

International Journal of Bio-Inorganic Hybrid Nanomaterials

Co-precipitation Synthesis of Zinc Oxide (ZnO) Nanoparticles by Zinc Nitrate Precursor

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Received: 11 June 2014; Accepted: 16 August 2014

ABSTRACT

Nanostructured zinc oxide (ZnO) materials have received considerable interest from scientists due to their remarkable performance in electronics, optics and photonics. ZnO nanoparticles were synthesized by co-precipitation method. ZnO nanoparticles were synthesized using $Zn(NO_3)_2$ and K_2CO_3 precursors. The structure of the obtained product was confirmed by the powder X-ray diffraction (XRD) analysis. The morphology, size and structure of the as prepared ZnO nanoparticles were investigated using scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) analyses. The composition of nanocrystals was determined by electron dispersive spectroscopy (EDS). XRD pattern showed that the zinc oxide nanoparticles exhibited hexagonal wurtzite structure. By SEM images, multiple layered structure of ZnO nanoparticles were observed after calcinations. The particles size were measured in the range of 20-80 nm for sphere-like shaped as-synthesized ZnO and 40-100 nm for pyramid-like shaped annealed ZnO with less agglomeration, as estimated by XRD technique and direct HRTEM observation. The EDS spectrum showed peaks of zinc and oxygen free of impurity.

Keyword: ZnO Nanoparticles; Pyramid-like shaped; Low temperature synthesis; Co-precipitation method; Crystal structure.

1. INTRODUCTION

In the last few decades, study of one-dimensional material has gained importance in nanoscience and nanotechnology. With reduction in size, novel electrical, mechanical, chemical and optical properties are introduced resulting from surface and quantum confinement effects. Although scientists have been extensively studied for many years but still research is going on to synthesize metal oxides with well-defined shape, size and composition. Zinc oxide (ZnO) is a versa-

tile material with diversified technological potentials as transparent electrodes in solar cells [1-3], catalysts [4, 5], waveguides [6, 7], transparent thin film transistors [8], piezoelectric transducers and actuators [9, 10], surface wave acoustic devices [11-13], gas sensors [14, 15], photonic crystals with tunable band gaps [16, 17], anti-reflection coatings [1], varistors [18, 19], and in flat panel displays as a low voltage phosphor. Besides, ZnO has several attractive properties, such as,

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high chemical stability, good piezoelectric properties, non-toxicity, and bio-compatibility, which have drawn tremendous attention in recent years. ZnO is a II-VI semiconductor with direct wide band gap semiconductor (3.3 eV at room temperature) with large excited binding energy (60 meV).

ZnO can be utilized in fabrication of solid state optoelectronic devices operating in near UV region [20, 21]. Moreover, intrinsic ZnO is a n-type semiconductor with maximum optical transparency in visible region of electromagnetic spectrum. The n-type semiconductor behavior is due to the ionization of excess zinc atoms in interstitial positions and the oxygen vacancies [22]. ZnO exists as hexagonal wurtzite structure with two lattice parameters $a = 0.324$ nm and $c = 0.5207$ nm. ZnO belongs to the space group of P63mc [21]. The structure is composed of two interpenetrating hexagonal close packed sublattices of oxygen ions displaced by 0.375 along the threefold c-axis with respect to Zn ions. In other words, ZnO structure may be described as planes of O^{2-} and Zn^{2+} stacked alternatively along the c-axis. Each sublattice has 4 atoms per unit cell. Every Zn cation is tetrahedrally coordinated with 4 O^{2-} at edges of a tetrahedron and vice versa. In other words, Zn^{2+} ions occupy tetrahedral sites in the hexagonal close packed sublattice of O anions. Schematic diagram of unit cell of wurtzite ZnO is shown in Figure 1. The tetrahedral coordination in ZnO leads to a lack in inversion symmetry and hence, ZnO exhibits piezoelectricity and pyroelectricity. Owing to the wurtzite structure, ZnO has low symmetry leading to spontaneous polarization along the c-direction. Surface defects play an important role in the photocatalytic activities of metal oxides as they increase the number of the active sites [23, 24]. Therefore, ZnO exhibits dielectric, piezoelectric, pyroelectric, acousto-optic, and photoelectrochemical properties also [21, 25]. ZnO nanoparticles have been grown using physical and chemical techniques: plasma assisted molecular beam epitaxy (MBE), rf-magnetron sputtering, metalorganic chemical-vapor deposition, pulsed-laser deposition, the sol-gel method [26-28], co-precipitation [29], hydrothermal method [30].

Chemical methods, such as precipitation methods, have been proved to be attractive due to the low growth temperature and easy operation, promising scale-up

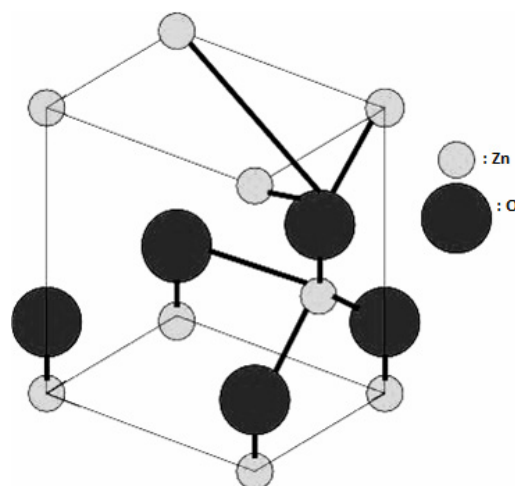


Figure 1: The wurtzite structure model of ZnO.

fabrication [31]. These wet chemical techniques are usually simple, economical, and versatile, and proved to be very effective for large scale production [32]. At present, the precipitation method is widely used in the synthesis of ZnO nanocrystals because the mole ratio can be accurately controlled, monodisperse samples can be synthesized, and the solubility can be increased [33]. In the present work, ZnO nanoparticles were prepared by employing a cost effective precipitation technique. The as prepared sample was characterized by powder XRD, UV, SEM and TEM analyses and the results are discussed.

2. EXPERIMENTAL DETAILS

Zinc nitrate (Merck) is the chemical compound with the formula $Zn(NO_3)_2 \cdot 6H_2O$, it is used as a precursor in preparing semiconducting zinc oxide nanoparticle in chemical methods. Potassium carbonate (K_2CO_3 , Merck) is used in the experiment as precipitator. All the reagents were purchased from Merck Chemicals and used without further purification. In a typical synthesis process, 0.03 M $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in a mixed solvent of water (100 mL) and added to solution of 0.05 M K_2CO_3 (50 mL) under magnetic stirring. The pH of the solution was adjusted to 5.5. The mixed solution stirred with a magnetic stirrer at 80°C and evaporated for 4 hours. The product was dried at 220°C for 1 hour then ground into a fine particle. The temperature of the dried precursor powder was

increased at the rate of 1°C/min to attain the required temperature and then allowed the sample to stay at 500°C for 4 hours to obtain the ZnO nanoparticles. All samples were characterized without washing and purification.

The specification of the size, structure and surface morphology of the as synthesis and annealed ZnO nanoparticles were carried out to study of the ZnO morphology. X-ray diffractometer (XRD) was used to identify the crystalline phase and to estimate the crystalline size. The XRD pattern were recorded with 2θ in the range of 4-85° with type X-Pert Pro MPD, Cu- K_{α} ; $\lambda = 1.54 \text{ \AA}$. The morphology was characterized by field emission scanning electron microscopy (SEM) with type KYKY-EM3200, 25 kV and transmission electron microscopy (TEM) with type Zeiss EM-900, 80 kV. The Ti and O elemental analysis of the samples was performed by energy dispersive spectroscopy (EDS) type VEGA, 15 kV. All the measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

X-ray diffraction (XRD) at 40 Kv was used to iden-

tify crystalline phases and to estimate the crystalline sizes. Figure 2(a) shows the XRD morphology of as-prepared ZnO nanoparticles and Figure 2(b) shows annealed sample at 500°C for 3 hours. In our case all the diffraction peaks at angles (2θ) of 31.36°, 34.03°, 35.8°, 47.16°, 56.26°, 62.54°, 67.64°, 68.79°, 69.45°, 72.82° and 77.33° correspond to the reflection from (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) crystal planes of the hexagonal wurtzite zinc oxide structure. The mean size of the ordered ZnO nanoparticles has been estimated from full width at half maximum (FWHM) and Debye-Sherrer formula according to equation the following:

$$D = \frac{0.89\lambda}{B \cos \theta} \quad (1)$$

where, 0.89 is the shape factor, λ is the x-ray wavelength, B is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. The mean size of as-prepared ZnO nanoparticles was around 25 nm from this Debye-Sherrer equation.

Figure 3(a) shows the SEM image of the as-prepared ZnO nanoparticles prepared by co-precipitation

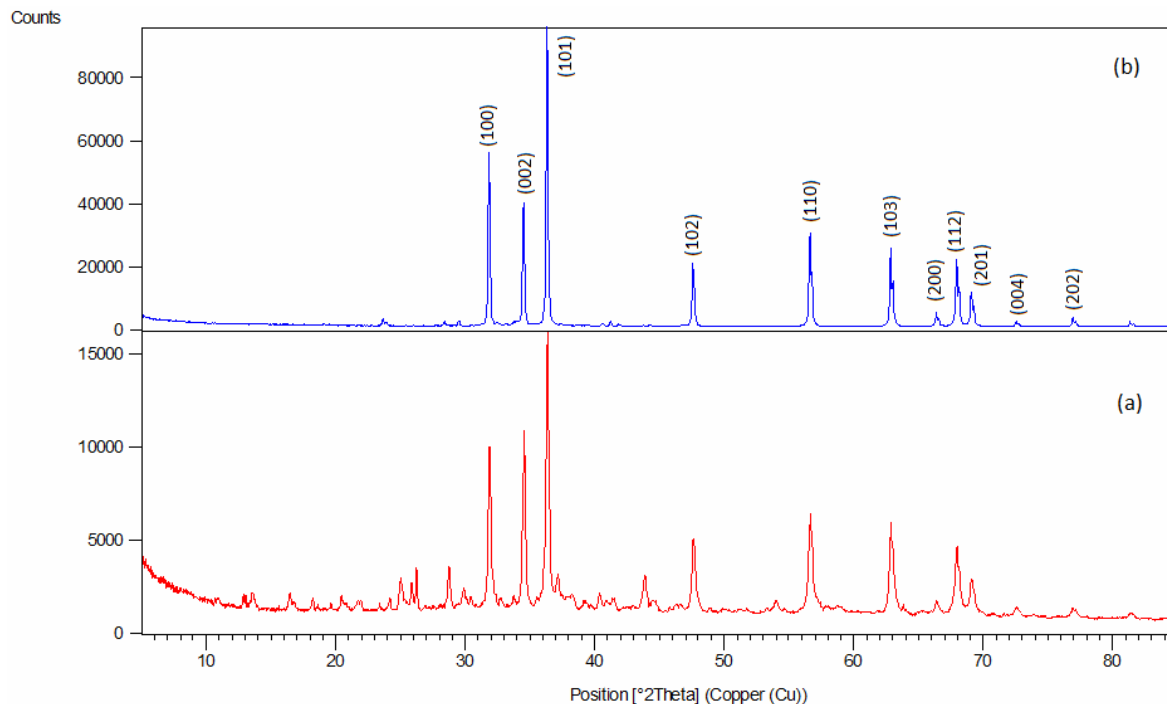


Figure 2: XRD pattern of annealed ZnO nanoparticles.

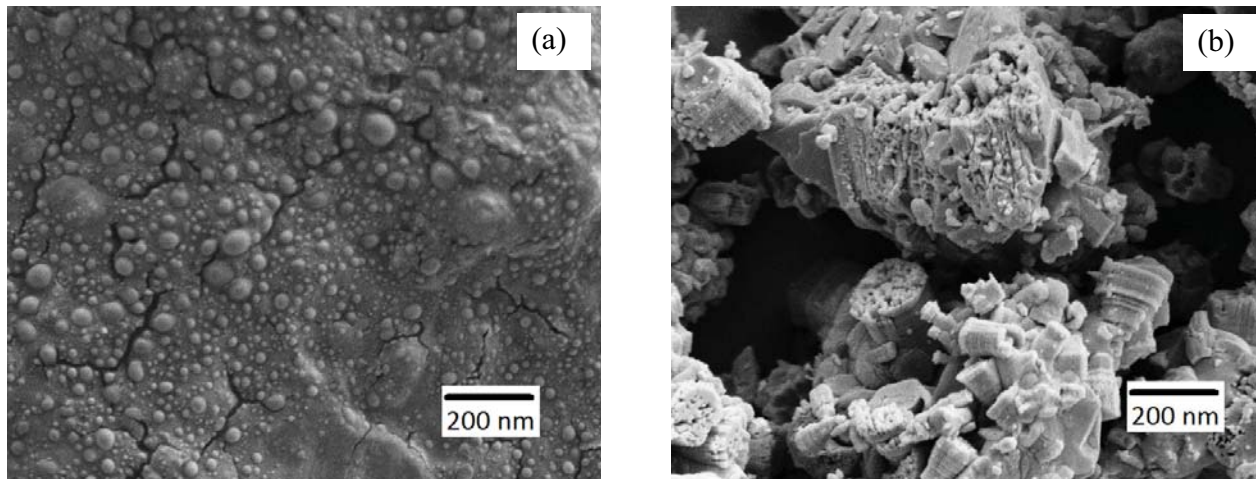


Figure 3: SEM images of the (a) as prepared (b) annealed ZnO nanoparticles at 500°C.

method. In this Figure, the particles size is in the range of 20-80 nm. Figure 3(b) shows the SEM image of the annealed ZnO nanoparticles at 500°C for 4 hours. The ZnO nanoparticles formed were less agglomerated with multiple layered structure of pyramidal shape with formation of clusters [34]. The crystallite size of annealed ZnO particles is in the range of 40-100 nm in diameter.

Energy dispersive spectroscopy (EDS) of ZnO prepared by wet synthesis is shown in Figure 4 which confirms the existence of Zn and O with weight percent.

EDS was used to analyze the chemical composition of a material under SEM. EDS measurement shows only peaks of titanium and oxygen and indicates the absence of impurities in prepared ZnO.

The transmission electron microscopy (TEM) analysis was carried out to confirm the actual size of the particles, their growth pattern and the distribution of the crystallites. Figure 5 shows the as synthesized TEM image of ZnO nanoparticles prepared by chemical co-precipitation route with less agglomeration.

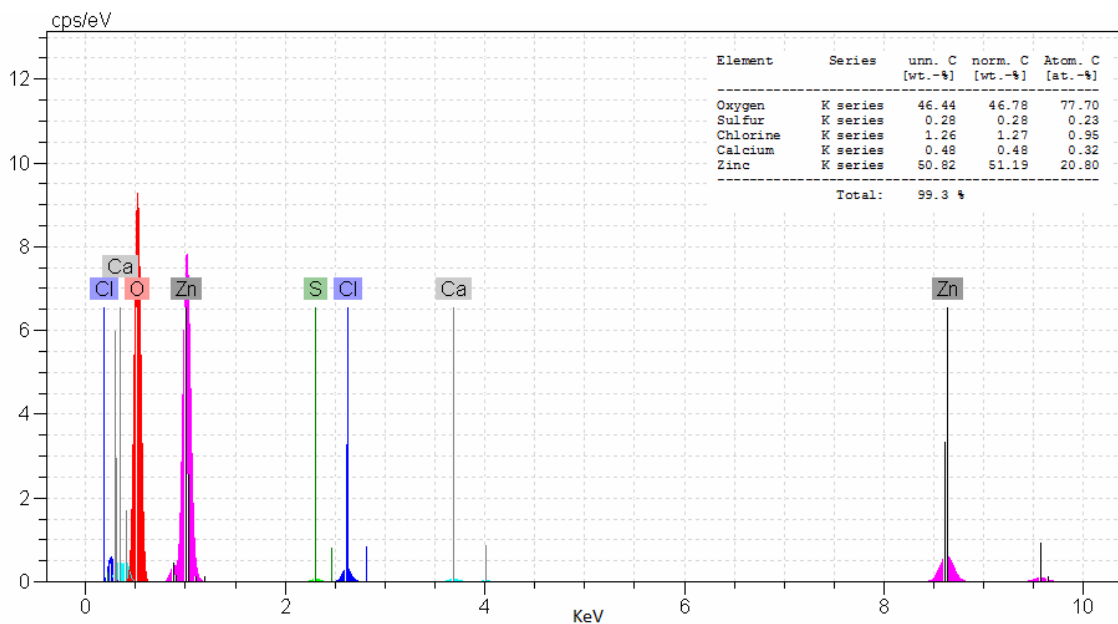


Figure 4: EDS spectra of the as synthesized ZnO prepared by wet synthesis.

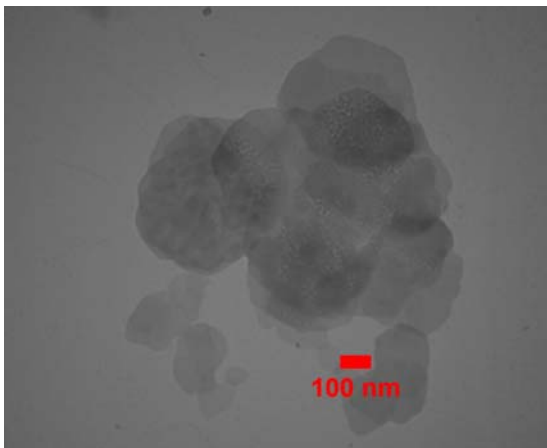


Figure 5: TEM images of the as prepared ZnO nanoparticles.

4. CONCLUSIONS

Pyramidal shape of ZnO nanoparticles were successfully synthesized by a simple co-precipitation method using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and K_2CO_3 as precursors. The XRD results showed hexagonal wurtzite structure of ZnO nanoparticles. From SEM images revealed that with increasing annealing temperature the morphology of the particles changes to the pyramid-like shaped with less agglomeration. The particles size were measured in the range of 20-80 nm for sphere-like shaped as-synthesized ZnO and 40-100 nm for pyramid-like shaped annealed ZnO, as estimated by XRD technique and direct HRTEM observation. Finally, EDS measurement showed only peaks of titanium and oxygen and indicated the absence of impurities in prepared ZnO.

ACKNOWLEDGEMENT

The authors are thankful for the financial support of varamin pishva branch at Islamic Azad University for analysis and the discussions on the results.

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