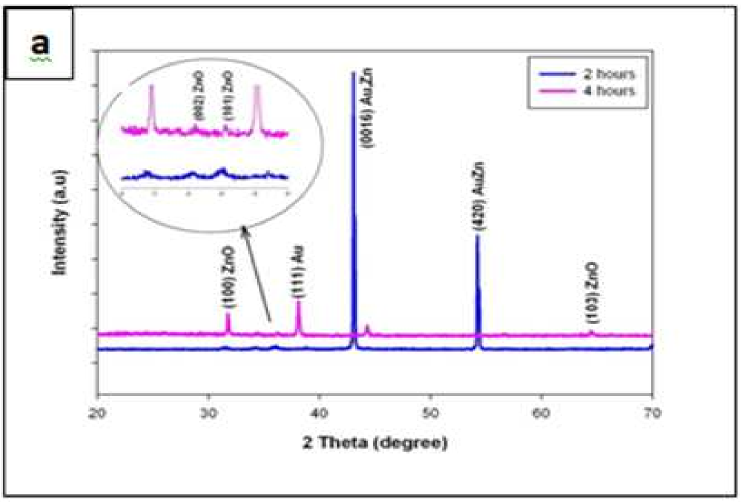
In the present work, we have demonstrated the fabrication of ZnOnanorod and nanotower directly on zinc foil substrate under different experimental conditions with using gold thin film as catalyst. Since the foil functions as both Zn source and substrate for the growth of ZnO nanostructures; thus, the synthesis and assembly of ZnO nanostructures on a metallic substrate is accomplished in one step, and the naturally good adhesion or electrical between the ZnO nanostructures and the conductive substrate has been realized.

Experimental:

ZnO nanostructures were prepared by a catalyst assisted thermal oxidation of Zn metal foil in air. A conventional horizontal tube furnace was used for the synthesis of ZnO nanostructures at different temperature (400, 450 °C) for two typical oxidation durations of 2 and 4 hoursrespectively. High purity Zinc foil from Alfa-Aesar(1cm× 1cm) were used as both the substrate and Zn^{2+}source. Zn foil were ultrasonically cleaned in acetone and in ethanol successively for 20 min in each solvent. A thin film of gold (40nm) was deposited by DC sputtering as a catalyst layer. Zinc foils were loaded onto a quartz boat; this boat was inserted close to the center of quartz tube inside the horizontal tube furnace. The furnace was heated to the certain temperature at a heating rate of (3 °C/min) and kept at this temperature for (2,4 h) respectively. Subsequently, the furnace was cooled naturally to room temperature.The structure of the ZnO nanostructures have been analyzed by X-ray diffraction (XRD) using (miniflex II Rigaku, Japan) x-ray diffractometer, the wave lengh of x-ray source radiation (Cu,kα) is 1.54°A and Field Emission scanning electron microscopy (FESEM) using (Hitachi- S4160, Japan).

RESULTS AND DISCUSSION

The X-ray diffraction (XRD) patterns of the samples oxidized at 400 °C and at 450 °C for 2 and 4 h are shown in figure (1). The diffraction peaks are in good agreement with the hexagonal wurtzite structure of ZnO(JCPDS card no. 36-1451).The presence of sharp and intens diffraction peaks for ZnO implies high crystallinity of the as-prepared sample. At 400 °C, a few diffraction peaks corresponding to metallic Au and Au-Zn alloy have been observed (see fig .1-a). It was also observed that the number of these diffraction peaks and their intensity were decreased with the increase of the oxidation time and temperature.No diffraction peaks from Zn or Au-Zn alloy can be detected in the samples oxidized at 450 °C .It can be concluded that, after oxidation, Zn was completely converted into ZnO (see fig.1-b).This result is in agood agreement with (F. J. Sheini *et al*.,2011).



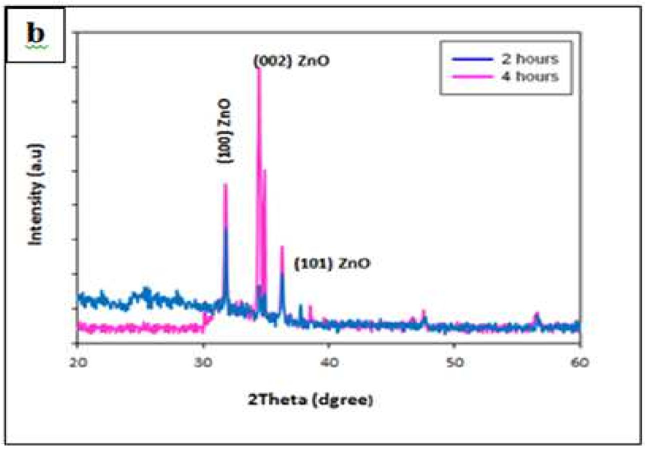


Fig. 1: XRD patterns of ZnO nanostructures synthesized on zinc foil: (a) at 400◦C for 2 and 4h; (b) at 450 ◦C for 2 and 4h time of oxidation.

For the microstructural analysis of the as-synthesized samples,FESEM are used. The morphologies of the Zn foils oxidized at different temperatures for 2h are shown in figure (2). The oxidation at 400 °C for 2 h resulted in the formation of short, sparse and randomly distributed ZnOnanorods on the Zn surface, (see Fig.2(a-b)) The growth of the nanorods was not uniform throughout the foil.The nanorods have a length and diameter averaged at (0.4) µm and (40) nm respectively.While the oxidation at 450 °C resulted in the formation of ZnOnanorods with a much higher surface density, longer length and larger diameter, most of nanorods became gradually thinner towards their tip. Smaller diameter nanorods are seen to branch out from the main rods, (see Fig.2(c-d).

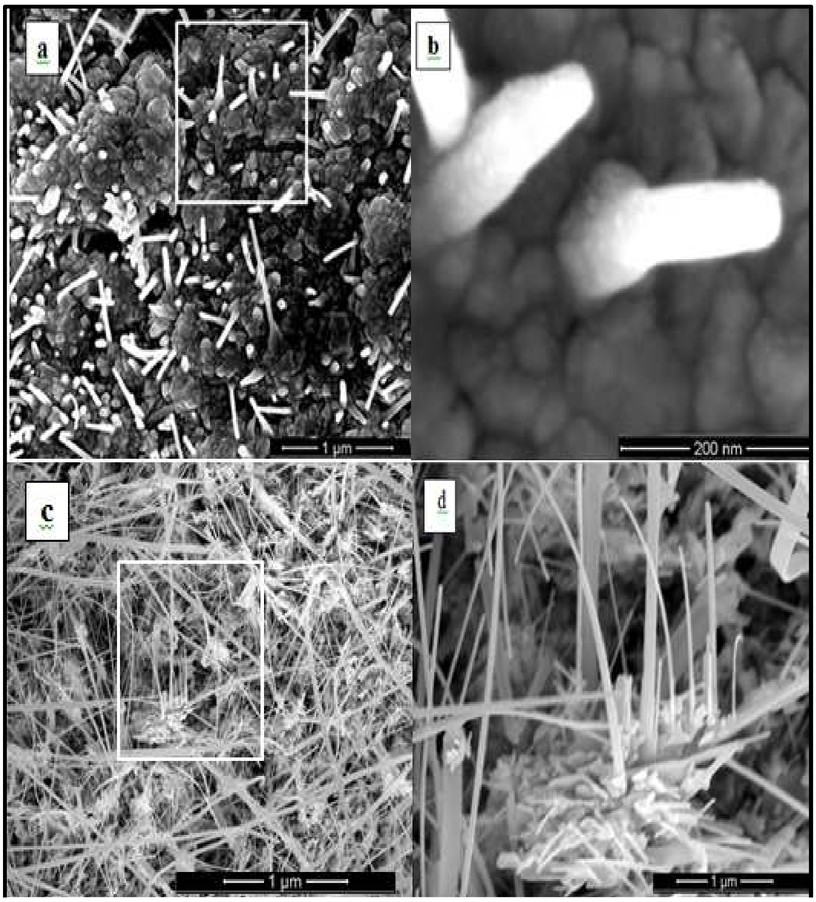


Fig. 2: FESEM images of ZnOnanostructure formed on zinc foil for 2h :(a) at 400°C; (b) the high magnification of the high light rectangle in (a);(c):at 450;(d) the high magnification of the high light rectangle in(c)

To investigate the effect of Oxidation time in the morphologies of the oxidized Zn foil, Oxidation at a longer time of 4 h was then carried out. As the oxidation time increased the surface density and length of the nanorods increased for the samples oxidized at 400°C in comparison with samples oxidized at 2 h The nanorods have a length up to (1.5 µm) and average diameter of (64 nm) at the base, (28 nm) at the tip (see Fig3(a-b).The samples oxidized at 450 °C for 4 h consist of branched nanorods with much higher surface density in comparison with the samples oxidized at 2h , (see Fig 3(c-d)). Tower like structure was also observed referred to by the white arrow as seen in fig (3 -d).

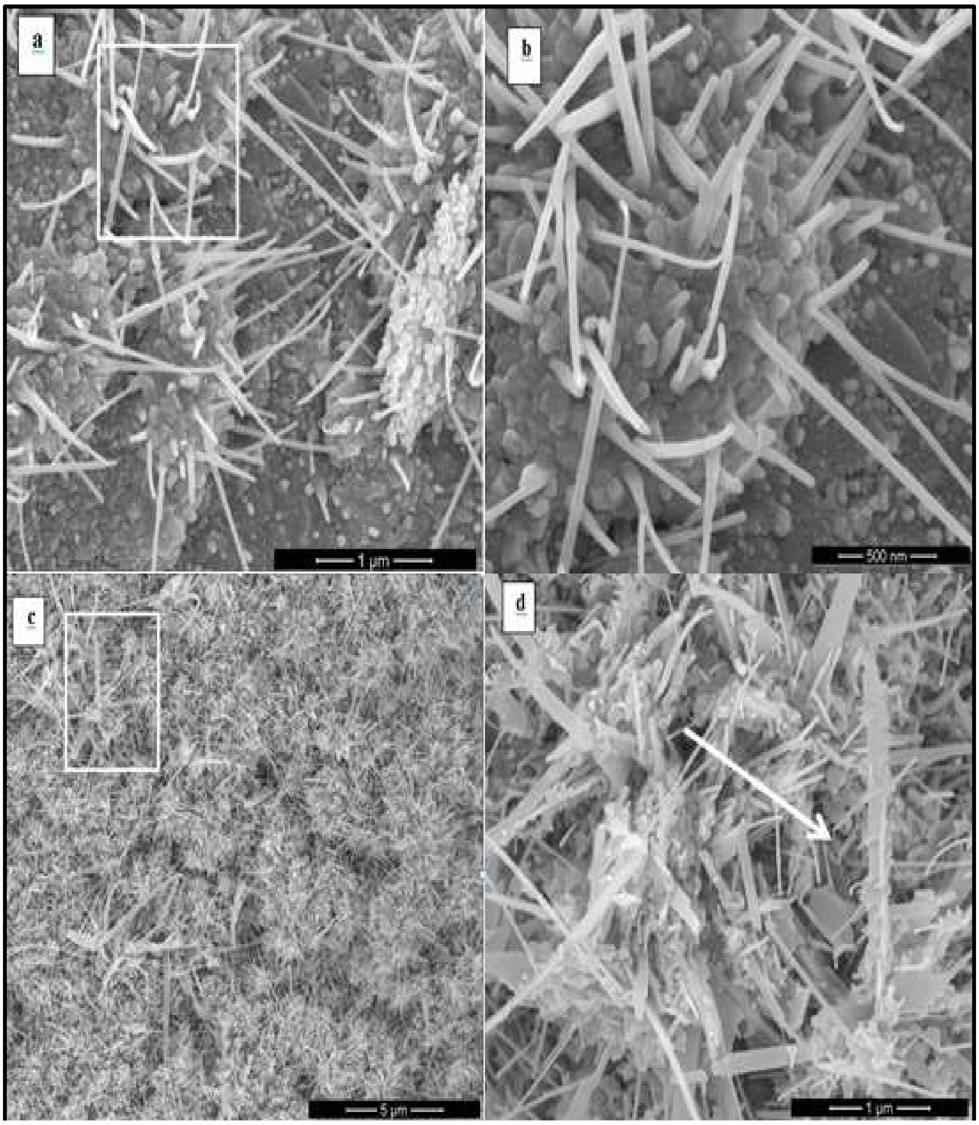


Fig. 3: FESEM images of ZnOnanostructure formed on zinc foil for 4h :(a) at 400°C; (b) the high magnification of the high light rectangle in (a);(c):at 450;(d) the high magnification of the high light rectangle in(c).

It was found that the oxidation reaction occurred with two mechanisms; lower melting point of zinc metal and above melting point of zinc metal (B. Behera and S. Chandra,2014). At the oxidation temperature below the melting of Zn, the formation of ZnO nanostructures occurs via a solid–solid transformation mechanism. where Zn in solid phase can be oxidized to form ZnOnanorods at temperature less than 419.6°c. For oxidation at temperatures above the melting point of Zn,the liquid–solid mechanism is the dominating process that results in the formation of ZnO nanostructures. where more than 419.6°c, Zn in liquid phase can be oxidized to form ZnOnanorods on the substrate.

At 400° C, the formation of the ZnOnanorods can be explained on the solid _solid mechanism (Lu Yuan,2014), as the temperature is below the melting point of Zn, the Zn atoms undergo solid phase diffusion from the substrate (Zn foil) to the surface, which form Au-Zn alloy particles. The Au/Au-Zn alloy particles play catalytic role in the growth of the ZnOnanorods,first acting as nucleation sites and then initiating the growth process. With The continued supply of Zn atoms from the substrate and $O_2$from the air,they react to form ZnO. ZnO start to adsorb on the surface of clusters and growing as nanorods as seen in fig(2-a).

When the oxidation of Zn takes place at 450°C (above the melting point of Zn) The growth was governed by liquid _solid mechanisms (Zhong Lin Wang ,2004).The Zn metal start to melt and form a large quantity of melting liquid alloy droplet with Au catalyst. The liquid droplet serves as preferential site for absorption of gas phase reactant and, when supersaturated, the nucleation site for crystallization. Nanorod growth begins after the liquid becomes supersaturated in reactant materials and continues as long as the catalyst alloy remains in a liquid state and the reactant is available. During growth, the catalyst droplet directs the nanorod's growth direction and defines the diameter of the nanorod. The length of the nanorod increase with increase the oxidation temperature and time. The increase of the nanorod length can also originate from the transport of zn atoms via a particular diffusion channel inside the rods towards the tip of the nanorods. The growing tip of a nanorod is expected to have restricted supply of zinc, so a needle shape develops. The increase of the nanorod diameter can also originate from the migration of material from one rod to the other, this result in formation of smaller rods emerge from the main nanorods. Due to higher concentration at the base additional nucleation and growth occur forming ananotower at this temperature secondary growth leads to the formation of branched nanorods and nanotower. The formation mechanism of nanotower can be illustrated in fig (4). At the first step(a) the nuclution take place,then the nanorod formation occur as the second step (b).At third step(c),With increasing the temperature and time the length and diameter increased and small rods emerge from the main rods due to secondary growth result in the formation of nanotower as the last step (d).

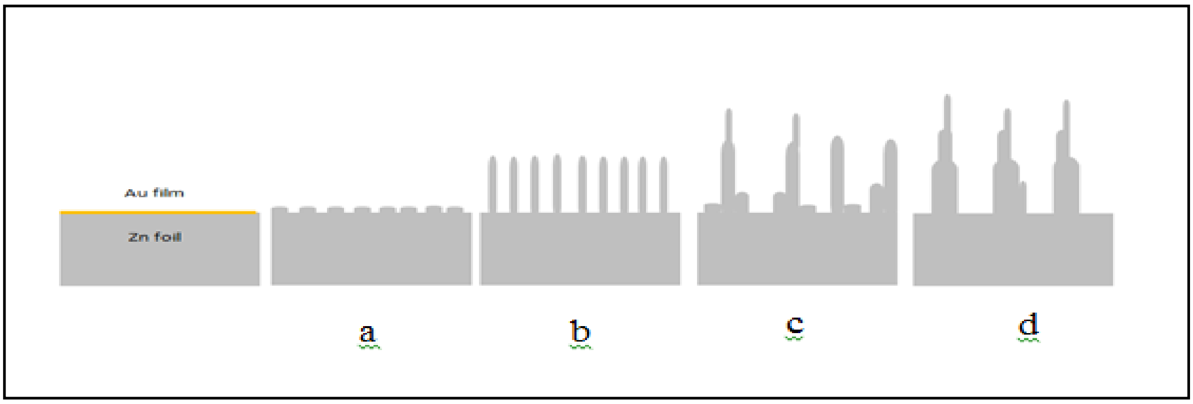


Fig. 4: Schematic illustration of growth of ZnOnanorods and nanotower on the surface of zinc foil by oxidation in air.

Conclusions:

Tow type of ZnO nanostructures: nanorod and nanotower,were successfully synthesized by thermal oxidation method of Zn foil in air. The oxidation temperature and time are believed to play important roles in the growth of the nanostructures. As oxidation temperature and time increases, density as well as the length of nanorodesincreases.The formation of nanotower was only observed at Oxidation temperature of (450 °C): at lower than this temperature, nanorods formation were observed.These nanostructures exhibited better performanceFor gas sensor and photocatalytic applications due to the very large specific surface area.

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