Sonochemically Assisted Synthesis of ZnO Nanoparticles: A Novel Direct Method

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ABSTRACT: *Nanocrystalline ZnO particles were prepared by a novel sonochemical route from zinc acetate and sodium hydroxide without any requirement of calcination steps at high temperature and without surfactants. Variations in several parameters and their effects on the structural (crystal size and morphology) properties of nanoparticles were investigated. Characterizations were carried out by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), IR spectroscopy, Thermal Gravimetry Analysis and Diffrential Thermal Analysis (TGA/DTA).*

KEY WORDS: *Sonochemistry; X-ray diffraction, Zinc oxide, Electron microscopy.*

INTRODUCTION

In recent years, synthesis of inorganic materials with specific size and morphology has attracted significant attention due to their possible use in different fields [1-4]. ZnO is a polar inorganic crystalline material with many applications due to its unique combination of interesting properties such as non-toxicity, good electrical, optical and piezoelectric behavior, stability in a hydrogen plasma atmosphere and low price [5-8]. ZnO is a well- known semiconductor with a wide direct band gap (3.37 ev) and a large exciton binding energy of 60 meV at room temperature [9, 10] and it has a wide range of applications such as solar cells, luminescent, electrical and acoustic devices, gas and chemical sensors, coatings, catalysts, micro lasers, memory arrays and biomedical applications [8, 11]. Till now, many methods have been developed to synthesize zinc oxide nanocrystals including vapor phase growth [12], vapor- liquid- solid process [13], soft chemical method [14], electrophoretic deposition [15], sol-gel process [16], homogeneous precipitation [17], etc.

The sonochemical method has been proven to be a useful technique to obtain novel materials with interesting properties. It is based on acoustic cavitation resulting from the continuous formation, growth and implosive collapse of bubbles in a liquid [18]. This method has been used for synthesis of many kinds of nanomaterials so far. Also some researchers have used this method to prepare different shapes of ZnO nanocrystallites. *Gedanken* and coworkers synthesized crystalline nanoporous ZnO spheres with a diameter of ca. 500 nm and 20 nm pore size via ultrasonic irradiation [19]. *Dong Qium et al.* [20] synthesized ZnO nanoparticles by sonicating a prepared zinc hydroxide sol and investigated the role of different

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Table 1: Experimental conditions for the preparation of ZnO nanoparticles.

sample	$Zn(OAc)_2.3H_2O$	NaOH (0.1 M)	Sonication time	Ultrasound power
1	50 ml (0.1 M)	100 ml	1 hr	60-90W
2	25 ml (0.2 M)	100 ml	1 hr	60-90W
3	10 ml (0.5 M)	100 ml	1 hr	60-90W
4	25 ml (0.1 M)	100 ml	1 hr	60-90W
5	25 ml (0.2 M)	100 ml	2 hr	60-90W
6	50 ml (0.2 M)	100 ml	30 min	150-180W
7	50 ml (0.2 M)	200 ml	1 hr	390-420W
8	50 ml (0.2 M)	200 ml	1 hr	60-90W
9	25 ml (0.2 M)	100 ml	1 hr	60-90W
10	25 ml (0.2 M) + 2g PVA	100 ml	1 hr	60-90W

solvents for precipitating the ZnO particles. *Hu et al.* [21] synthesized linked single-crystal ZnO rods with an average diameter over 150 nm under ultrasound irradiation. *Zhang et al.* [22] synthesized ZnO nanorods by sonochemical method in the paraffin oil with the assistance of stearic acids at high temperature.

In the present work, we found that ultrasonic irradiation can greatly enhance the conversion rate of precursor to nanometer- sized ZnO crystals without needing to use heating at high temperatures and surfactants. Also the role of calcinations on the size, morphology and chemical composition of nanoparticles was investigated. For the precursor we used zinc acetate dissolved in ethanol and with the addition of a solution of sodium hydroxide, ZnO nanoparticles were directly obtained. The influence of several parameters on the size and morphology of the ZnO particles is reported. The powders were characterized by means of powder X- Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), IR Spectroscopy, Thermal Gravimetry Analysis and Diffrential Thermal Analysis (TGA/DTA).

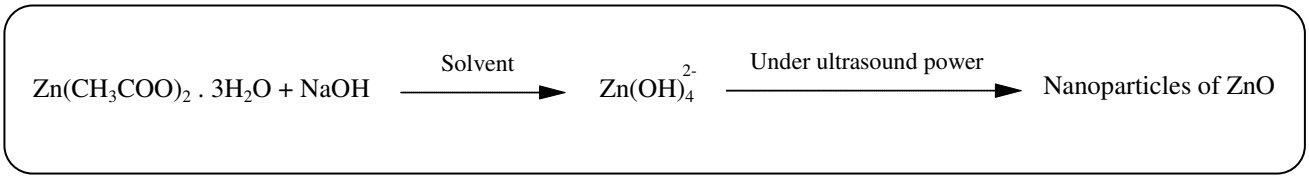
EXPERIMENTAL SECTION

Different amounts of NaOH solution with a concentration of 0.1 M were added to the 0.1, 0.2, 0.5 M solutions of $Zn(CH_3COO)_2.3H_2O$ in ethanol. The mixtures were sonicated for 30 min, 1 h and 2 h with different ultrasound powers. To investigate the role of surfactants on the size and morphology of nanoparticles, we used 2g of PolyVinyl Alcohol (PVA) in the reaction with optimized conditions. Table 1 shows the conditions of reactions in detail. A multiwave ultrasonic generator (Sonicator-3000; Misonix, Inc., Farmingdale, NY, USA), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 600 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level. The wave amplitude in each experiment was adjusted as needed. X-Ray powder Diffraction (XRD) measurements were performed using a Philips diffractometer of X'pert company with mono chromatized Cuk_α radiation. The crystallite sizes of selected samples were estimated using the sherrer method. TGA and DTA curves were recorded using a PL-STA 1500 device manufactured by Thermal Sciences. The samples were characterized with a Scanning Electron Microscope (SEM) (Philips XL 30) with gold coating. IR spectra were recorded on a SHIMADZU- IR460 spectrometer in a KBr matrix.

RESULTS AND DISCUSSION

The reaction between zinc acetate and sodium hydroxide to form zinc oxide has been shown in scheme 1.

Fig. 1 shows the XRD patterns of the ZnO nanoparticles. Fig.1a shows the XRD pattern of the direct sonochemicaly synthesized ZnO nanoparticles and Fig. 1b shows the XRD pattern of this sample after calcinations for 4 hours by a temperature of 400°C. As it can be observed the XRD patterns are quite the same and are in agreement with the typical wurtzite structure ZnO



Scheme 1: The mechanism of ZnO formation.

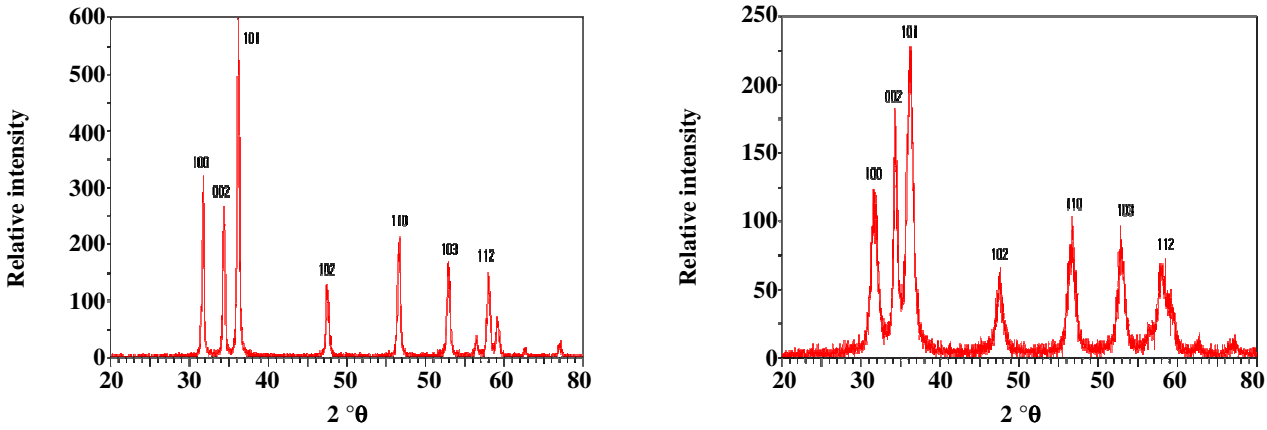


Fig. 1: X- ray powder diffraction pattern of ZnO nanoparticles (sample No. 2) (a) after calcination, (b) befor calcinations.

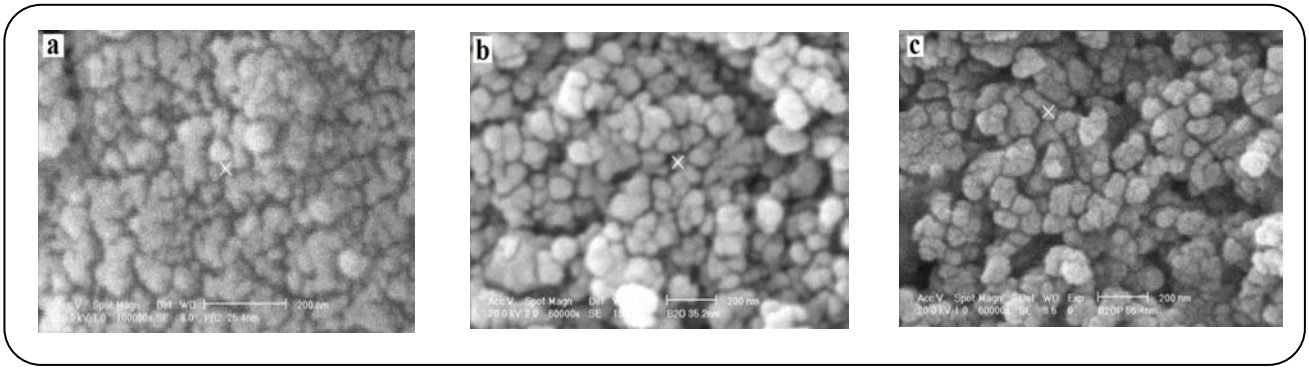


Fig. 2: SEM images of ZnO nanoparticles (a) sample No. 2 before calcination, (b) sample No. 2 after calcination, (c) sample No. 10 after calcinations.

diffraction (hexagonal phase, space group $P6_3mc$, with lattice constants a = 3.24982(9) Å, c = 1.6021 Å, Z = 2, JCPDS No. 36-1451). Sharp diffraction peaks shown in Fig. 1 indicate good crystallinity of ZnO nanoparticles. No characteristic peak related to any impurity was observed. The broadening of the peaks indicated that the particles were of nanometer scale. Estimated from the sherrer formula, $D = 0.891\lambda/\beta\cos\theta$, where D is the average grain size, λ is the X-ray wavelength (0.15405 nm), and θ and β are the diffraction angle and full-width at half maximum of an observed peak, respectively [23], the average size of the particles of sample number 2 was 25.4 nm, and the average size of this sample after calcination at 400°C for 4 hours has been calculated about 57.5 nm which are in agreement with that observed from SEM images.

Morphology, structure and size of the samples are investigated by Scanning Electron Microscopy (SEM). Fig. 2a indicates that the original morphology of the particles is approximately spherical with the diameter varying between 20 to 100 nm. The best morphology with smaller particles and good distribution was obtained for the sample number 2 before cacination and Fig. 2b shows the SEM image of this sample after calcination,

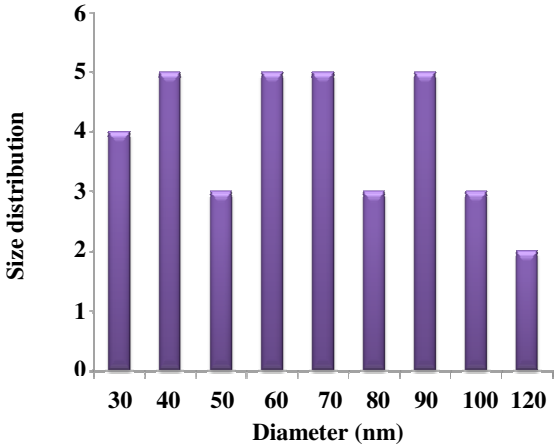


Fig. 3: Particle size histogram of sample 2.

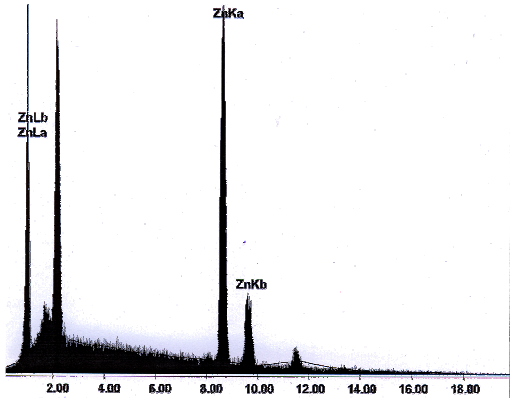


Fig. 4: EDAX analysis of sample No. 2.

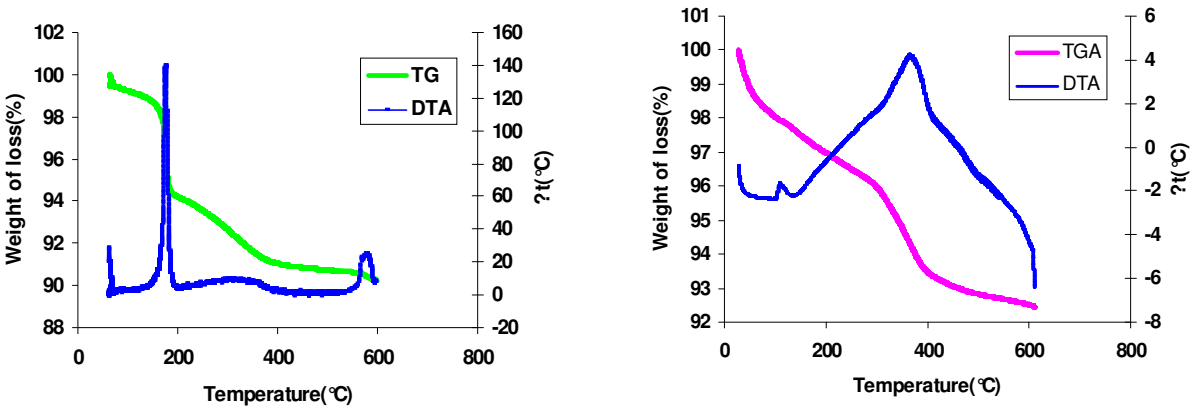


Fig. 5: TG- DTA curves of the ZnO nanoparticles of sample No. 2 (a) befor calcinations, (b) after calcinations.

as it is observed the size of the particles has become larger after calcination. Fig. 2c shows the SEM image of the sample number 10. The role of PVA on the morphology of this sample is obvious. It has been reported that the presence of a capping molecule (such as polyvinyl alcohol) can alter the surface energy of crystallographic surfaces, in order to promote the anisotropic growth of the nanocrystals [24, 25]. In this work PVA adsorbs on the crystal nuclei and it helps the particles to grow separately. To investigate the size distribution of the nanoparticles a particle size histogram was prepared for sample 2, (Fig. 3). Most of the particles possess sizes in the range from 40 to 90 nm. For further demonstration, the EDAX was performed for the sample No. 2. The EDAX spectrum given in Fig. 4 shows the presence of Zn as the only elementary component.

ThermoGravimetric Analyses (TGA) were carried out to show that there is not any difference between the curves of intermediate product and the one after calcinations. There is not any reportable loss of weight in the TGA curves that proves the existence of zinc oxide which does not decompose in this temperature range and the similarity of the TG curves of two samples shows the direct synthesis of ZnO. Fig. 5a shows the TGA and DTA diagrams of sample No. 2 and Fig. 5b shows the TGA and DTA diagrams of this sample after calcinations.

Infrared spectra of the powders were recorded in the range of 4000- 400 cm^{-1}. Fig.6 (a) shows the IR spectrum of sample No.2 before calcination. The relatively sharp absorption bands in the range of 1380-3400 cm^{-1} are probably due to the presence of solvent remaining in the powder or a little $Zn(OH)_4^{2-}$ that has not been

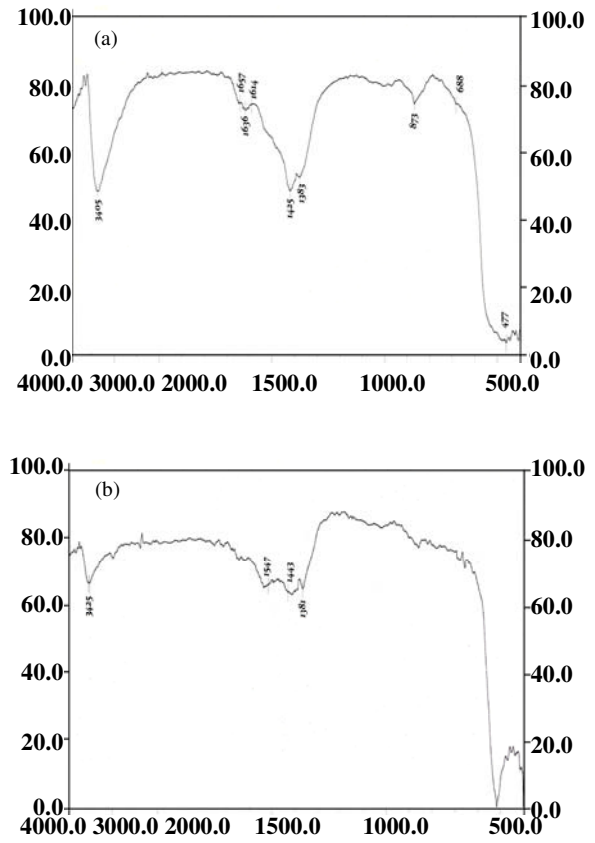


Fig. 6: IR spectrum of sample No.2 (a) before calcinations, (b) after calcinations.

converted to ZnO. Fig.6 (b) shows the IR spectrum of sample No.2 after calcination. The absorption bands at about 500 cm^{-1} can be attributed to the stretching modes of Zn-O and the weak bands in the range of 1380-3425 cm^{-1} are probably attributed to the presence of water in the KBr matrix.

In order to investigate the role of sonication on the composition, size and morphology of the products, we have done the reaction without sonication with the same conditions of the optimized sample. The XRD pattern of the obtained product is corresponding to ZnO but the SEM images show that the particles of the sample without using sonication have larger sizes comparing with the samples obtained via the sonochemical route.

CONCLUSIONS

A simple sonochemical method has been presented by the direct transformation of $Zn(OAc)_2.3H_2O$ precursor to create the ZnO nanoparticles. The properties of nanoparticles were studied by SEM, XRD, IR and TG- DTA. SEM analysis shows that ZnO nanoparticles have an average diameter of 20- 50 nm which varied by different factors. Comparing with the gas-phase approaches such as thermal evaporation and chemical vapor deposition which require high temperature and expensive equipment, wet chemical methods have been proven to be simple and versatile approaches for preparing ZnO nanostructures due to their relatively low growth temperature and good potential for mass production, so preparation of ZnO via solution chemical routes provides a promising option for large-scale production of this material [26-29]. Comparing with the wet chemical routes such as hydrothermal or solvothermal methods [8], this sonochemical method does not require pressure controlling and high temperature. Comparing with the sol-gel method [30], which requires long aging times, this procedure takes place in 2 hours at the most. The differences between this method and other sonochemical routes [20, 21, 31, 32], are in the starting materials, the procedure, adding surfactants and also the shape of the products which is one dimensional such as nanorod, nanobelt and so on in all cases, but we have obtained nanoparticles by this procedure. The most important benefit of this method is preparing ZnO nanoparticles directly and by a one-step reaction. It has been proved that the products of the reactions under ultrasound radiation are special and sometimes unexpected. In our previous work we had obtained cadmium carbonate from the reaction of cadmium acetate and tetra methyl ammonium hydroxide under ultrasound radiation [33], in the present work we have expected to obtain zinc carbonate as the intermediate product but zinc oxide was prepared directly by the reaction of zinc acetate and sodium hydroxide under the ultrasound power. It shows that the type of the metal ion, the type of the sonicator device and the power of ultrasound have probably affected on the type of the product.

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