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Research Paper

Synthesis and Characterization of Gelatin Capped Zno Nanoparticles

Chemistry

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ABSTRACT

ZnOnanoparticles (NPs) have been synthesized using gelatin as surface modifyingagent by co-precipitation method. Linear optical investigations have been performed using ultraviolet-visible (UV-vis) spectroscopy and fourier transform infra-red (FT-IR) spectroscopy. Strong blue-shift of maximum absorption wavelength in the UV-vis spectra clearly attests the formation of ZnO NPs. Maximum blue-shift has been observed for the sample prepared using highest concentration of gelatin. FT-IR spectrum shows rotational-vibrational peaks corresponding to ZnO and gelatin which clearly indicates the attachment of gelation on the surface of ZnO. Particles sizes of all uncalcined and calcined NPs have been calculated using Effective Mass Approximation (EMA) method. X-ray diffraction (XRD) pattern confirms the formation of pure phase wurtzite structure of ZnO and particle size was calculated using Debye-Scherrer formula and agrees with UV-vis data. Field emission scanning electron microscopy and transmission electron microscopy reveals the uniform surface morphology of ZnO NPs.

Introduction

Nanomaterials having particle size in the range of few nanometers show properties which are of scientific and technological importance [1, 7]. Nano crystalline ZnO semiconductor is one of the best promising materials as it has potential applications in optics and optoelectronics. ZnO is a wide band gap semiconductor having bulk energy gap of about 3.3 eV at room temperature. The energy band gap can be increased in the nano regime and optical properties of such materials can be tuned for the specific applications. ZnO nanoparticles (NPs) can be synthesized by various methods among which polyol synthesis technique is mostly favored. To avoid agglomeration of the NPs, capping agents play important role. These capping agents can be removed by the process of calcination at slow heating rate by which un-agglomerated nanostructures can be retained.

Amino acids belong to an important class of water soluble organic surface modifying agents that play critical role in the synthesis of narrow range NPs. They are commercially available, inexpensive and non-biohazard materials. Researchers have demonstrated the use of L-histidine and L-cysteine as capping agents for semiconducting nanomaterials. We have used amino acids as a capping agent in our previous works [8-12]. The amino group has a loan pair of electrons and capable of forming hydrogen bonds [13, 14].

In this paper, we report synthesis of ZnO NPs by using gelatin as surface modifying agent. ZnO NPs with particle size of 8 nm can be effectively synthesized by using gelatin. ZnO NPs have been characterized by ultraviolet-visible (UV-vis) spectroscopy. Powder X-ray diffraction (XRD) technique has been utilized for the structural evaluation of ZnO NPs.Morphological studies have been performed using field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM).

2.1 Experimental

ZnO NPs were synthesized using co-precipitation method. All chemicals used were of analytical reagent grade and used without further purification. Zinc chloride ($ZnCl_2$) AR grade, Sodium Hydroxide pellets (NaOH) AR grade and gelatin were procured from SD-fine Chemicals, Mumbai.

Firstly, solutions of 1M $ZnCl_2$ and 2M NaOH were prepared in double distilled water in separate beakers. 0.5g of gelatin was dissolved into 100 ml double distilled water and stirred vigorouslyto form 0.5% gelatin solution. Double distilled water was used as a solvent for the synthesis of ZnO NPs. Then four samples of ZnO NPs containing different concentrations of gelatin capping agent were prepared.For synthesis of pure ZnO NPs (sample name ZnO-Pure), 5ml of 1M $ZnCl_2$ was dissolved into 100 ml double distilled water and it was stirred for 30 minutes using magnetic stirrer at room temperature. Then 5ml of 2M NaOH was added drop wise into this solution which immediately resulted into white precipitate. ZnO NPs capped with gelatin has been synthesized by adding and stirring gelatin before addition of NaOH in the solution. Three such samples were synthesized by adding 1 mL (sample name ZG1), 2 mL (sample name ZG2) and 5 mL (sample name ZG5) gelatin into the solution and precipitate were recovered after drop by drop addition of NaOH.

The precipitate was then separated using centrifuge machine at 4000 rpm (REMI Model-4RC) for 30 minutes and washed 2-3 times with double distilled water. White precipitate was dried in an electric oven at 100°C for 2 hours and fine particles were obtained after grinding in agate mortar. Table 1 shows the samples prepared by using different concentrations of gelatin.

Table 1. Details of synthesized ZnO NPs

Sample Name	$ZnCl_2$ 1M	NaOH 2M	Gelatin 0.5%
ZG1	5 ml	5 ml	1 ml
ZG2	5 ml	5 ml	2 ml
ZG5	5 ml	5 ml	3 ml

2.2 Characterization

All samples of ZnO NPs were subjected to structural and morphological characterization by X-ray diffraction (XRD) using RigakudiffractometerMiniflex II with nickel filtered CuK_α radiation (λ=1.5406 Å) and angle 2θ ranging from 10 to 70°; transmission electron microscopy (TEM) using JEM-2100 HR-TEM (Make-JEOL, Japan; operating voltage 200kV) and field emission scanning electron microscopy (FE-SEM) using Hitachi S-4800, Japan at an operating voltage 15kV. Fourier transform infra-red (FT-IR) spectra were recorded using IR double beam spectrophotometer, 8400S-Shimadzu, Japan. Ultraviolet-visible (UV-vis) spectroscopy was performed using UV-visible spectrophotometer (BLK-C-SR, Stellarnet, USA) in the wavelength range 190-1100 nm.

Results and Discussion

3.1 UV-visible study

Figure 1 shows UV-vis spectra for calcined and uncalcined samples of ZnO NPs as described in Table 1. A spectrum clearly shows the maximum absorption at wavelengths near 353 nm, 352 nm and 347 nm for samples ZG1, ZG2 and ZG5 respectively. Strong blue shift is evident for all ZnO NPs capped using gelatin. This blue shift and increase in the band gap gives clear indication of formation of nano phase material. The particle size is calculated from UV-vis spectra by using Effective Mass Approximation (EMA) [15]. The EMA formula can be stated as:

$$E_g = E_{bulk} + \frac{h^2}{8r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{e^2}{4\pi\varepsilon_o\varepsilon_r\gamma_e}$$

where, is band gap energy for NPs, is energy gap for bulk semiconductor, and are effective electron and hole mass (for ZnO, = 0.19 m_0, = 0.21 m_0). is Bohr exciton radius, is relative dielectric constant, is dielectric constant of air. Calculations suggest that the particle size decreases with increase in the concentration of capping agent.

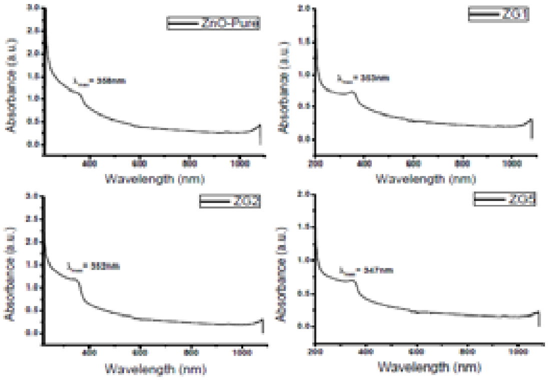

Figure 1. UV-visible spectra of uncalcined ZnO NPs

Table 2: Optical data calculated from UV-visible spectra of calcined and uncalcined ZnO NPs

Sample Name	Particle Size (nm)		
	EMA model	XRD	TEM
ZnO-Pure	20		
ZG1	10		
ZG2	9.5		
ZG5	8	9	9

3.2 FTIR Spectroscopy

The functional groups and bonding structure of ZnO NPs capped with gelatin sample was investigated by FT-IR spectroscopy. The FT-IR spectrum has been recorded using powder KBrpellete method. Small fraction of powder sample of ZnO NPs capped with gelatin (sample ZG5) is mixed with KBr and a pellete is formed. The pellete is subjected to IR measurements. **Fig. 2** shows FT-IR spectra of ZnO NPs capped with gelatin.Peaks assignments are summarized in the **Table 3**[16- 20].

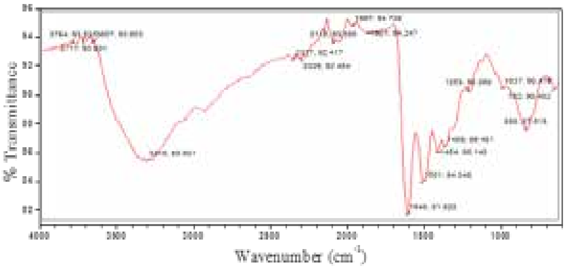

Figure 2. FT-IR spectrum of Gelatin capped ZnO NPs

Table 3. FT-IR peak assignments

Peaks (cm^{-1})	Assignments
3310	vibrations of amide A
2377	vibrations of amide B
1648	vibrations of amide I
1551	vibrations of amide II
1454	deformation vibrations of –C-H- groups and the symmetrical stretching vibrations of –C=O groups of ionized –COO$^-$ grouping
1409	
1253	
1037	

3.3 XRD studies

Figure 3 shows XRD pattern of ZnO NPs. All diffraction peaks can be indexed in hexagonal crystal structure with cell parameter a= 3.264 A° and c= 5.219 A° (JCPDS file no. 79-0208). The peaks obtained at 2θ° values of 31.62, 34.33, 36.12, 47.33, 56.31, 62.64, 66.03, 67.64, and 68.73 can be attributed to the planes (100), (002), (101), (102), (110), (103), (200), and (112) respectively. Diffraction peaks are broadened that can be seen from the profile which confirms the nano crystalline nature of zinc oxide. XRD pattern also confirms the high purity of nano crystals as no peak related to impurity is observed.Considering the spherical nature, particle size of these NPs are calculated by Debye-Scherrer formula [21], $d = k\lambda/(\beta\cos\theta)$; where k is a constant (k=0.93) and β is width of the diffraction peak at half maxima.

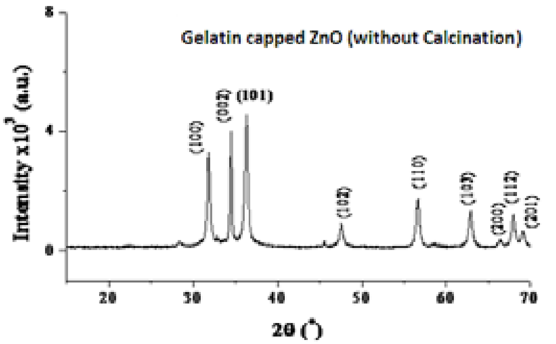

Figure 3.XRD of gelatin capped ZnO

3.4FESEM and TEM analysis

ZnO NPs capped using gelatin have been subjected to FESEM and TEM. Figure 4 shows FESEM micrographs and figure 5 shows TEM images of ZnO NPs. All micrographs attest the formation NPs having uniform morphology. The observed particle size agrees with EMA theory and XRD data.

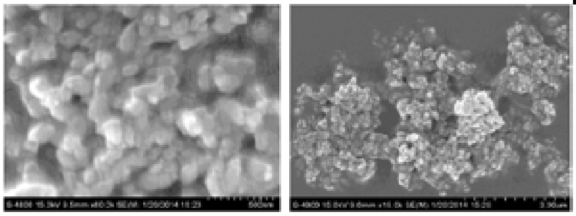

Figure 4. FESEM micrographs of ZnO NPs

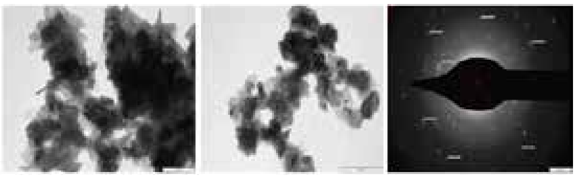

Figure 5. TEM micrographs of ZnO NPs

Conclusions

Gelatin capped ZnO NPs have been successfully synthesized using co-precipitation method. ZnO NPs of narrow size distribution (8 to 10 nm) can be synthesized by properly adjusting the concentration of gelatin. Particles having such narrow size distribution are capable of showing properties due to quantum size effect and quassi-quantum size effect. The synthesized NPs were characterized by UV-visible spectroscopy and particle size for various samples was calculated using EMA theory. FT-IR analysis confirms the role of gelatin as capping agent. XRD analysis confirms the formation of pure phase hexagonal nanocrystals of ZnO. No impurity peaks were seen in the XRD pattern. FESEM and TEM investigations attest the formation of ZnO NPs with uniform morphology. Particle sizes calculated using EMA theory and XRD analysis agree with FESEM and TEM images. Such NPs may be proved important for nonlinear optical applications.

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