Synthesis of Zinc Oxide Nano Rods, Sheet and Flower at 80°C by the Sol-gel Method

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Abstract

Synthesis of zinc oxide nanorods, sheets and flower like structure were done by the sol-gel method using zinc acetate dihydrate and sodium hydroxide at 80°C with 12 hours refluxing time nanorods, in case of as synthesized powder, with diameter of 20-60nm. Annealing at higher temperature (300 and 500ºC,) in air ambient changes the morphology to sheet and flower like structre. The standard peak of zinc oxide was observed in IR at 523cm^{-1}. The UV-VIS spectroscopy of zinc oxide shows a characteristic peak at 375nm.

Keywords : Nanorods, Sol-Gel, X-ray diffraction, ZnO

1. Introduction

Semiconductor zinc oxide is a unique material that can be easily grown with properties like high mechanical, thermal, and chemical stability. In the past decade, the interest has been focused on nanostructured zinc oxide for instance nanorods, nanowires, and nanoneedles [1-2]. The Wurtzite zinc oxide is a promising semiconductor material due to its large applicationareas such as solar cells, sensors, optoelectronic devices, surface acoustic waves and wave-guides, light emitting diodes and laser diode etc. In addition to this; chemical routes are easier and economical for preparation of micro and nanorods of zinc oxide for the large-scale industrial production.

We are reporting here sol-gel process for the preparation of zinc oxide nano and microstructures with handy checmials. The chemical analysis was carried out by the XRD, FTIR, and SEM, whereas the optical properties were investigated using UV-Vis spectroscopy.

2. Experimental and Results

All the chemicals were purchased from Aldrich Chemical Corporation and used without further purification. 0.2M Zinc acetate di hydrate ($ZnAc_2$.$2H_2O$) and 3M Sodium hydroxide were dissolved in de-ionized water and stirred for 30 min. White precipitates were observed in few minutes of stirring but the stirring was continued for 30 minute while maintaining the pH of the solution as 12.9. Later the solution was refluxed for 12 hours at 80°C. After refluxing the white aqueous gel of zinc oxide was washed with methanol, for the removal of ionic impurities. After washing, the gel was dried at room temperature. The dried powder was then calcined at 300°C and 500°C for two hours in ambient air. The crystallinity and phase of the powder samples were analysed by X-ray diffraction spectroscopy (XRD, Rigku) with CuKα Radiation (λ=1.54178Å) with Bragg angle ranging from 30 to 65°. The morphology of the as synthesize and annealed zinc oxide powder was visualized by the Field Emission Scanning Electron microscopy (FE-SEM-HitachiS -4700). The chemical composition of the sample was analyzed by the FTIR in the range of 400-4000cm^{-1} and the optical property was observed by the UV-VIS spectrophotometer.

Fig1 (a-c) shows the XRD spectra of as synthesized zinc oxide powder, annealed at 300 and 500°C respectively. The diffraction peaks in the three speactra are well matched with the standard ZnO (JCPDScard no. 36-1415) showing the typical zinc oxide sturcutre. Since other peaks except zinc oxide were not observed, the synthesized powder appears pure zinc oxide. The crystallinity of the powder increases with increasing annealing temperatuer, which is clealy evident from the XRD pattern showing increase in the peak intensities.

Fig.2 presents the FESEM image of as synthesized powder showing nanorods. The diameter of the rod varies from 20-60nm and the lengthening up to 2-3μm. A sheet like structure is observed when annealed at 300°C, as shown in Fig. 3. Annealing at 500ºC results in the agglomeration of the particles forming a flower like structure, above 500º C results in total agglomeration of the particles and the flower like structure was not observed. The composition of the as-synthesized zinc oxide powder was analyzed by the FTIR spectroscopy in the range of 500-4000cm^{-1}; the characteristic peak of zinc oxide was observed at the 523cm^{-1}. The O-H mode of vibration and starching mode of vibration of C=O is observed at 3200-3600cm^{-1} and 1547 cm^{-1} and 1647 cm^{-1} respectively. The UV-vis absorption spectra of as synthesized zinc oxide powder shows the standard peak corresponding to ZnOat ~ 375 nm.

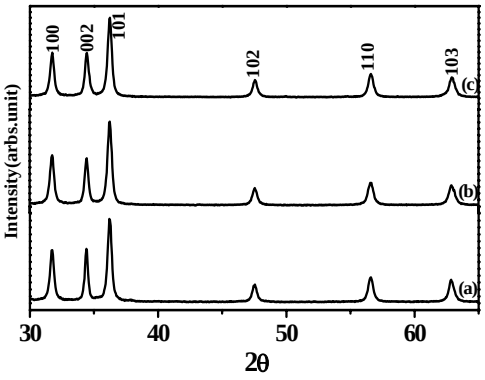

Fig. 1. XRD spectraof as grown zinc oxide Nanorods (b) annealed at 300°C and (c) 500°C.

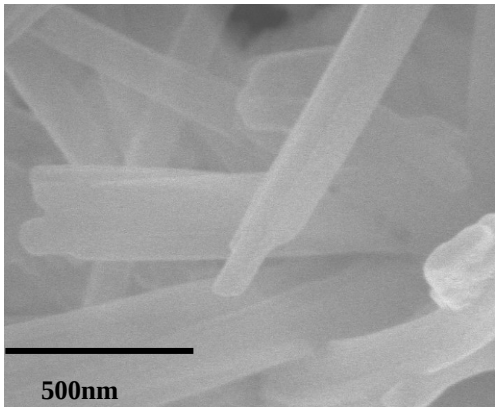

Fig. 2. FESEM image of as prepared Zincoxide powder.

The expected growth process of the flower-shaped ZnO nanostructures composed of hexagonal nanorods can be explained by the initial precipitation of the $Zn(OH)_2$. The formed $Zn(OH)_2$ dissolves to a considerable extent in water to form the Zn^{2+} and OH^- ions. Therefore, as the concentration of these Zn^{2+} and OH^- ions exceeds the critical value, the precipitation of ZnO nuclei starts.

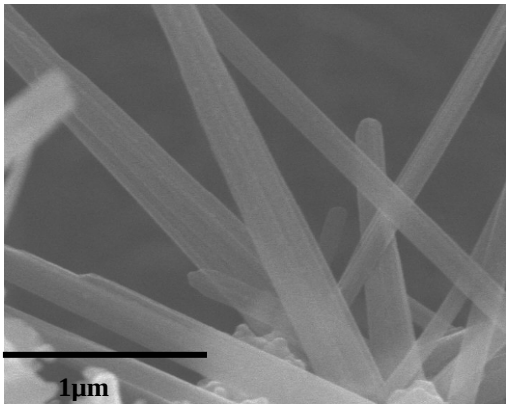

Fig. 3. FESEM image of Zincoxide nano Sheets annealed in air at 300°C.

TheTransformation of the $Zn(OH)_2$ precipitates into the ZnO crystals proceed through these simple reactions:

$$Zn(OH)_2 \rightarrow Zn^{2+} + 2OH^- \quad \text{.....(I)}$$

$$Zn^{2+} + 2OH^- \rightarrow ZnO + H_2O \quad \text{.....(II)}$$

The $Zn(OH)_2$ precipitates are more soluble as compared to the ZnO precipitates hence the formed $Zn(OH)_2$ precipitates tend to produce continuously Zn^{2+} and OH^- ions which formed the ZnO nuclei (reaction I).The formed ZnO nuclei are expected to be the building blocks for the formation of the final products (reaction II). As the ZnO is a polar crystal, where zinc and oxygen atoms are arranged alternatively along the c-axis and the top surfaces is Zn-terminated (0001) while the bottom surfaces are oxygen-terminated (000$\bar{1}$).The Zn-(0001) is catalytically active while the O-(000$\bar{1}$) is inert Furthermore, the growth depends upon the growth velocities of different growth planes in the ZnO crystals. In ZnO, the growth velocities of the ZnO crystals in different directions are [0001] > [01$\bar{1}$ $\bar{1}$] > [01$\bar{1}$0] > [01$\bar{1}$1] > [000$\bar{1}$], under hydrothermal conditions.

3. Summary

In this work, nano-structured ZnO was prepared using sol-gel method and the effect of annealing temperature was studied. It was found that the crystallinity of the particles increases with annealing temperature. Annealing at 500°C results in a flower like structure. Annealing above 500°C results in total agglomeration of the particles and the flower likestructurecouldnotbe formed.

4. References

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