

# Growth Mechanism of ZnO Nanostructures in the Presence of Surface Active Molecule

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**Abstract**—Zinc Oxide (ZnO) nanoparticles (NPs) have recently drawn the attention of scientific community due to different morphologies (dumbbells and nanotubes), which are synthesized with surface active molecules. A wet chemical method is developed to synthesized ZnO nanotubes (NTs) in the presence of sodium dodecyl sulphate (SDS). Dumbbells like structures to NTs are obtained in the presence of SDS by varying temperature of the reactions. The synthesized samples are characterized using X-Ray diffraction (XRD), transmission electron microscopy (TEM) and Ultraviolet-visible analysis (UV-vis), which shows the chemical nature of SDS, is responsible for the variation of ZnO morphologies.

## 1. INTRODUCTION

There is growing interest in studying the self-assembly of surface active molecules on the inorganic surface. This is due to the number of possible applications ranging from gas-sensor, biosensor, optical and electrical devices and window materials for displays [1-4]. ZnO is an n-type semiconductor with a large direct band gap of 3.37 eV and a large excitation binding energy of 60 meV. For desire morphologies, numbers of methods are available like sol-gel, spray pyrolysis, hydrothermal synthesis and electrochemical [5-8]. These methods have some drawbacks like vacuum environment, high temperature and complicated controlling process. However, most of these methods yield arrays of one dimensional ZnO crystals whose morphologies are limited to dumbbell like and needle-like structures. In this work, we present chemical route to synthesized dumbbells and NTs like structures of ZnO using SDS (anionic surfactant) as the modifying and protecting agent. Further, by increasing the temperature, their adsorption mechanisms are explained on the basis of their functional groups:  $\text{SO}_4^-$ ,  $-\text{OH}$ ,  $-\text{OCH}_2\text{CH}_2$ ,  $-\text{CH}_2$ ,  $-\text{CH}_3$ . The synthesized samples are characterized using TEM, XRD and UV-Vis spectroscopy.

## 2. EXPERIMENTAL SECTION

### 2.1 Materials and Methods

Zinc acetate  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and SDS from MERCK, Xylene rectified Extrapure, ammonia ( $\text{NH}_3$ ), ethanol from

HIMEDIA are purchased. Triply distilled water is used for all preparations. All reactants are of analytical grade and used as received without any further purification.

In a typical process,  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (1mM) and SDS (2g) is mixed together in 30 ml of xylene by stirring at room temperature until a homogenous slightly-turbid mixture is obtained.  $\text{NH}_3$  diluted by ethanol is added drop-wise to the well-stirred mixture until pH is reached to 10. In order to homogenize the reaction mixture, the stirring process must last for at least 1h after adding  $\text{NH}_3$ . The mixture is refluxed at  $100^\circ\text{C}$  for 5 hours; a milky-white suspension is obtained and centrifuged to separate the precipitate, which is rinsed with absolute ethanol and distilled water for several times. Further, the reaction mixture is carried out at  $150^\circ\text{C}$  with 2g of SDS keeping other conditions to be same. A blank sample of ZnO is also prepared in the absence of surface active molecules keeping other conditions to be constant.

## 3. METHODS

The ZnO NPs are centrifuged (Eppendorf Centrifuge 5418) at 14,000 rpm for 25 min and then are washed two times with triply distilled water. After each washing, the sample is then centrifuged at 14,000 rpm for 10 min. The obtained sample is then used for further studies (TEM, XRD and UV-Vis spectroscopy). TEM images are recorded with Tecnai FEI working at 200 kb voltage. The analysis are conducted by placing a drop of working solution on carbon coated copper grid and are followed by solvent evaporation at room temperature. The X-ray diffraction spectrometric studies are carried out with Philips X<sup>2</sup>-Pert PRO X-ray diffractometer. The samples are taken on a glass slide and the diffraction spectrum is recorded using nickel-filtered  $\text{Cu K}\alpha$  radiation. UV-Vis spectroscopy is used to characterize the optical absorption properties of ZnO. The UV-Vis absorption spectra of the samples are recorded in the wavelength range of 250-800 nm using a U-3900 UV-Vis spectrometer (Hitachi Corporation, Tokyo, Japan). Spectra are recorded at room temperature and the data is transformed through the Kaleidagraph function.

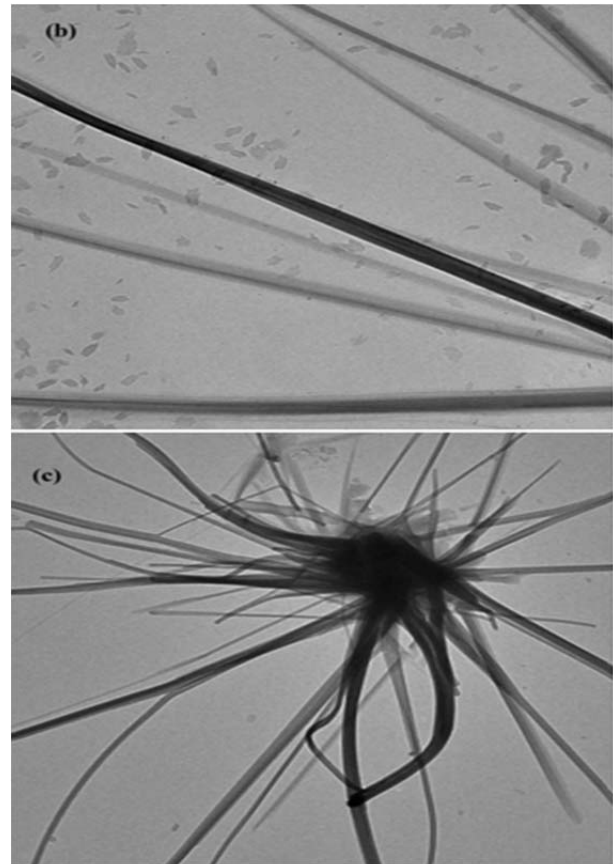
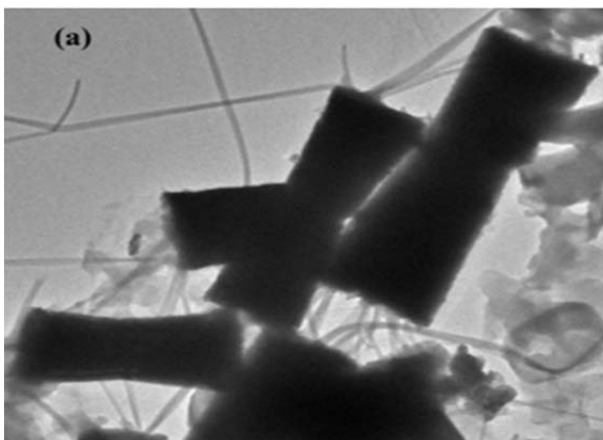
## 4. RESULTS AND DISCUSSION

### 4.1 Structure and Morphology

The morphology of the material is investigated by TEM. As synthesised ZnO-SDS dumbbell like structures on addition of 2g of SDS at 100°C (S1 sample, Fig. 1a) have an average diameter and length of about 0.65 and 2.10  $\mu\text{m}$ , respectively. However, an increase in temperature to 150°C with 2g SDS (S2 sample, Fig. 1b) results in the formation of NTs. The XRD patterns of ZnO nanostructures prepared at different temperatures 100°C and 150°C are shown in Fig. 2. It reveals the presence of single phase ZnO (JCPDS card No. 89-7102) in each sample. The diffraction peaks can be indexed to (100), (002), (101), (102), (110), (103) and (112) planes of the hexagonal structure of ZnO, demonstrating the excellent crystalline nature of the ZnO nanostructures, which is further supported by the sharp diffraction peaks.

### 4.2 Growth Mechanism

In the presence of surface active molecule, we have planned to fabricate ZnO particles by the decomposition of  $\text{Zn}(\text{NH}_3)_4^{2+}$  precursor directly under thermal conditions. The most stable crystal of ZnO is a wurtzite structure consisting of polar [0001] and [000 $\bar{1}$ ] planes and nonpolar [10 $\bar{1}$ 0] and [11 $\bar{2}$ 0] planes. At 100°C, SDS being anionic surfactant but less polar due to long hydrophobic chain may adsorb on polar plane (0001) thus leading to the formation of dumbbell like structures. With increase in temperature 100°C to 150°C, adsorption may lead to repulsive interactions among sulphate groups on the (0001) plane. Thus, adsorption increases on non-polar plane (10 $\bar{1}$ 0), thereby exposing the (0001) plane for epitaxial growth. Also the surface free energies of (0001) facet planes is suggested to be relatively higher than that of other low-indexed facet planes, hence the growth velocities of ZnO crystal to be as follows: [0001]



**Fig. 1: TEM images of ZnO in the presence of SDS (2g) at (a)100°C (b) 150°C (c) bushlike NTs .**

$\gg[10\bar{1}0] \gg [000\bar{1}]$  which results in the formation of NTs. It may be explained further by considering major role of SDS in the growth of ZnO dumbbell and NTs. It would act as transport carrier in Oswald ripening. However, at higher temperature of S2, there is a fast growth of ZnO dumbbells as ostwald's ripening is more operative as evidenced in the transformation of dumbbell morphology to NT morphology with significant reduction in the length and diameter of dumbbells. In addition to NTs, large ZnO NTs are also observed in central parts of product aggregates, which may be assigned as ZnO NTs are glued together. With the increase in temperature, the majority of ZnO NTs are assembled into the bushlike aggregates (Fig. 1c).

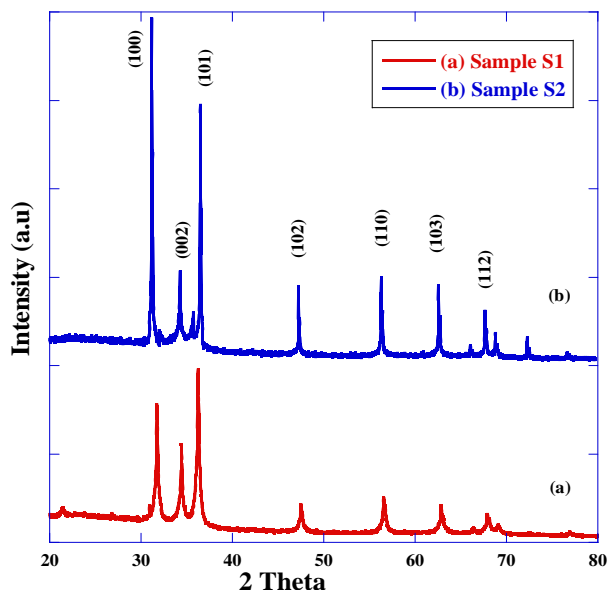


Fig. 2: XRD patterns of ZnO nanostructures in the presence of SDS (2g) at (a) 100°C (b) 150°C.

## 5. OPTICAL MEASUREMENT

UV-visible absorption spectroscopy is widely being used technique to examine the optical properties of nanosized particles. Fig. 3 shows the UV-visible optical absorption spectra of the colloidal suspension of ZnO and different samples (S1 & S2).

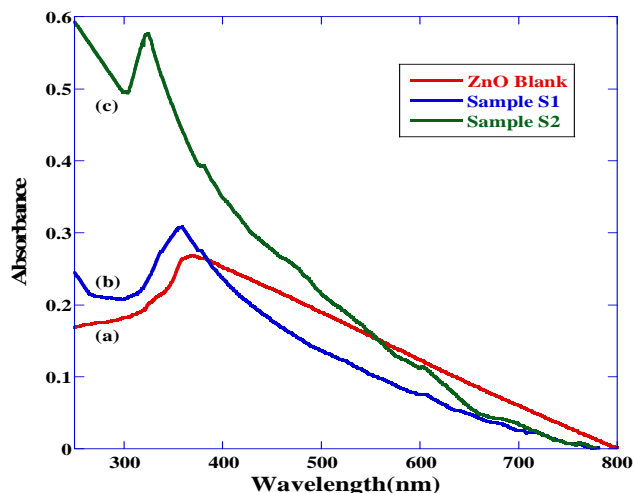


Fig. 3: UV-Vis absorption spectra of ZnO (a) blank and in the presence of SDS (2g) at (b) 100°C (c) 150°C.

The absorption peak for ZnO in the absence of surface active molecule is at 368 nm. There are two absorption peaks at about 355 and 323 nm corresponding to two different temperature of SDS (100°C and 150°C), respectively. The blue shift in the excitation absorption clearly indicates the morphology of ZnO changed and the band gap of the NTs increases resulting in the shift of absorption edge to lower wavelength, as the diameter decreases.

## 6. CONCLUSION

We report a simple method of preparing ZnO nanostructures with controllable sizes using surface active molecule as a shape-directing/capping agent. We have observed that different shapes of ZnO nanostructures such as dumbbell like and NTs are obtained by varying the reaction temperature. Corresponding mechanistic details for the formation of various nanostructures of ZnO are tentatively suggested.

## 7. ACKNOWLEDGEMENTS

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