Digest Journal of Nanomaterials and Biostructures Vol. 5, No 1, March 2010, p. 297 – 301

HYDROTHERMAL SYNTHESIS OF NANO ZnO STRUCTURES FROM CTAB

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In recent days Zinc oxide (ZnO) attracted much interest due to its versatibility and size dependent opto-electronic properties. ZnO flake structures have been hydrothermally synthesized in the reaction of aqueous solution of cetyl trimethyl ammonium bromide (CTAB) and NaOH at 373.15 K. It was found that, the volume of added ammonia, surfactant (CTAB), and mixed solvent play crucial roles in morphological control of ZnO nanostructures. Based on the structural information of XRD and SEM, a growth mechanism was proposed for the formation of ZnO flake structures.

(Received March 20, 2010; accepted April 1, 2010)

Keywords: CTAB, Zinc Oxide, Nanostructures, Hydrothermal Process Morphology, SEM, XRD

1. Introduction

Zinc oxide (ZnO) is a versatile material. Nanosized ZnO crystals have attracted a great deal of attention because of their size-dependent opto-electronic properties. A chemical synthesis of nano-sized ZnO crystals in aqueous solution, which was suitable for a large-scale production, has been developed [1].

During the past decades, reports on the synthesis of various structures of ZnO have increased rapidly, Viz., rods, wires, tubes, towers, stars, dendrite and flower like, etc. These structures are expected to have more potential applications in building functional electronic devices with special architectures and distinctive optoelectonic properties. Therefore, it is attempted to synthesize ZnO nano or microstructures in a controllable shape and size to meet the demand and to explore the potentials of ZnO. It is still a challenging task for material scientists, to directly fabricate large-scale ZnO crystals with controlled morphology [2].

In the present study, ZnO flake shaped micro structures were synthesized hydrothermally by using CTAB as a surfactant. The results suggested that, by using CTAB as a surfactant, morphology of ZnO could be changed in hydrothermal process.

2. Experimental

The Zinc acetate dehydrate [Zn $(CH_3COO_2)_2H_2O$] and Sodium hydroxide [NaOH] were procured from Merck limited, Mumbai and cetyl trimethyl ammonium bromide ($C_{19}H_{42}BrN$) form Sd fine chemical, Chennai. These chemicals were used as such without further purification.

2.1 Sample Preparation

The sample was prepared by the normal hydrothermal synthesis which involves the addition of 0.5 g of zinc acetate dehydrates was put into 110 ml of deionized water and stirred vigorously for 15 min. This was followed by addition of 0.5 gm of cetyl trimethylammonium

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bromide (CTAB). After the dissolution of CTAB, 10 ml of 2M NaOH aqueous solution was introduced into the above aqueous solution, which resulted in a white aqueous solution. The prepared solution was transferred into a stainless steel autoclave with a external temperature of 373.15K, sealed and maintained for 3 hours. The resultant white solid products were centrifuged and washed with distilled water and ethanol for several times to remove the ions adhering to the final products. Then the sample was dried in a hot air oven at 333.15 K.

2.2 Instrumentation

To investigate the ZnO structures, an X-ray diffractometer XPERT PRO (λ=1.541) was used. The mean crystallite size D was obtained from the Scherrer formula [3], as given below:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

where K=0.9, λ = 1.541, θ is the diffraction peak angle, and β denotes the full width at half maximum of the corresponding diffraction peak. IR spectra of the nanoparticles were obtained at room temperature with a Nicolet Avatar Impact 330 series FTIR spectrometer with the range of 4000~400cm^{-1}. The scanning electron microscopy (SEM) model JSM-5610 LV was used to take the images. The composition of elements like Zn was confirmed by energy dispersive X-ray spectra (EDX).

3. Results and discussion

Fig 1 showed the typical XRD patterns of ZnO with the higher & narrower diffraction peaks implied a good crystallization of ZnO. No characteristic peak of other impurities was observed in this pattern. The sharp diffraction peaks indicated the good crystallinity of the prepared crystals [4 -7]. Larger crystalline size of 21.16 and 39.05 nm was obtained for the ZnO crystals. The crystal size of the ZnO nanoparticles calculated from FWHM was tabulated in Table 1.

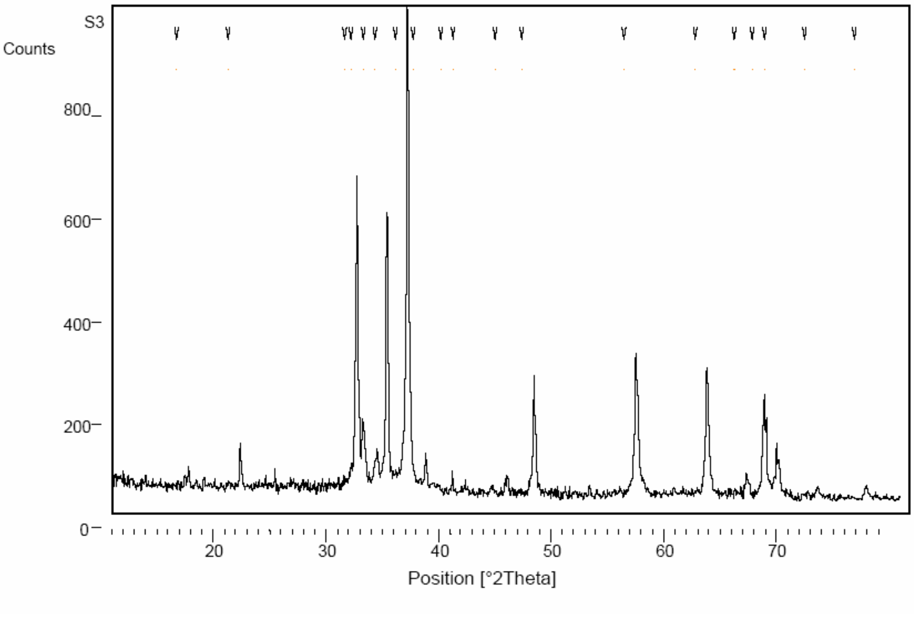

Fig. 1. XRD diffraction pattern of ZnO porous structures synthesized by CTAB assisted hydrothermal Process.

The morphology of product Fig. 2 (a) showed the general morphologies of the CTAB assisted hydrothermally synthesized ZnO flake structures. It was inferred from fig 2 (b) shows most of the structures were uniform. Hiroyuki Usui [1] and yazhuo shang et al [8] reported various morphologies such as rod-like, spheroidal, hexahedron structures and other irregular structures of CTAB-assisted hydrothermal synthesis of ZnO. They also reported that the formation of flower like ZnO is much more difficult in CTAB assisted hydrothermal synthesis of ZnO.

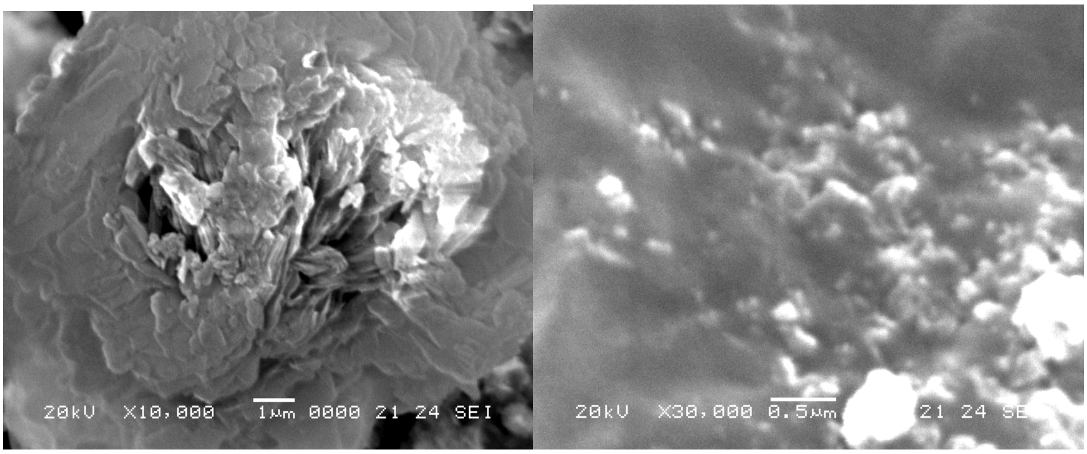

Fig. 2. SEM images of the ZnO Flake and Dot Structures obtained by CTAB assisted hydrothermal process: (A) low magnification (B) high magnification.

Raghvendra S. Yadav [9] and Mei Li et al [10] reported solvothermal synthesis of ZnO porous nano solids, with deionized water and CTAB solution, as pores forming agent. The pore size of the later being larger than the former, with decreased surface area and a slight increase in porosity.

The FTIR spectrum of synthetic ZnO powder (Fig. 3) showed main absorption bands due to O-H stretching of hydroxyl group at 3401 cm^{-1}, asymmetric and symmetric C=O stretching of Zinc acetate at 1634 and 1506 cm^{-1}, O-H bending of hydroxyl group at 569 cm^{-1} and Zn-O stretching of ZnO at 428 cm^{-1}. These data are similar to the result of an another study [11].

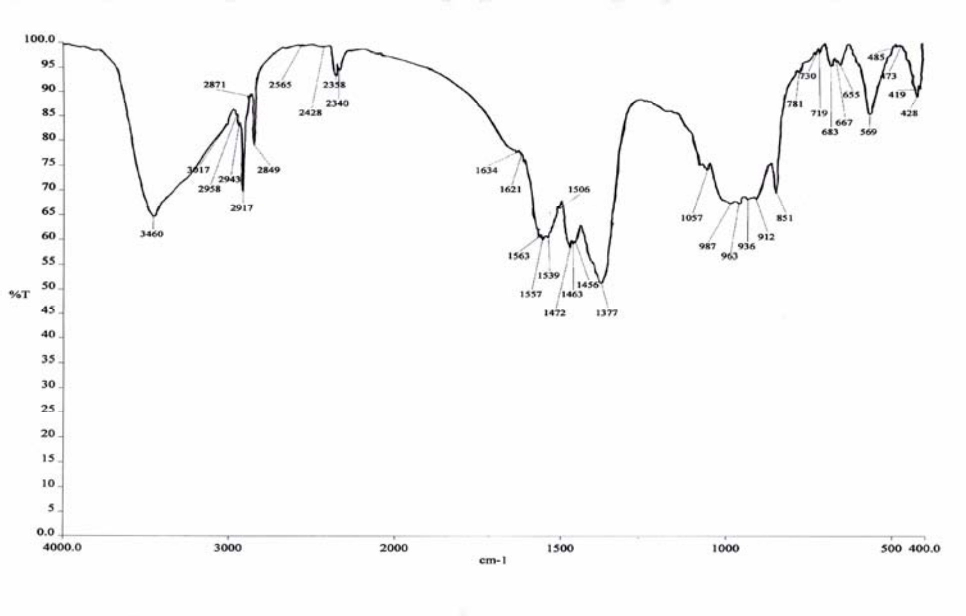

Fig. 3. FTIR spectrum of ZnO nanoparticles

It was stated that, the formation of the ZnO flake structures was due to the presence of a suitable surfactant. The energy dispersive spectroscopy (EDS) given in fig.4 showed the presence of Zn (Na, Si, Cu and Al comes from substrate) [12].

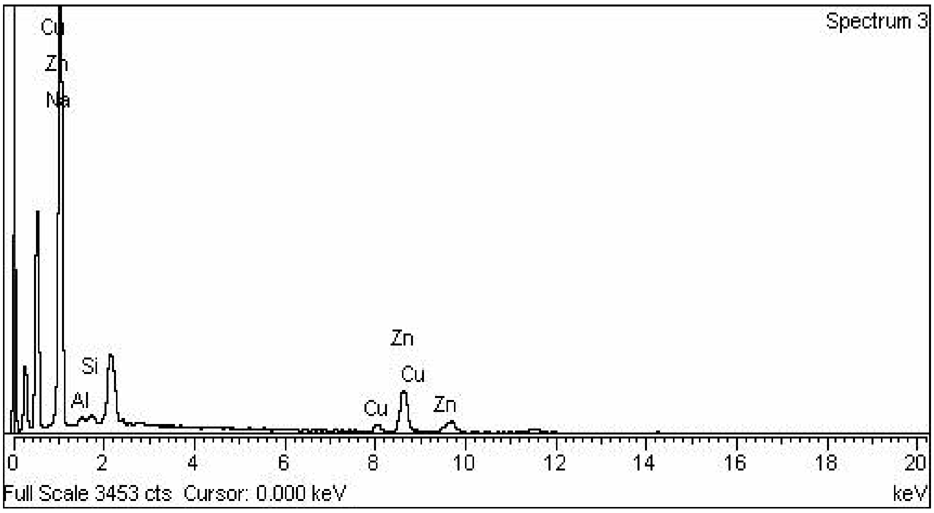

Fig. 4. EDX spectrum of ZnO nanoparticles.

4. Growth mechanism

The improvised approach to synthesis ZnO by hydrothermal process was closely related to a new understanding of the growth mechanism

$$Zn^{2+}+4OH^{-} \rightarrow [Zn\ (OH)_4]^{2-} \qquad [a]$$
$$[Zn\ (OH)_4]^{2-} \rightarrow Zn(OH)_2+2OH^{-} \qquad [b]$$
$$Zn(OH)_2 \rightarrow ZnO+H2O \qquad [c]$$
$$[Zn(OH)_4]^{2-} \rightarrow ZnO+2H_2O+2OH^{-} \qquad [d]$$

The elements Zn existed as $[Zn\ (OH)\ _4]\ ^{2-}$ a negatively charged tetrahedrons that were formed according to the reaction (a), whereas CTA^+ was positively charged with a tetrahedral head and a hydrophobic tail. It was found from the $CTAB^-$assisted hydrothermal process, CTA^+-[Zn (OH)$_4$]2- ion pairs were formed initially by electrostatic interaction.

The CTAB could accelerate the ionization of [Zn (OH)$_4$]2- as it was a strong-acid-weak-base salt. The CTA^+-[Zn (OH)$_4$]2- ion pairs formed a combination of CTAB and ZnO according to the reaction (d).It was inferred that, the CTAB aggregated in between the ZnO crystallites during hydrothermal crystallization and on washing the material with ethanol, the flake structures of ZnO were formed. A detailed study on the effect of surfactant in the formation of ZnO structures during hydrothermal process is in progress.

5. Conclusions

ZnO flake structures nanomaterials were successfully synthesized by hydrothermal method using Zinc acetate dihydrate sodium hydroxide and CTAB as the reactants. The XRD pattern revealed that the synthesized materials were crystalline in nature. Spectroscopic studies showed that the absorption of nano structured ZnO were determined by their morphologies.

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