Research Paper

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Surface Area Study of the Nanocrystalline Zinc Oxide Synthesized by Reverse-Micellar Method

Environmental Science

KEYWORDS : ZnO nanoparticles, reverse micellar method, Surface area

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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. The specific surface area of ZnO nanoparticles as calculated using BET method was found to be 62.922 m2g-1

1. Introduction

Nanotechnology can be defined as a technology of design, fabrication and applications of nanostructures and nanomaterials. Several methods have been explored for the synthesis of nanomaterials. These processes involve both physical and chemical methods [1-5].

Many scientists are currently working on molecular and nanoscaled electronics. The current development in this field is due to shrinkage of semiconductor in semiconductor industries along with the availability of characterization and manipulation techniques at the nanometer level. Nanotechnology offers a wide range of applications in field of electronics, optical communications and biological systems. There are two general ways available to produce nanomaterials. The first way is to start with bulk material and then break it into smaller pieces using mechanical, chemical or other form of energy (top-down). An opposite approach is to synthesize the material from atomic or molecular species via chemical reactions and allow the precursor particles to grow in size (bottom-up). Both approaches can be done in either gas, liquid, supercritical fluids, solid states or in vacuum. 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.

Zinc oxide due to its versatility and multifunctionality creates attention in the research field related to its applications. 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. ZnO is an important material because of its broad applications in electronic industries such as piezoelectric transducers, gas sensors, photonic crystals, light-emitting devices, photodetectors, photodiodes, optical waveguides, transparent conductive films, varistors, solar cell windows and bulk acoustic wave devices [6-8].

The total surface area of the filler is the most important parameter that influences the reinforcement. Particle size naturally is directly related to surface area by simple geometric considerations, in the absence of porosity. Other factors like shape of particle, size distribution and pattern of particle packing etc, affect the total surface area of a given quantity of filler.

In our previous article [9], we report on the synthesis and characterization of ZnO by reverse micelle method using a cationic surfactant. In this article, we report the BET Surface area analysis of ZnO nanoparticles synthesized by reverse micellar route.

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 Z_n^{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 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.

2.3. Surface area

Surface area of samples was determined by Brunauer-Emmett-Teller (BET) and pore size and pore volume analysis was performed by Barrett-Joyner-Halenda (BJH) method using Quantachrome instruments (Model NOVA 2000e surface area and pore size analyzer).

2.3.1. Sample preparation: Outgassing: Before the specific surface area of the sample can be determined, it is necessary to remove gases and vapours that may have become physically adsorbed onto the surface after manufacture and during treatment, handling and storage. If outgassing is not achieved, the specific surface area may be reduced or may be variable because an intermediate area of the surface is covered with molecules of the previously adsorbed gases or vapours. The outgassing conditions are critical for obtaining the required precision and accuracy of specific surface area measurements on pharmaceuticals because of the sensitivity of the surface of the materials.

Procedure: Admit a small amount of dry nitrogen into the sample tube to prevent contamination of the clean surface, remove

the sample tube, insert the stopper, and weigh it. Calculate the weight of the sample. Attach the sample tube to the volumetric apparatus.

3. Results and Discussion

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 1. The TEM micrographs of ZnO nanoparticles indicates that most of the individual particles are in range of 18-38 nm.

Approximately 0.26 g of the sample powder was placed in the sample cell and allowed to degas at one of the degassing stations for 3 hours at 250°C in a vacuum degassing mode. This removes contaminants such as water vapor and adsorbed gases from the sample. The degassed sample was then subjected to analysis at one station and the data was recorded by admitting known quantity of adsorbing Nitrogen gas into the sample cell containing the solid adsorbent maintained at constant temperature (77 K). As the adsorption occurs the pressure in the sample cell changes until equilibrium is reached. From the BET plot the specific surface area is calculated using the BET equation.

$$\frac{1}{W\left[(P_0/P)-1\right]} = \frac{c-1}{W_m c}\left(\frac{P}{P_0}\right) + \frac{1}{W_m c} \quad \text{--------- (1)}$$

where P and P0 are the equilibrium and the saturation pressure of adsorbate, W is the adsorbed gas quantity and Wm is monolayer adsorbed gas quantity and c is the BET constant. The BET equation requires a linear relation between 1 / W [(P_0/P) – 1] and (P/P_0). This plot should yield a straight line usually in the approximate relative pressure range 0.05 to 0.3. From the resulting linear plot, the slope, which is equal to (C – 1)/WmC, and the intercept, which is equal to 1/WmC, are evaluated by linear regression analysis.

Figure 2 shows the BET plots of of ZnO nanoparticles and their surface area was found to be 62.922 m^2g^{-1} which is smaller in comparison to the as-prepared sample at room temperature. The decrease in specific surface area at high temperature may be attributed to the increase in grain size. On heating the sample at high temperature (450°C), the particles become agglomerated which may lead to decrease in the specific surface area. It can be clearly seen from figure 3 that the adsorption isotherm of the sample was of type II according to BDDT (Brunauer, Deming, Deming and Teller) type of classification [10]. The pore size distribution (pore radius and pore volume) was calculated using Barrett-Joyner-Halenda (BJH) method [11]. The BJH pore size and pore volume distributions of these samples are shown in figure 4 and 5. As can be seen from the graphs, the pore radius obtained from BJH method comes out to 15.877 Å and pore volume is 0.089 cc/g. Table 1 summarizes the BET surface area and BJH pore diameter of ZnO nanoparticles.

4. Conclusion

Nanoparticles of ZnO synthesized by reverse micellar method using CTAB as a surfactant via Reverse micellar route. 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), SEM, FTIR, TGA etc. in our previous article. Specific surface area of these nanoparticles was found to be 62.922 m^2g^{-1}

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Table 1 summarizes the BET surface area and BJH pore diameter of ZnO nanoparticles.

Sample	BET surface area (m^2g^{-1})	BJH	
		Pore radius (Å)	Pore volume (cc/g)
ZnO	62.922	15.877	0.089

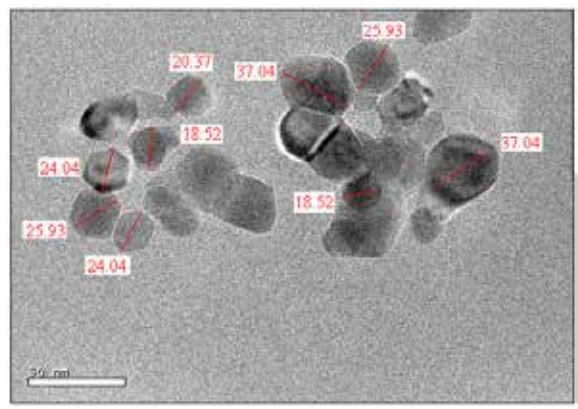

Figure 1. Transmission electron microscopy (TEM) shows the particle size of

ZnO nanoparticles.

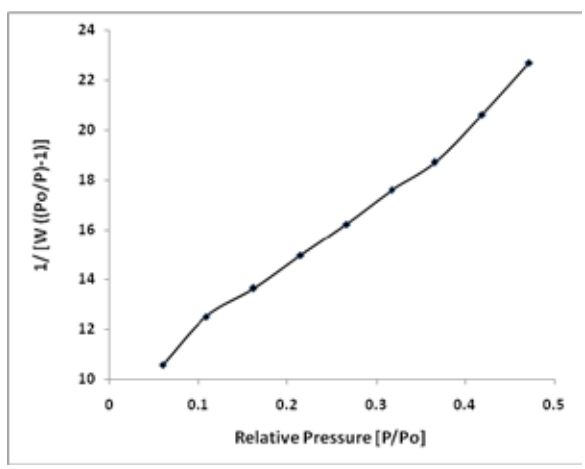

Figure 2. BET plots of ZnO nanoparticles.

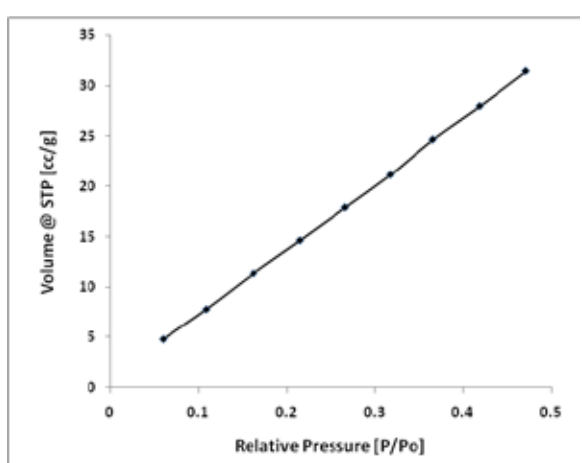

Figure 3. Nitrogen adsorption-desorption isotherm of ZnO nanoparticles.

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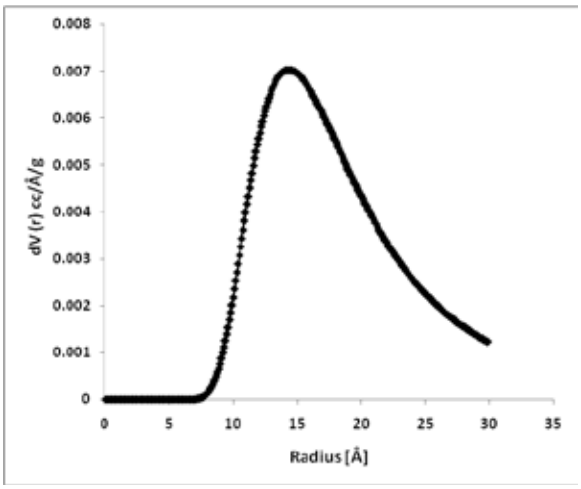

Figure 4. BJH plot for pore size of ZnO nanoparticles.

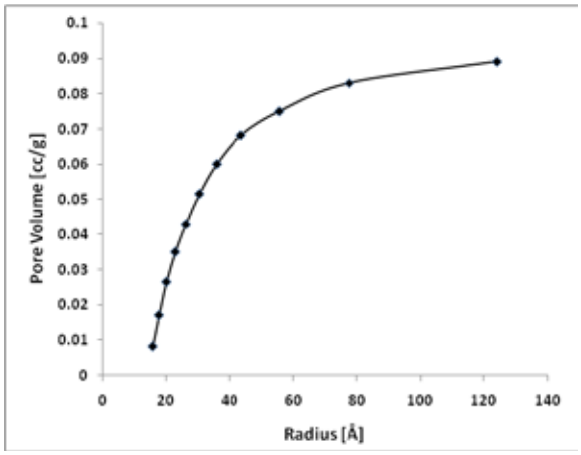

Figure 5. BJH plot for pore volume of ZnO nanoparticles.

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