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Preparation and Synthesis of ZnO Particles by Precipitation Method at Low Temperature

Research Article

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Abstract: Using zinc nitrate as a precursor and NaOH starch as a stabilizing agent, hexagonal zinc oxide (ZnO) particles has been synthesized by precipitation method at low temperature. The scanning electron microscopy (SEM) images show particles of nearly uniform spherical size of around 10 to 20 nm. The infrared spectroscopy (FT-IR) measurement reveals the peak at 500 cm^{-1}, corresponding to the Zn-O bond. Thus the ZnO particles of nanostructure may be confirmed. UV studies reveal that the particles may be of micron size.

Keywords: ZnO particles, low temperature precipitation, XRD, SEM, FTIR, UV.

1. Introduction

Research on semiconductor nanocrystals has grown significantly in recent years owing to their novel optical, electrical and catalytic properties. Unique optical and electronic properties of semiconductor nanocrystals are due to size quantization effect and surface state on the nanometer scale [1]. Various semiconducting nanomaterials of single elements, compound semiconductors and metal oxides have been successfully synthesized and studied [2–4].

In particular, the zinc oxide (ZnO) nanoparticles is promising material for nanoscale devices such as Ultraviolet lasers [5–7] light-emitting diodes [8], flat panel displays [9–11], photodetectors, gas sensors [12–14], catalysis and solar cells [15–18]. ZnO is a n-type semiconductor and has a large energy band gap of 3.37 eV. The ZnO nanoparticles can be synthesized using various techniques such as hydrothermal [19], sol–gel [20], wet chemical [21], precipitation [22], microemulsion [23], chemical vapor deposition [24], solid state reaction [25] and laser ablation.

In this work, the ZnO nanoparticles were synthesized using the cost competitive and simple precipitation process. The single step process with the large scale production without unwanted impurities is desirable for the cost-effective preparation of ZnO nanoparticles. As a consequence, the low cost precursors such as zinc nitrate hexahydrate and sodium hydroxide to synthesize the ZnO nanoparticles through a simple precipitation route are used here. In order to reduce the agglomeration among the smaller particles, the starch molecule which contains many O–H functional groups could bind surface of nanoparticles in initial nucleation stage, is used. The as-prepared ZnO nanoparticles are coated with starch molecules.

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2. Experimental

2.1. Chemical Reagents

All the chemicals used in the experiment were of analytic reagent (AR Grade, 99.9% pure) grade. Zinc nitrate hexahydrate and soluble starch were procured from the Merck, India, while the sodium hydroxide platelets were supplied by the Loba Chemie Pvt. Ltd. All chemicals were used as received without any further purification. De-ionized water was used throughout the synthesis process.

2.2. Synthesis

The ZnO nanoparticles were prepared by the precipitation method using zinc nitrate and sodium hydroxide as precursors and soluble starch as a stabilizing agent. 0.3 gm of starch was dissolved in 100 ml of distilled water at 27°C. 10 ml of the different ratio sample are 0.2, 0.3 and 0.4 M zinc nitrate was added to the starch solution. The obtained solution was stirred constantly using the magnetic stirrer for 2 hrs until the complete dissolution occurs. Subsequently, 10 ml of 0.2 M sodium hydroxide solution was added drop by drop to the above solution from the sidewalls. The reaction was allowed to proceed for 2 hrs after the complete addition of sodium hydroxide solution. After the completion of the reaction, the solution was allowed to settle down for 24 hrs. The supernatant solution was discarded carefully and the remaining solution was centrifuged. In order to remove the byproducts and excessive starch bound to the nanoparticles, the precipitate was washed with ethanol repeatedly. The powder of the ZnO nanoparticles was obtained after drying at 100°C for 2 hrs. Figure 1 shows the flowchart for the preparation of ZnO nanoparticles.

2.3. Characterization

The powder X-ray diffraction (XRD) was performed using Philips Holland, XRD system PW 1710 with nickel filtered CuKa (k = 1.5405 A) radiation. The average crystallite size (t) has been calculated from the line broadening using the Scherrer's relation: $t = 0.9k/Bcosh$, where k is the wavelength of X-ray (k = 1.5405 A) and B, the width of the peak at half height (maximum) in radians. The Scanning electron microscopy (SEM) studies were performed with Tecnai 20 G2 under the 200 kV. The samples were prepared by dispersing the drop of colloid on the copper grid, covered with the carbon film and the solvent was evaporated. For the measurement of Fourier transform infra-red (FTIR) spectra, Bomem Hartmann and Braun MB Series Fourier Transform Infrared spectrometer was used. The ZnO nanoparticles were dispersed and mixed with the KBr particles together and pressed into pellets.

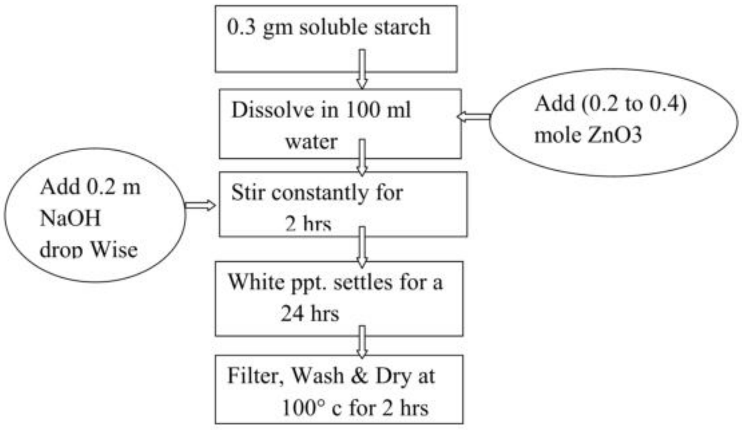

Figure 1.

3. Results and Discussion

3.1. XRD Study

The XRD pattern of ZnO nanoparticles prepared at 100°C is shown in Figure 2. The ZnO nonoparticles is observed to be highly crystalline. ZnO is called the zincite and has the hexagonal wurtzite type structure. The lattice parameters are $a = 3.18(1)A$, $c = 5.27(1)A$. These parameters are matching with the reported values (JCPDS file No. 36-1451). The XRD peaks are broad due to the nano-size effect. The average crystallite size of prepared ZnO nanoparticles as calculated using Scherrer's relation is about 21 nm.

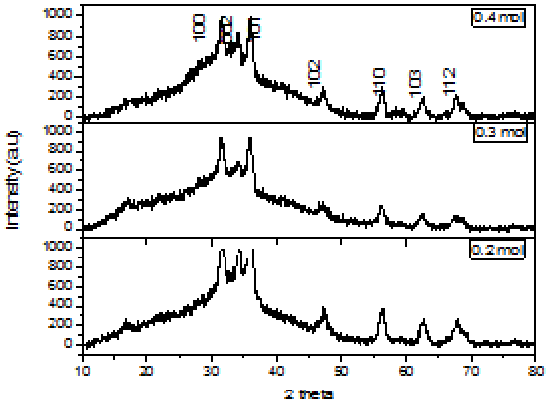

Figure 2.

3.2. SEM Study

Figure 3.2 represents the SEM image of ZnO nanoparticles at different magnifications which confirms the formation of ZnO nanoparticles. These images shows approximate spherical shape to the nanoparticles and most of the particles exhibit some agglomeration. From the pictures, it also can be seen that the particle size is more than the calculated valus from the Debye-Scherrer formula indicating the agglomeration of crystallites in ZnO particles. The aggregation of particles should had been originated from the large specific surface area and high surface energy of ZnO nanoparticles the aggregation occurred probably during the process of drying from SEM analysis it is seen that only zinc and oxygen are present in the sample and no other impurities are found.

SEM for 0.4 mol concentration:

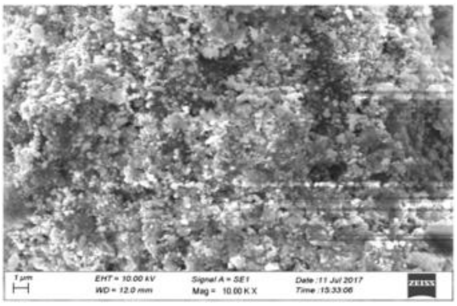

Figure 3. S1

SEM for 0.3 mol concentration:

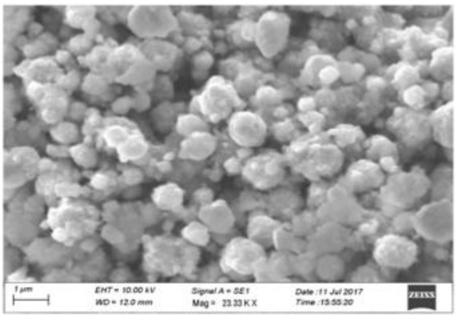

Figure 4. **S2**

SEM for 0.2 mol concentration:

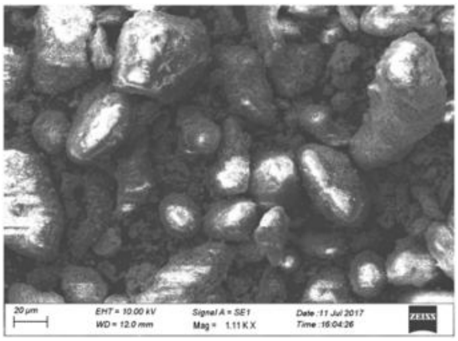

Figure 5. **S3**

SEM image of synthesized ZnO for different mol concentration (a) 0.2 mol (b) 0.3 mol (c) 0.4 mol

3.3. FT-IR Study

The FT-IR spectrum of ZnO nanoparticles prepared at 100°C is displayed in Figures Prominent peaks at 500, 1600 and 3435 cm^{-1} are clearly observed. The peak at 500 cm^{-1} corresponds to the Zn–O and remaining peaks 1600 and 3435 cm^{-1} may be due to the absorption of water during the preparation of IR pellet or O–H present in the starch molecule. Earlier, the broad bands between 500 and 800 cm^{-1} were attributed to the vibration of Zn–O bond. The peaks at 910, 1020 and 2926 cm^{-1} are due to the presence of C–O and C–H vibration modes of starch, which acts as a capping agent.

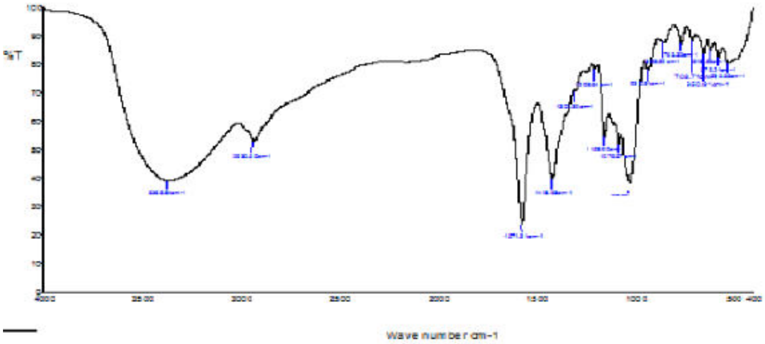

Figure 6. **FTIR spectra for synthesized ZnO particle**

3.4. UV Study

The optical characterization of the sample was recorded on UV absorption spectrometer fig shows the UV-Visible absorption spectra of ZnO nanopatricles as a function of wave length. The UV-Visible absorption spectroscopy of ZnO nanoparticles in ethanol solvent shows an excitonic absorption peak at 192 nm, which lies much below the band gap wavelength of ZnO. The blue shift in the peak centered at $\sim$192 nm in absorption spectra (figure) may be due to the transition of electron from the more inner shell of to the uppermost shell as time passes. It is possible that, due to aggregation and agglomeration, particle size increases and material settled down on the bottom of container causing decrease in the absorbance. The optical band gap (Eg) was calculated using the absorption spectra by formula (Ahϑ)n=B (h$\vartheta-$Eg), Where A is absorbance, B is characteristic of the material. This behavior is typical for many semiconductors due to internal electric fields within the crystal and inelastic scattering of charge carriers by phonons. From the graph the band gap of the zinc oxide is from the values (2.25ev-2.6ev).

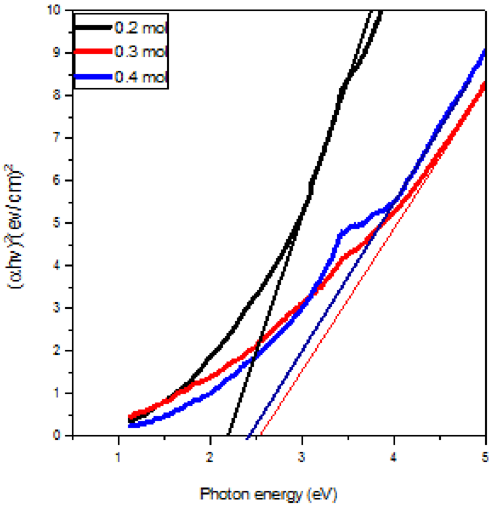

Figure 7.

4. Conclusion

The ZnO nanoparticles with hexagonal structure have been synthesized by simple competitive precipitation method after anneling the precursor. The prepared ZnO particles were characterized by XRD, SEM, FTIR, UYstudy. XRD, SEM studies confirmed the nanostructures for the prepared Zno nanoparicles. SEM micrograph illustrates that the particle size increases at high annealing temperature. The optical direct band gap of the synthesized nanoparticles is found to be (2.25ev-2.6ev) The ZnO nanoparticles can be used in different industrial application, namely, luminescent material for fluorescent tubes, active medium for laser, sensor, and so forth.

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