

Synthesis and Photoluminescence Property of Bentonite Doped Zinc Oxide Nanoparticles

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Abstract: Zinc oxide (ZnO) has recently achieved special attention regarding potential electronic application due to its unique optical, electrical and chemical properties. Due to its near-UV emission and visible light transparency, ZnO is useful for the fabrication of light-emitting diodes, UV-radiation detectors, and transparent contacts in solar cells. In order to increase the carrier concentration and modify the optical properties of ZnO nanoparticles, the bentonite doping is proposed in present work. The undoped and bentonite doped ZnO nanoparticles, was successfully prepared by chemical technique. The functional group and structure was confirmed by FTIR and XRD analysis. The optical properties of ZnO and bentonite doped were analyzed by UV-Visible and Photoluminescence spectra.

Keywords: Zinc Oxide; Bentonite; X-ray diffraction; Photoluminescence

1. Introduction

The availability of a wide range of nanostructures makes ZnO an ideal material for nanoscale optoelectronics and piezoelectric nanogenerators. As a semiconductor, ZnO has a wide direct band gap ($E_g = 3.37$ eV), with a large excitonic binding energy of 60 meV [1]. Zinc oxide has high refractive index, high thermal conductivity, antibacterial and UV-protection properties. Recent progress in optical devices such as lasers and optical amplifiers, based on electronic transitions of rare earth ions have inspired a lot of work in different materials doped with these ions [2, 3]. In proposed work, bentonite clay was used as dopant and tried to enhance photoluminescence property. Bentonite clays find wide industrial application and rich in Montmorillonite which is nano-structured and nano-porous member of smectite group and the dominant constituent of a bentonite. The chemical formula for Bentonite is $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$. Bentonite is a native, colloidal, hydrated aluminum silicate. Due to its special properties, bentonite is a versatile material for geotechnical engineering as well as in many products in daily use.

2. Experimental Details

Zinc oxide nanoparticles were prepared by wet chemical method using Zinc Chloride and sodium hydroxide as precursors without further purification. 1M of sodium hydroxide was added drop wise over a period of 2 hours in 1M of Zinc Chloride solution in room temperature. After the completion of reaction, the solution was allowed to settle for 24 hours. The solution was centrifuged at 4500 rpm for 10 minutes and washed with ethanol and distilled water to remove the byproducts for several times. After washing, the

material was calcined at 80°C for 24 hours in oven. During calcinations, zinc hydroxide converted into zinc oxide. The obtained ZnO powder was observed to be white in colour.

For the preparation of Bentonite doped zinc oxide nanoparticles, the procedure was the same. However, different ratios of Bentonite (0.004 and 0.006 gm) were dissolved along with 1M of sodium hydroxide solution. The obtained ZnO powder was observed to be dirty white in colour which may be due to the addition of bentonite.

The obtained samples were characterized by Bruker AXS D8 X-ray diffractometer using advanced with monochromatic CuK α - radiation ($\lambda = 1.5406\text{\AA}$). The crystallite size of the powders was determined by Scherer equation. FT-IR spectra were obtained using a SHIMADZU infrared spectrometer. A UV-vis spectrophotometer was used to record the absorption spectra of samples.

3. Result and Discussion

3.1. XRD Analysis

Fig. 1 shows the XRD pattern of the as prepared sample. All diffraction peaks could be perfectly indexed to the wurtzite ZnO reported in JCPDS (2003) (file no. 89-7102) [4]. This result suggested that the nanopowders had a pure hexagonal wurtzite structure with well developed crystallinity. The lattice constants were calculated to be $a = 3.249\text{\AA}$, $c = 5.206\text{\AA}$. The formation of nanocrystalline ZnO is reflected through the broadening of the XRD characteristic lines for ZnO. The XRD pattern shows the presence of ZnO, due to the reflection peaks located at 31.1(100), 34.4(002), 36.2(101), 47.5(102), 69(201) and 72.5(004). In bentonite doped ZnO the peaks become broader and more intense, which indicates the decrease of particle size and the improvement of crystallinity. By recording the full width at half maxima (FWHM) of these peaks, the average size of the nanocrystallites is determined using the Debye- Scherrer equation

$$D = k\lambda / \beta \cos \theta,$$

where D is the average crystallite size, K is a constant (0.89 here), λ is the wavelength of the X-ray radiation (0.154 nm), β is the band broadening (full width at half-maximum) and θ is the diffraction angle. The particle size of pure and bentonite doped ZnO nanoparticles was calculated and given in the Table 1.

Table 1. Particle Size of Synthesized Sample

Samples	Particle Size
ZnO	47
ZnO/0.04 Bentonite	40
ZnO/0.06 Bentonite	23

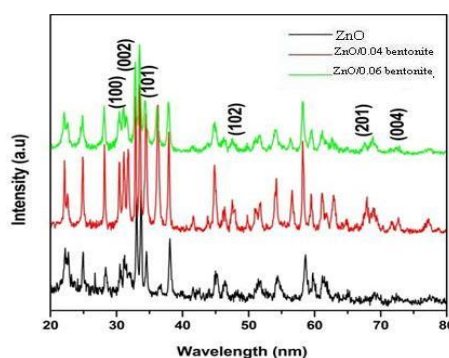


Fig. 1. XRD pattern of Pure ZnO; ZnO/0.04Bentonite;ZnO/0.06Bentonite

3.2. FT-IR Analysis of ZnO and Bentonite Doped ZnO Nanoparticles

The FTIR spectrum of the pure and bentonite doped ZnO, synthesized by wet chemical method, which was acquired in the range of 500-4000 cm^{-1} were shown in the Fig. 2, 3 &4. The band between 450-500 cm^{-1} correlated to metal oxide bond (ZnO). The broad band starting at 3452 cm^{-1} corresponds to the O-H bond. The peak at 1662 cm^{-1} corresponds to O-H bonding of absorbed water. The main absorption band between 424 and 623 cm^{-1} group was attributed to the Zn-O stretching mode frequency [5-7]. The FTIR spectrums of bentonite doped samples are shown in Fig. 3 and 4. The absorption band at 3774, 3493, 1033, 912, 536 and 469 cm^{-1} are due to the coexistence of bentonite in ZnO. The absorption at 3774 cm^{-1} is attributed to stretching vibration of OH groups [8]. It was reported that the Al-OH stretching frequency is observed at 3774 cm^{-1} , while the bending frequency is at 906 cm^{-1} . This can be considered as characteristic of dioctahedral clay [9]. While absorption at the frequencies at 1033 cm^{-1} , 528 cm^{-1} and 468 cm^{-1} are attributed to Si-O stretching, for Si-O-Al bending and Si-O-Mg bending respectively [10,11], while that at 3493 cm^{-1} has been assigned to OH groups bonded to absorption water. However we have not estimated precisely the quantity of the dopant present in the material.

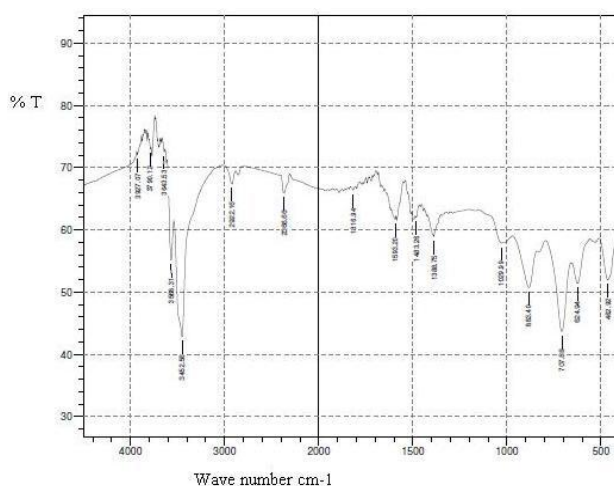


Fig. 2. FTIR spectrum of pure ZnO nanoparticles

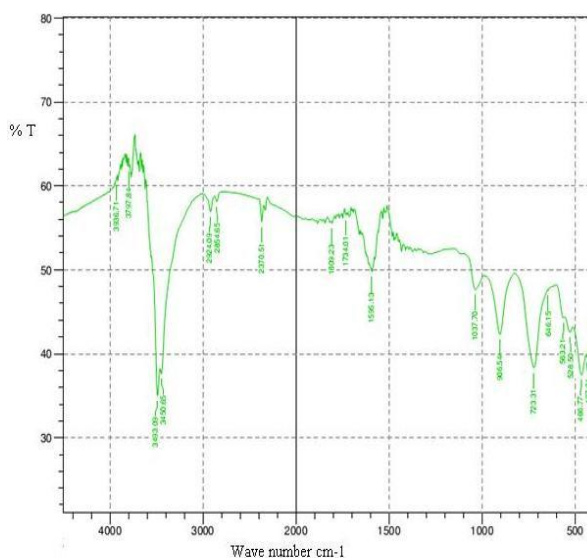


Fig. 3. FTIR spectrum of ZnO/0.04Bentonite nanoparticles;

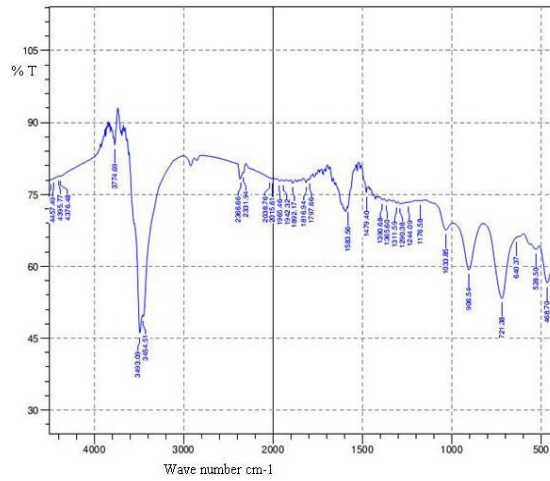


Fig. 4. FTIR spectrum of ZnO/0.06Bentonite nanoparticles.

3.3. UV-Visible Spectra Analysis of ZnO and Bentonite Doped ZnO Nanoparticles

The UV absorption peaks of the prepared pure ZnO sample are shown in Fig. 5. The absorption peaks of pure ZnO are 327 and 335nm. The absorption peaks of bentonite doped samples A and B are shown in Fig. 6 & 7 respectively and their absorption peaks are 330 and 336nm, 344 and 358nm and is significantly red shifted when compared to pure ZnO.

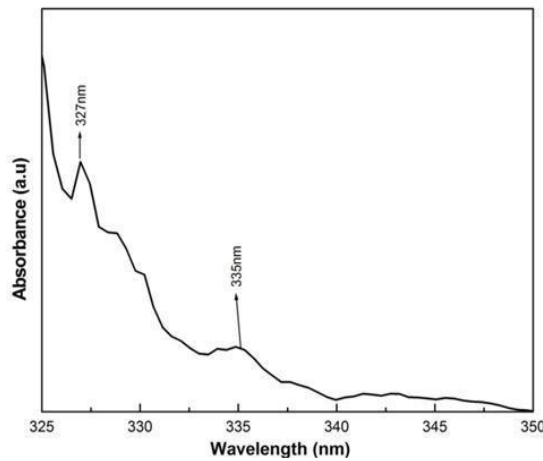


Fig. 5. UV-Vis spectrum of pure ZnO

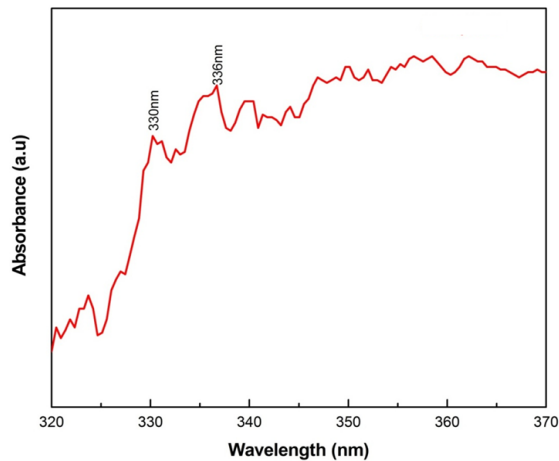


Fig. 6. UV-Vis spectrum of ZnO/0.04bentonite

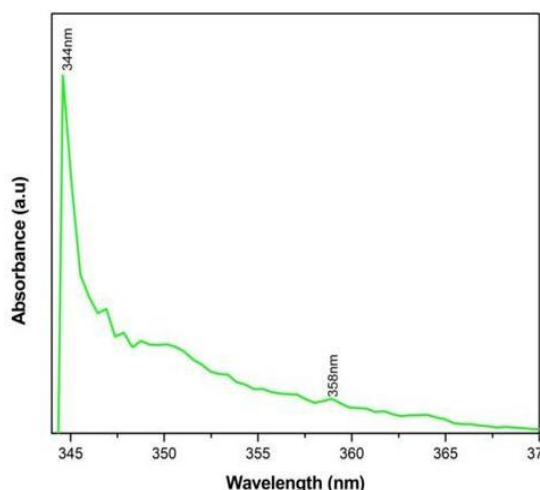


Fig. 7. UV-Vis spectrum of ZnO/0.06Bentonite

3.4. Photoluminescence Analysis of ZnO and Bentonite Doped ZnO Nanoparticles

The room-temperature PL spectroscopic study enables to determine the electronic energy levels from where emission is particularly observed which in turn helps to corroborate the band structure of the ZnO nanoparticles [12]. Photoluminescence spectra of pure and bentonite doped Zinc oxide nanoparticles were observed under excitation 210 nm was shown in Fig.8. A strong and sharp emission is observed at 485 and 419nm at the blue and violet band. In addition weak emission at \sim 460nm in the blue band was observed. The blue band emission perhaps originated from the recombination of oxygen vacancies with oxygen interstitials or other defects [13]. Because of the large surface-to-volume ratio of bentonite doped ZnO particles shows efficient and fast trapping of photo-generated holes at surface sites.

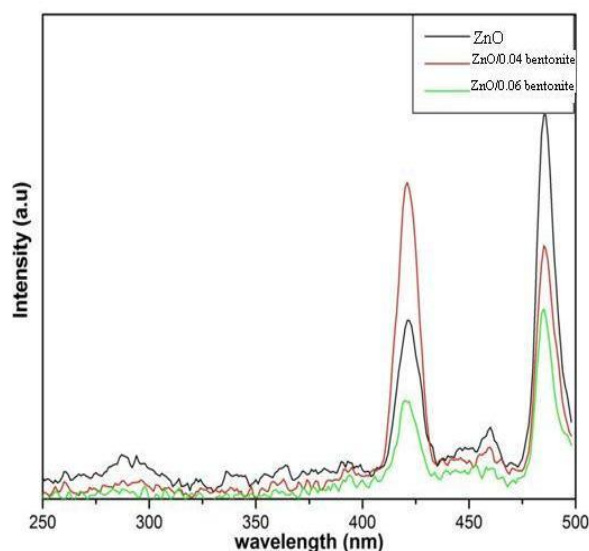


Fig. 8. PL Spectrum of Pure ZnO; ZnO/0.04Bentonite;ZnO/0.06Bentonite

4. Conclusion

Bentonite doped ZnO nano particles was prepared by wet chemical method. Powder XRD, FTIR, UV and PL studies confirmed that the Bentonite was doped in ZnO. XRD result showed that the obtained ZnO nanoparticles were hexagonal system. The particle size decreases while increasing the concentration of

Bentonite. Because of the large surface-to-volume ratio of bentonite doped ZnO particles, efficient and fast trapping of photo-generated holes at surface sites. This concluded that bentonite doped ZnO will have improvement in photoluminescence property. This preliminary idea which confirms that bentonite doped ZnO acts as a good photocatalytic agent due to the presence of large oxygen deficiency.

References

- [1] Roy, V. A. L., Djuricic, A. B., Chan, W. K., Cao, J., Lui, H. F. & Surya, C. (2003). Luminescent and structural properties of ZnO nanorods prepared under different conditions. *Appl. Phys. Lett.* 83, 141 - 143.
- [2] Blasse, G. & Grabmaier, B.C. (1994). *Luminescent Materials*. Springer, Berlin.
- [3] Scheeps, R. (1996). Upconversion Laser Processes. *J. Prog. Quantum Electron.* 20, 271-358.
- [4] *Organic Index to the Powder Diffraction File*, Joint Committee of Powder Diffraction Standards, 2003.
- [5] Kwon, Y. J., Kim, K. H., Lim, C. S. & Shim, K.B. (2002). Characterization of ZnO nanopowders synthesized by the polymerized complex method via an organochemical route. *J Ceram Proc Res* 3,146-149.
- [6] Silva, R. F. & Zaniquelli, M. E. D. (2002) Morphology of nanometric size particulate aluminium-doped zinc oxide films. *Colloid Surf Physicochem Eng Aspect.* 198, 551-558.
- [7] Li, H., Wang, J., Liu, H. (2004). Sol-gel preparation of transparent zinc oxide films with highly preferential crystal orientation. *Vacuum.* 77, 57-62.
- [8] Cailere, S., Henin, S., & Rautureau, M. (1982). Structural proprieties physico-chimiques. *Mineralogie des Argiles*. Ed. Masson, 70-80. (in French).
- [9] Van Der Marel, H. W. & Beutelspacher, H. (1976) *Atlas of Infrared Spectroscopy of Clay Minerals and Their Admixtures*, Elsevier, Amsterdam, 31-58.
- [10] Benguella, B. & Yacouta-Nour, A. (2009). Adsorption of Bezanyl Red and Nylomine Green from aqueous solutions by natural and acid-activated bentonite. *Desalination* 235, 276-292.
- [11] Tavani, E. L. & Volzone. C. (1999). Adsorption of sulphuric acid on smetite from acidic aqueous solution. *Ceramica*, 45, 133-136.
- [12] Xu, F., Chen, J., Guo, L., Lei, S. & Ni, Y. (2012) In situ electrochemically etching-derived ZnO nanotube arrays for highly efficient and facilely recyclable photocatalyst. *Appl Surf Sci* 258, 8160-8165.
- [13] Mahamuni, S., Borgohain, K., Bandre, B.S., Leppert, V.J. & Risbud, S.H (1999). Spectroscopic and structural characterization of electrochemically grown ZnO quantum dots. *J. Applied Phy.* 85. 2861-2865.

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