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Synthesis and Characterization of Zinc Oxide Nanoparticles via a Novel Reverse-Micellar Route

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Abstract: ***Zinc Oxide (ZnO) nanoparticles were synthesized by water-in-oil microemulsions with CTAB as the surfactant, 1-butanol as the cosurfactant, isooctane as the non-polar phase. These nanoparticles were decomposed at 450 °C in air to obtain nanoparticles of zinc oxide. Transmission electron micrographic (TEM) analyses revealed the particle size of the nanoparticles to be in the range 18–38nm. The average grain size is 25 nm. Variety of techniques likes Powder x-ray diffraction studies (PXRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), thermogravimetry analysis (TGA), FTIR are used to carry out structural characterization of the nanoparticles.***

Keywords: ZnO nanoparticles, reverse micellar method, TEM, SEM, FTIR.

1. Introduction

Nanocrystalline materials may be considered as the challenge of this age. Intensive investigations were stimulated for several applications for these new classes of materials. Zinc oxides of particle size in nanometer range have been paid more attention for their unique properties. They are widely used for solar energy conversion, non-linear optics, catalysis, varistors, pigments, gas sensors, cosmetics etc [1-7]. As a wide band gap semiconductor, ZnO has been widely studied in varistors, transparent conductors, transparent U.V. protection films, chemical sensors and so on [8-11]. Also ZnO has been commonly used in its polycrystalline form over hundred years in a wide range of applications. This ignites many research minds all over the world and creates enthusiasm to develop proper growth and processing techniques for the synthesis of Zinc oxide. Zinc oxide (ZnO), a versatile semiconductor material, has been attracting attention because of the commercial demand for optoelectronic devices operating at blue and ultraviolet regions [12]. ZnO is a wurtzite-type semiconductor with band gap energy of 3.37 eV and it has very large excitation binding energy (60 meV) at room temperature [13,14].

A wide number of synthesis techniques also been developed by which ZnO can be grown in different nanoscale forms and thereby different novel nanostructures can be fabricated with different shapes ranging from nanowires to nanobelts and even nanosprings. A number of techniques have been used for the synthesis of ZnO, such as co-precipitation [15], hydrothermal [16], sol-gel [17], combustion method [18], rheological phase reaction precursor method [19] and other physical methods. Among all chemical methods, the reverse micellar method is a versatile method which does not require any specialized or expensive equipments for obtaining the uniform, homogenous and monodisperse nanoparticles of wide ranging compositions. The reverse micelles or water pools act as a nano reactor which determines the size and shape of nano particles and also inhibit the excess aggregation of particles [20-22]. The reverse-micelles obtained at a particular ratio of the aqueous phase to the surfactant leads to uniform-sized nanoreactors and have an aqueous core (in the nanometer range) in which precipitation of the inorganic compound or the initial precursor is carried out. It is possible to control not only the size but also the morphology of the nanoparticles by proper choice of the composition of the micro-emulsion system. There have been reports on the synthesis of metal oxides through the reverse micellar route of oxides [23–27].

In this paper, we report on the synthesis, characterization and of ZnO by reverse micelle method using a cationic surfactant. The synthesis via this method does not require specialized or expensive equipments as is required by several physical methods. The nanoparticles have been characterized by Powder X- Ray diffraction and Transmission Electron microscopy.

2. Experimental Details

2.1 Reagents and chemicals

All reagents were of analytical grade and used without further purification. The main reagents used for the synthesis were: cetyltrimethyl ammonium bromide (CTAB) (99%), 1-butanol (99.5%), isooctane (99%), zinc nitrate, ammonium oxalate, chloroform and methanol. All other reagents and chemicals were of analytical reagent grade.

2.2 Synthesis of ZnO nanoparticles

Zinc Oxide nanoparticles were prepared using the reverse micellar route. Microemulsions with cetyltrimethyl ammonium bromide (CTAB) as the surfactant, 1-butanol as the cosurfactant, isooctane as the non-polar phase and 0.1M aqueous solutions of Zn^{2+} and $C_2O_4^{2-}$ were prepared. Microemulsion I contained 0.1 M zinc nitrate solution while microemulsion II contained 0.1 M ammonium oxalate solution. The weight fraction of various constituents in the microemulsion was 16.76% of CTAB, 13.9% of n-butanol, 59.29% of isooctane and 10.05% of aqueous phase. The two microemulsions were slowly mixed and stirred overnight on a magnetic stirrer. The precursor was separated from the surfactant and non-polar phase by centrifugation. The precursor was then washed with a 1:1 chloroform/methanol mixture to remove the surfactant and other impurities if

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present and dried in an oven at 120 ˚C for 1 hr. Dried the precipitate and ground it with an agate mortar and pestle. White powder of ZnO was obtained. The nanocrystalline ZnO was annealed in air at 450º C for 6hrs. The flow chart and reaction scheme for the preparation of ZnO nanoparticles are shown as **Figure 1.**

3. Characterization

Powder x-ray diffraction studies (PXRD) were carried out on a Bruker D8 Advance diffractometer using Ni filtered Cu Kα radiation. Normal scans were recorded with a step size of 0.02◦ and step time of 1 s.

Microphotographs of the original form of ZnO with surfactant were obtained by the scanning electron microscope (SEM) at various magnifications. The crystal size and morphology have been studied by transmission electron microscopy (TEM) using JEOL JEM 200CX transmission electron microscope with an accelerating voltage of 200 kV. The TEM specimens were prepared by dispersing the powder in acetone by ultrasonic treatment. A few drops were poured onto a porous carbon film supported on a copper grid, and was then dried in air.

Thermal decomposition of samples were studied by thermogravimetry analysis (TGA) with a Perkin Elmer TGA/DTA system instrument in nitrogen atmosphere at a heating rate of 30ºC min^{-1} with alumina as a reference sample. On the basis of the TGA/DTA studies, we calcined the precursor (cadmium oxalate dihydrate) obtained by the reverse micellar route at 450 ◦C for 6 h to effect the complete conversion to cadmium oxide nanoparticles.

The FTIR spectrum of ZnO in the original form dried at 40 °C were taken by KBr disc method at room temperature using a Nicolet Protege 460 FTIR spectrometer.

4. Results and Discussion

The PXRD diffraction patterns in figure 2 show that the as-prepared ZnO nanoparticles belonging to hexagonal structure, which is very close to the values in the literature (JCPDS 80-0074). The XRD pattern of ZnO nanoparticles indicates the prominent diffraction peaks at 2Θ values of 30.79˚, 33.48˚, 35.35˚, 46.59˚, 55.60˚, 61.93˚, 67.08˚ and 68.1˚ which are attributed to the typical Hexagonal type of ZnO.

The average particle size (D) may be calculated for the selected samples by using Scherrer equation given below:

$D = K\lambda \beta \cos \theta$

where K is the shape factor for the average crystallite (expected shape factor is 0.9), λ is X-ray's wavelength for Kα, β is full width at half maximum of the diffraction line, and θ is Bragg's angle.

SEM photographs of ZnO nanoparticles obtained at different magnifications (Fig. 3a-b). The image of Fig 3a demonstrate that a bulk quantity of plate-like or rod-like bunches exist. Each bunch is gathered of closely packed nanometer scale rods and forms radiating structures.

Transmission electron microscope (TEM) image (Figures 4) of PTh/ZnO nanocomposite was obtained using JEOL JEM 200CX electron microscope. TEM image suggests that the particles of the nanocomposite are in nanometer range. TEM images of ZnO shows hexagonal nanoparticles (with few spherical nanoparticles) with average particle size of 25 nm. The extent of agglomeration is very less which can be clearly seen from figure 4. The TEM micrographs of ZnO nanoparticles indicates that most of the individual particles are in range of 18-38 nm which is in close agreement with that estimated by Scherer formula based on the XRD pattern.

Figure.5 shows the FTIR spectrum of the ZnO nanoparticles synthesized by reverse micellar method method, which was aquired in the range of 400-4000 cm^{-1}.The band between the 450-500 cm^{-1} corelated to metal oxide bond (ZnO). From this FTIR we can also observe that increasing the annealing temperature sharpens of the characteristic peaks for metal oxide, suggesting that, the crystalline nature of ZnO increases on increasing the calcination temperature. The peaks in the range of 1400-1500cm^{-1} corresponds to the C=O bonds. The adsorbed band at 1626 cm^{-1} is assigned O-H bending vibrations. The peak at 1319$cm^{-1}$and 1530cm^{-1} corresponds to C=O and O-H bending vibrations respectively diminishes gradually for sample annealed at higher temperature.

Figure.6 shows a plot of TGA. To determine the crystalline conditions, TGA of ZnO gel nanoparticles were carried out. The specimens were heated from room temperature to 1000^{o}C with an increment of 10 ^{o}C/min in air. Notably, the TGA data plots the weight loss of the nanoparticles which shows that a small amount of weight loss has occurred around 100^{o}C, thereby indicating the evaporation of water and/or moisture.

5. Conclusion

We have demonstrated a new morphology, nanometer particles of ZnO synthesized by reverse micellar method using CTAB as a surfactant. After decomposition of zinc oxalate at 450°C for 6 hrs, the samples were characterized using powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM). Different structural characterization including electron microscope images and spectroscopy analyses data clearly indicated that the ZnO nanoparticles were synthesized successfully by this novel route. The TEM and SEM results suggest the uniform distribution of zinc oxide nanoparticles. TEM photograph shows the particle size of ZnO within the range of 18.0-38.0 nm.

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Figures Caption

Figure 1	Flowchart for the reverse micellar synthesis of ZnO nanoparticles
Figure 2	Powder X-ray diffraction pattern of ZnO nanoparticles.
Figure 3	SEM photographs of ZnO nanoparticles at different magnifications.
Figure 4	Transmission electron microscopy (TEM) shows the particle size of ZnO nanoparticles.
Figure 5	FTIR spectra of as prepared ZnO nanoparticles.
Figure 6	Simultaneous TGA curve of ZnO nanoparticles (as prepared).

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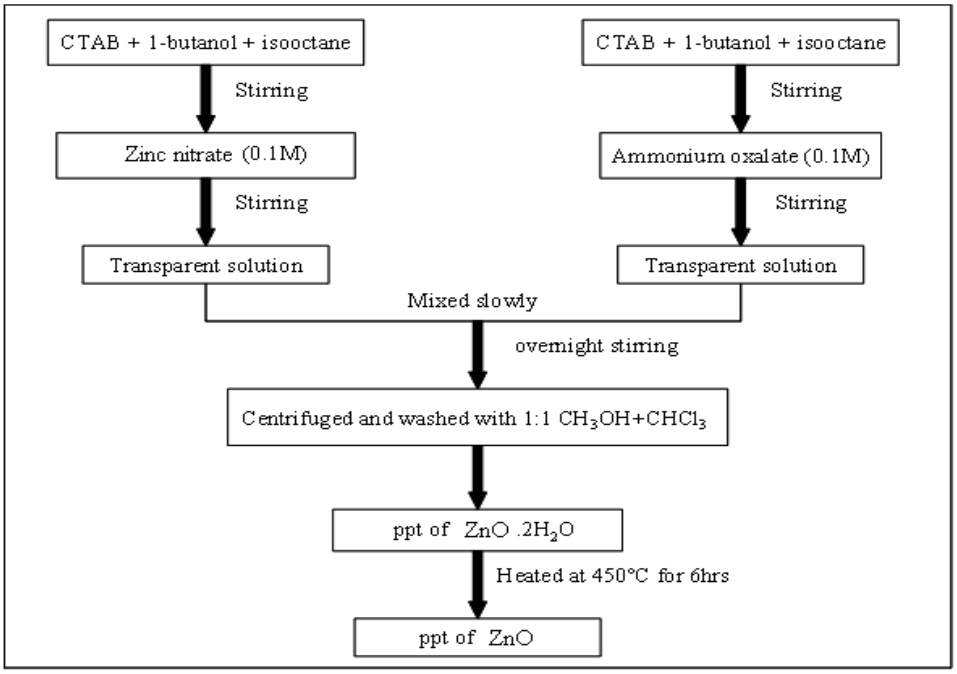


Figure 1: Flowchart for the reverse micellar synthesis of ZnO nanoparticles

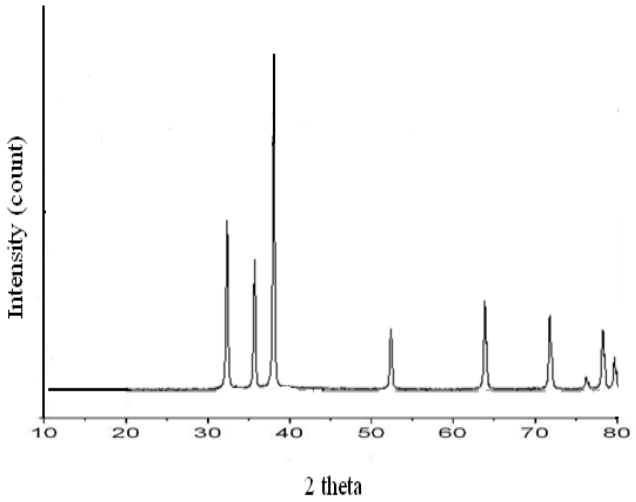


Figure 2: Powder X-ray diffraction pattern of ZnO nanoparticles.

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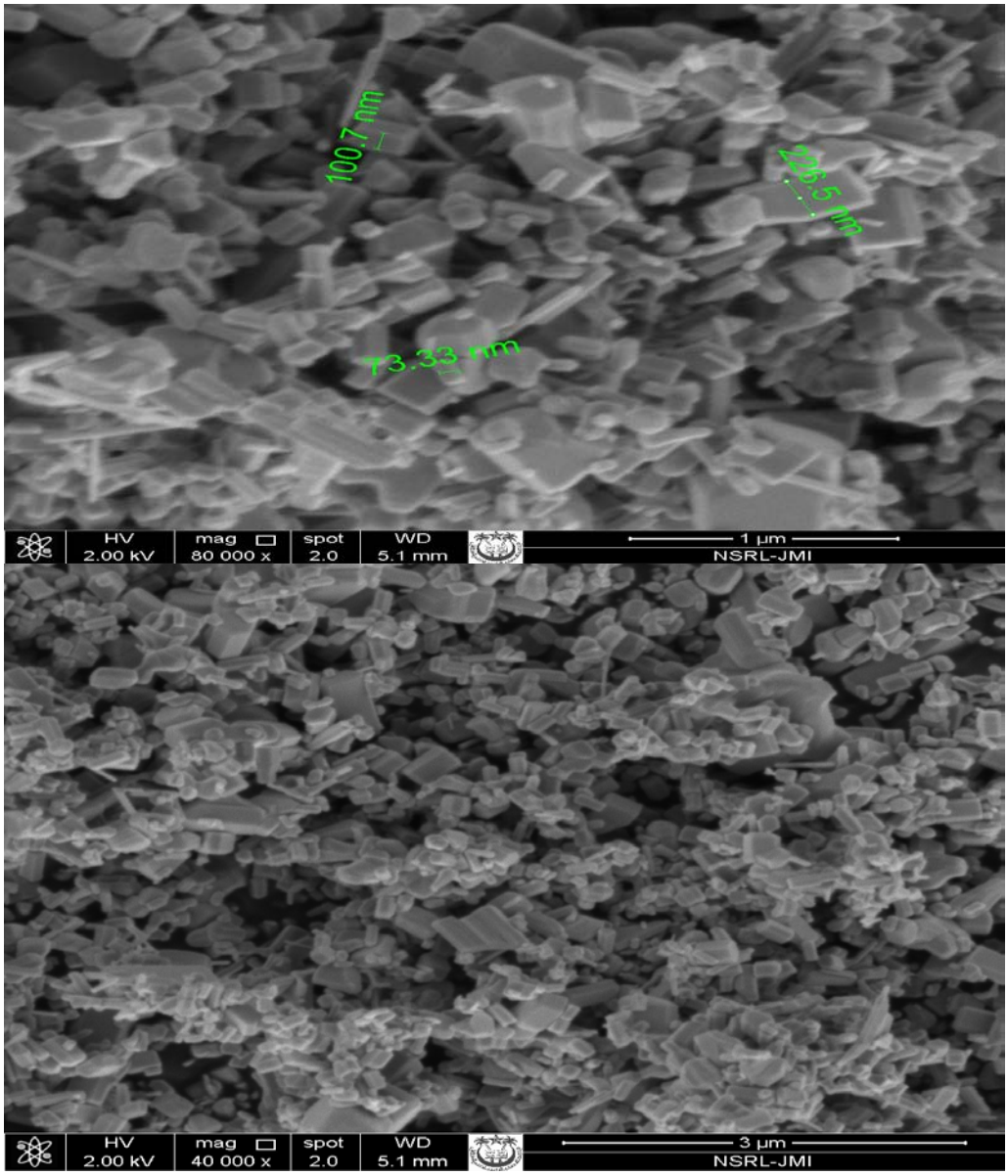


Figure 3: SEM photographs of ZnO nanoparticles at different magnifications.

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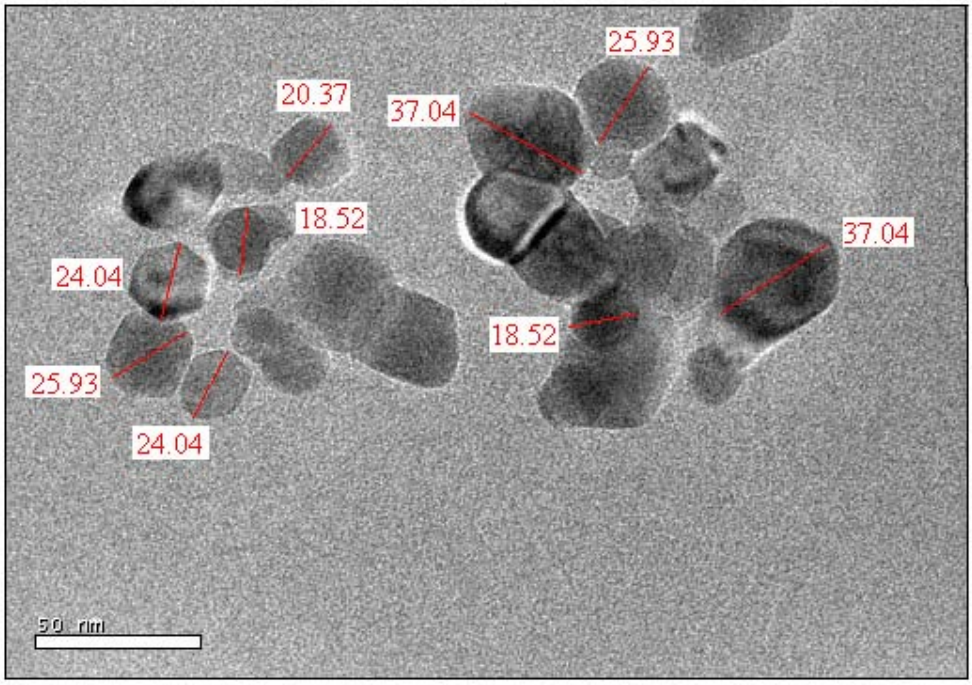


Figure 4: Transmission electron microscopy (TEM) shows the particle size of ZnO nanoparticles

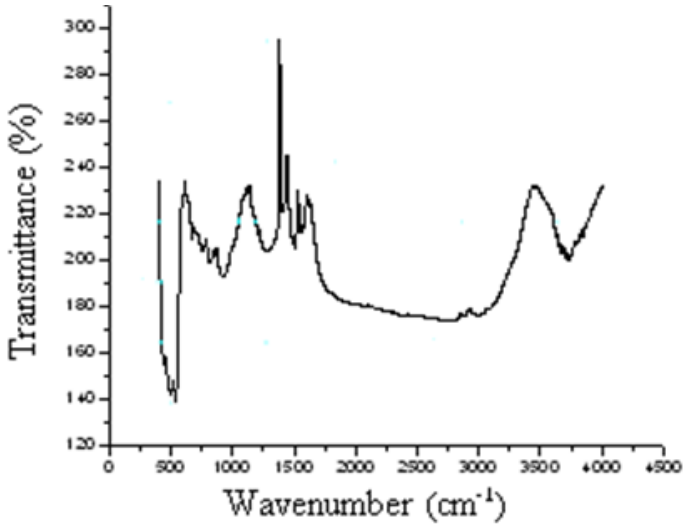


Figure 5: FTIR spectra of as prepared ZnO nanoparticles.

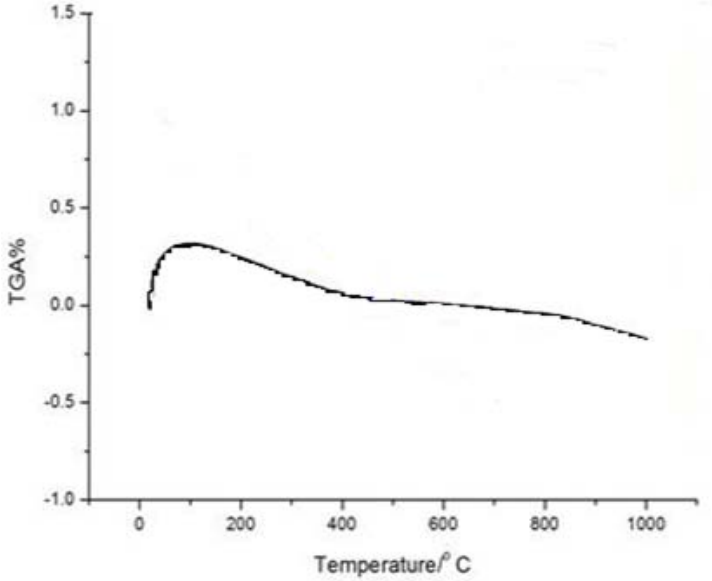


Figure 6: Simultaneous TGA curve of ZnO nanoparticles (as prepared).

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