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ZnO Nanostructures: Simple Routes of Synthesis

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***Abstract*—In this contribution we are presenting simple methods to synthesize zinc oxide (ZnO) nanostructures using aqueous zinc nitrate solution as precursor. Two methods were employed, one by co-precipitation using a base and the other by heating in presence of poly ethlylene glycol (PEG). The obtained precipitated compounds were calcined at different temperatures and structurally characterized by Powder X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy Dispersive X-ray diffraction (EDX) and UV-Vis spectroscopic techniques. The powder X-ray data indicates that the calcined compounds exhibit hexagonal structure. Scanning electron micrographs show that ZnO formed during co-precipitation shows a fascinating nanoflower morphology and ZnO formed by simple heating in presence of PEG shows hexagonal blocks which transform in to sword shaped rods on increasing the amount of PEG. All the SEM images confirm the particle sizes in the range of 150-200 nm. The band gap was higher for synthesized ZnO particles than their bulk counterparts. The results indicate that interesting nanostructures can be obtained by applying simple routes of synthesis.**

***Keywords*—Coprecipitation; Nanostructures; Morphology; Sword Shaped Nanorods; Micrographs**

I. INTRODUCTION

Zinc oxide, with its unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photostability, is a multifunctional material [1]. In materials science, zinc oxide is classified as a semiconductor in group II-VI, whose covalence is on the boundary between ionic and covalent semiconductors. A broad energy band (3.37 eV), high bond energy (60 meV) and high thermal and mechanical stability at room temperature make it attractive for potential use in electronics, optoelectronics and laser technology [2]. ZnO nanostructures have a great advantage in catalytic reaction process due to their large surface area and high catalytic activity [3]. Since zinc oxide shows different physical and chemical properties depending upon the morphology of nanostructures, not only various synthesis methods but also the physical and chemical properties of synthesized zinc oxide are to be investigated in terms of its morphology. Many methods have been described in the literature for the production of ZnO nanostructures such as laser ablation [4], hydrothermal methods [5], electrochemical depositions [6], sol–gel method [7], chemical vapor deposition, thermal decomposition [8], and combustion method [9]. Recently, ZnO nano particles were prepared by ultrasound [10], microwave-assisted combustion method [11], two-step mechanochemical-thermal synthesis [12], anodization [13], co-precipitation [14], and electrophoretic deposition [15]. Rodrigues-Paez et al. synthesized zinc oxide nanoparticles with different morphologies by controlling different parameters of the precipitation process such as solution concentration, pH, and washing medium [16]. In the present study, ZnO nanostructures were synthesized using simple routes. Zinc nitrate heptahydrate and sodium hydroxide were used as precursors to formulate ZnO nanostructures in the co-precipitation method while the second method involves simple heating process in the presence of PEG. The prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and the purity of the sample was tested by energy dispersive X-ray diffraction (EDX)

II. EXPERIMENTAL

A. *Co-precipitation method (CP)*

All the chemicals were analytic grade reagents used without further purification. The aqueous solution of zinc nitrate is prepared by dissolving 2g of zinc nitrate in 30mL of water. To this aqueous zinc nitrate solution 4g sodium hydroxide is added and the reaction mixture was heated at 50°C along with stirring and the process is carried out for one hour after which the white precipitate was obtained. The formed oxide wet precipitate is neutralized by adding few drops of hydrochloric acid. Then the wet precipitate is washed with de-ionized water to remove impurity ions present in it and further heated in the oven at 150°C to dry the precipitate (ZnO-CP) formed.

During stirring,

$$Zn(NO_3)_2.6H_2O + 2NaOH \longrightarrow Zn(OH)_2 + 2Na(NO_3)$$

During drying,

$$Zn(OH)_2 \longrightarrow ZnO + H_2O$$

B. *Heating method in presence of PEG*

ZnO nano particles (ZnO-PEG) are also prepared by simple heating method. This process involves dissolving a salt precursor i.e $Zn(NO_3)_2.6H_2O$ in water (or other solvent) to precipitate the oxide at higher temperatures (70ºC) with the help of various amounts of PEG (0 gm, 8 gm, 12 gm) (as shown in table 1). The salt precursor in dissolved in water to prepare 10 ml of metal salt solution (0.6 M) and after that various amounts of PEG added to the metal cation solution followed by heating along with manual stirring and the

process is carried out for 20 minutes at higher temperatures (70°C) to obtain homogeneous viscous solution. The obtained viscous material should be heat treated at (500°C and 800°C) for 1 hour.

TABLE I. Experimental details

Sample ID	Volume of solution(ml)	Amt of PEG in g
ZnO -0 PEG	10	0
ZnO-8 PEG	10	8
ZnO-12 PEG	10	12

C. Characterisation

The crystal structure of the synthesized particles was determined by X-ray diffractometer (D8 Discover, Bruker AXS Co. Ltd, Germany) with Cu- Kα radiation λ= 1.54056 A°. The particle size and morphology was derived from field emission gun scanning electron microscope (Carlzeiss Co. Ltd., Germany) and the elemental composition was obtained from energy dispersive X-ray diffraction attached to FESEM (EDX INCA, OXFORD Instruments.). UV-Visible spectrum was obtained from UV-Visible spectrophotometer (Evolution 201, Thermo scientific Co. Ltd)

III. Results and Discussion

A. UV-Visible spectroscopy

The UV-Visible absorbance spectrum of the ZnO nano particle colloids is shown in Fig1(a). The absorption spectrum shows an exciton band at 325- 330 nm and the significant blue shift relative to bulk exciton absorption (373 nm). This shift can be attributed to the confinement effect of small size ZnO nanoparticles. Energy band gap calculated using UV-Visible spectrum and observed as 3.41eV (Fig1(b)).

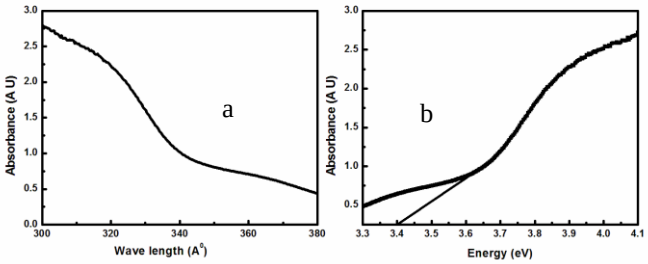

Fig. 1. (a) UV-Visible spectrum of ZnO
(b) Energy band gap calculation

B. EDX analysis

The elemental compositions of the ZnO nanoparticles prepared by both co-precipitation method and simple heating with PEG method were determined by energy dispersive X-ray diffraction (EDX INCA, OXFORD Instruments) as shown in Fig. 2 indicating the high purity of ZnO nanoparticles.

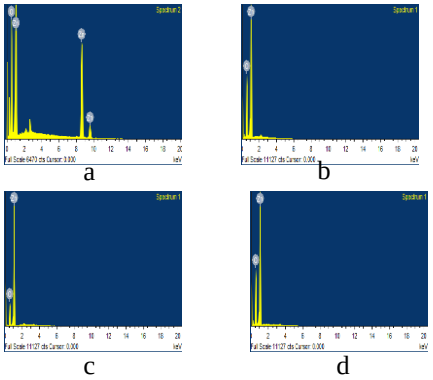

Fig 2. EDXof (a) ZnO-CP, (b) ZnO-0PEG, (c) ZnO-8PEG and (d) ZnO-12PEG

TABLE II. Elemental composition from EDX

	CP	0 PEG	8 PEG	12 PEG
Zn%	73.81	79.66	83.43	76.95
O%	26.19	20.34	16.57	23.05
Total	100	100	100	100

C. Structure

The typical X- ray diffraction patterns of all ZnO nanoparticles are shown in Fig. 3 which is well matched with **pdf 00-003-0752** from the data base and indexed to the hexagonal structured ZnO. ZnO crystallizes in the typical wurtzite hexagonal structure where oxygen and zinc atoms are spatially arranged in a way that O atoms are arranged in a closed hexagonal structure, while the Zn atoms occupy the centre of the distorted tetrahedron structure. X-ray analysis of all the four samples suggest a good crystallinity and no diffraction peaks of any other impurity detected. It indicates that the high purity of the ZnO nanoparticles is obtained. However, it was also observed from XRD pattern of ZnO -CP with peak broadening indicating a smaller crystallite size.

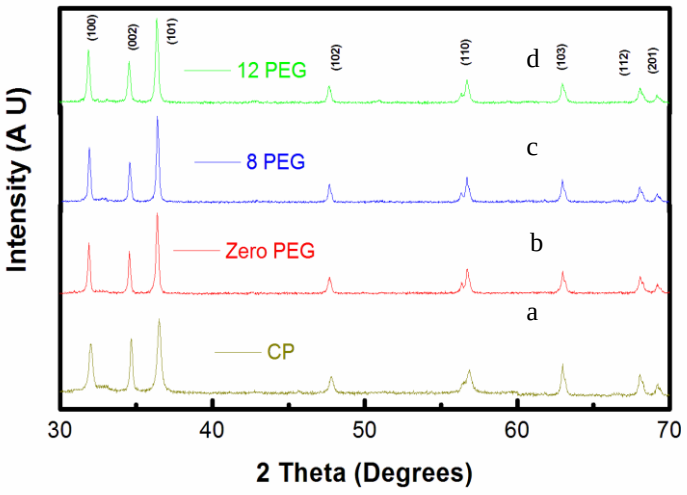

Fig. 3. Powder XRD of (a) ZnO-CP, (b) ZnO-0PEG (c) ZnO-8PEG and (d) ZnO-12PEG

D. Morphology

1) ZnO-CP

Fig. 4 illustrates the SEM image of Nano flowers of ZnO-CP. The high resolution image clearly reveals that obtained ZnO exhibits the well-defined flowery morphology. The flowers seem uniform with multi-layered petals. Moreover, all flower petals exhibit the tapering feature with the root size 70-90 nm and tip size 40-50 nm. The morphology looks similar to flower like morphology obtained by thermolysis of Zinc-Ethylenediamine complex [17], but the nanoflowers obtained in [17] were of three types with accumulation of different flowers, an isolated flower with multi layered petals and an isolated flower with monolayer petals and it was also observed that petals exhibit root size 300-500 nm with a very small tip size of 30-50 nm. In comparison to the nanoflowers obtained by the above process, the ZnO-CP nanoflowers are better fitting into the nano range commonly referred to 1-100 nm. ZnO-CP nanoflowers are also very different from the ZnO nanoflowers synthesized using PVD technique, which appear like multi-sheets grown on one another [18]. Interestingly this is the only case where in fascinating nanoflowere are obtained by simple precipitation method but all other cases report the precipitation of nanoparticles with irregular shapes [19].

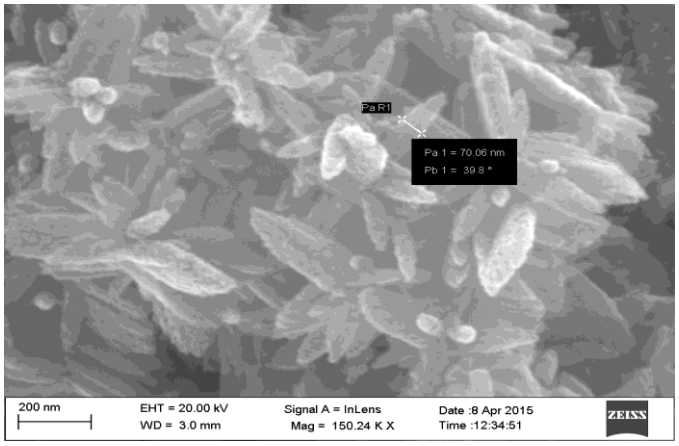

Fig. 4. Nanoflowers of ZnO-CP

2) ZnO -PEG

In this method it was observed that the hexagonal shape ZnO nanoparticles were prepared from the same precursor (zinc nitrate hexahydrate) by simple heating method with polyethylene glycol (PEG). The effect of PEG on the particle properties such as shape and size were investigated by using different amounts of PEG: 0 g, 8 g and 12 g. All the precursors were heated at 800^{o}C in air for 1h. Heating at temperatures of less than 500°C gave a large amount of carbon residue and the sample colour was black. Since the organic material must be removed to obtain pure oxide, precursor must be heated at high temperatures to decompose organic material so that low temperature processing is not allowed in this process. When using PEG, the heating temperature must be higher than 500°C. As shown in the SEM image of Fig. 5, the larger irregular shaped particles of several nanometer sizes were obtained without PEG and the average particle size was found to be 150 nm. Coagulation process intensively occurred during the heating process since the absence of separating medium between particles to permit as produced particles coalescence easily. Adding polymer in the precursor significantly decreased in particle size as shown in Fig. 6 and Fig. 7. It is clear from Fig. 6 that the uniform hexagonal ZnO blocks with 130-140 nm in size were prepared by using 8g of PEG and later by using excess amount of PEG (12g) the hexagonal blocks grow in to sword shaped nano rods with a diameter in the range of 130-140nm as shown in Fig. 7. It was observed that the similar sword shaped ZnO nanorods synthesized by the cetyl trimethyl ammonium bromide (CTAB)–assisted hydrothermal process [20] but the process used in was not as simple as it is in this case

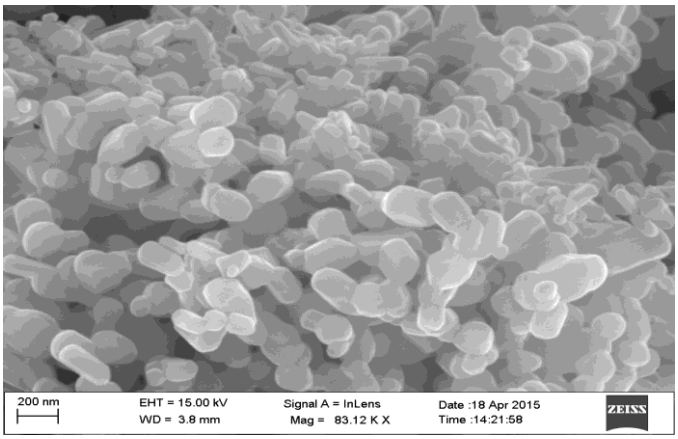

Fig. 5. Nanoparticles of ZnO-0PEG

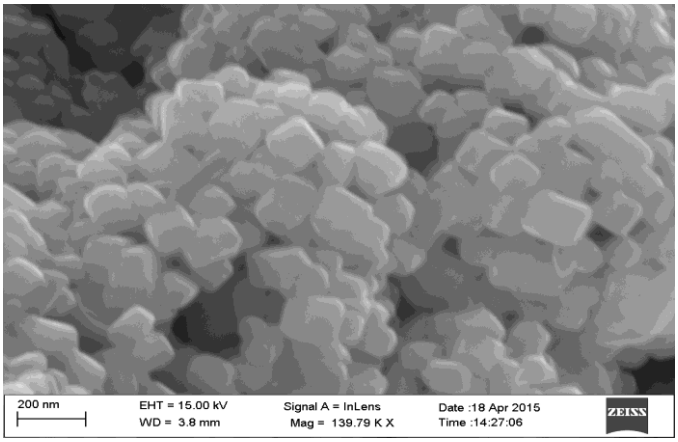

Fig. 6. Nano hexagonal bocks of ZnO-8PEG

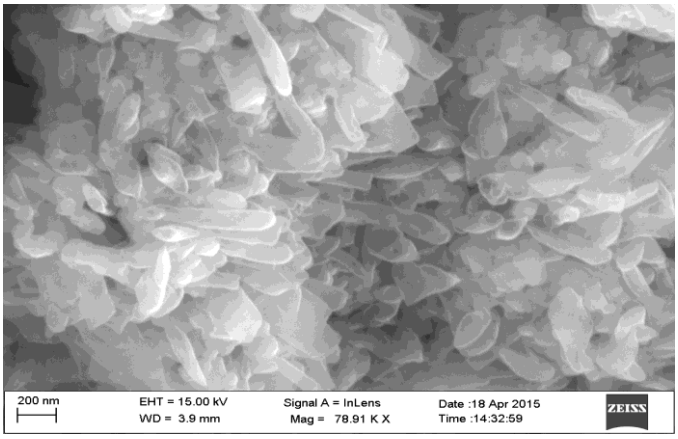

Fig. 7. Sword shaped nanorods of ZnO-12PEG

CONCLUSIONS

In summary, ZnO nanoflowers, nanoparticles, hexagonal nanoblocks and sword shaped nanorods have been prepared in a controlled way by applying simple methods of synthesis. All ZnO nanomaterials synthesized here can be indexed to hexagonal structure. SEM images clearly shows that as the amount of PEG increases the blocks grow into rods. Interestingly all the ZnO nanomaterials synthesized have a size less than 200nm and can be very useful in the applicative perspective.

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