

Synthesis and Characterization of Zinc Oxide nanoparticles: Effect of annealing on structural and optical properties

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Abstract-Zinc oxide nanoparticles have been prepared by chemical precipitation method. The structural, morphological and optical properties were investigated by annealing at three different temperatures 3000C, 4000C and 5000C. The synthesized nanoparticles were characterized by X-ray diffraction analysis (XRD), scanning electron microscope (SEM), UV-Vis absorption photoluminescence studies and FTIR spectra. The XRD pattern reveals that, ZnO sample has hexagonal wurtzite structure. The morphological studies show that the accumulation of particles at different temperature. The optical energy band gap (E_g) showed a decrease from 3.5 to 3.9 eV with increasing temperature. Both physical and applied aspects of ZnO nanoparticles can be well understood from the luminescence studies of them. FTIR analysis confirmed Zn- O bond formation of the synthesized nanomaterial.

Keywords-Zinc Oxide nanoparticles, FTIR, UV and XRD.

I. INTRODUCTION

The group II-IV semiconductors play an important role in the field of optoelectronics [1].Therefore; it is usually used in light emitting diodes and solar cells.In typical wurtzite hexagonal structure, ZnO crystallizes with the arrangement of Oxygen atoms in hexagonally closed structure, while the distorted tetrahedron structure is occupied by Zinc atoms. It has a wide band gap between 3.37 eV and large exciton binding energy of 60 meV even at room temperature.Among II-VI semiconductors ZnO is one of the most important materials which have wide number of applications. Different synthesis methods are available to prepare ZnO nanoparticles such as SILAR, hydrothermal method, microwave irradiation, solid state pyrolytic reaction, chemical spray pyrolysis, chemical bath deposition etc., [2-7]. In this paper ZnO nanoparticle prepared by chemical precipitation method.The morphology, crystallite size and optical properties of ZnO nanopowders synthesized by simple precipitation method were investigated. They also correlated the optical properties with morphology and crystallite size [8].Zinc oxide has been produced commercially for considerably more than century,

originally for use as a pigment in paints and also for rubber, glass, porcelain enamels and pharmaceuticals.

II. EXPERIMENTAL METHODS

This paper deals with the preparation of ZnO nanoparticles using chemical precipitation method. 0.5 M of zinc acetate was dissolved in deionized water. The sodium hydroxide solution was added to above solution drop wise with constant stirring. The white precipitate were formed and it was allowed to settle for overnight. Then filtered and washed several times of distilled water. It was dried at 100°C for 6 hours and then grinded using mortal pestel. The resulting powder was annealed at 300°C, 400°C and 500°C in for 2 hours.

The ZnO nanoparticles were prepared by precipitation method and the samples were annealed at different temperatures 300°C, 400°C and 500°C. The prepared CdO nanoparticles were characterized by XRD, SEM, UV, PL and FTIR. Powder X-ray diffraction patterns of the samples were obtained by using Bruker Eco D8 Advance X-ray diffractometer. The surface morphology of nanoparticles was examined by means of BRUKER DS Advance scanning electron microscope and EDAX. The FTIR spectra were taken on Perkins Elmer spectrophotometer. The PL emission spectra of samples were recorded at room temperature using spectrofluometer equipped with a 450 W Xenon lamp as the excitation source.

III. RESULTS AND DISCUSSION

XRD:

XRD patterns of the grown ZnO sample are recorded with the intensity data onto a 2θ range of 10°-80°.The X Ray Diffraction spectrum of synthesized ZnO nanoparticles confirms the hexagonal wurtzite structure according to JCPDF data (No: 74 – 0534). The XRD result shows that the sharp, narrow and the well-defined diffraction peaks indicate that the material has good crystallinity confirms the formation of ZnO

nanoparticles and also indicate the good crystalline of synthesized material. No characteristic peaks other than ZnO are observed which confirms that the synthesized products are of high purity. The intensity of the diffraction peaks increases and becomes sharper with increase in temperature, implying that the crystalline structure tends to have more integrity. No peaks of impurity were observed, suggesting that the high purity ZnO was obtained at 500°C. The crystalline size of ZnO nanoparticles was calculated using the value of FWHM from the most intense XRD peaks as around 45nm by using Scherrer formula [9].

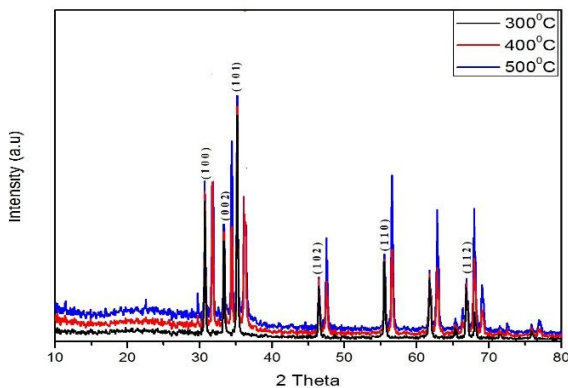


Fig 1: XRD pattern of the ZnO nanoparticle (0.5 M) annealed at (a) 300°C (b) 400°C and (c) 500°C.
Morphological Studies: SEM:

Figure 2 shows the morphology of the samples observed in SEM. The morphology is analyzed for various temperatures such as 300°C, 400°C and 500°C. SEM pictures reveal the morphology as near-spherical prismatic nanoparticles. These analyses show that high homogeneity emerged from the samples surface by increasing annealing temperature. With increasing temperature the morphology of the particles changes in the particles is closely accumulated each other. The crystallite size of annealed nanocrystals is in the range of 20-80 nm in diameter [10].

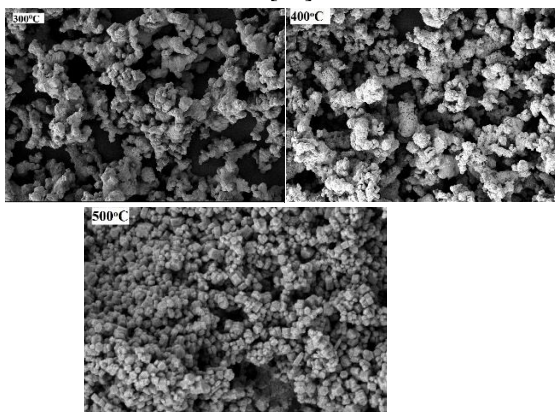


Fig 2: SEM image of the ZnO nanoparticle (0.5 M) annealed at (a) 300°C (b) 400°C and (c) 500°C.

IV. OPTICAL STUDIES

UV – Visible spectral analysis:

Figure 3 depicts the spectra of optical absorption in ZnO nanoparticles prepared by chemical precipitation method annealed at various temperatures, 300°C, 400°C and 500°C. UV-Vis absorption of ZnO nanoparticles was recorded in the wavelength range of 200 – 800 nm. ZnO has a band gap of 3.37 eV and hence a peak in the absorption spectra is expected to occur around 350 nm [11] and almost all the visible spectrum radiations are transmitted by the ZnO nanoparticles. The absorbance increases in temperature, and hence, there should be a decrease in band gap. UV spectrum gives information about excitonic or internal transition of nanomaterials.

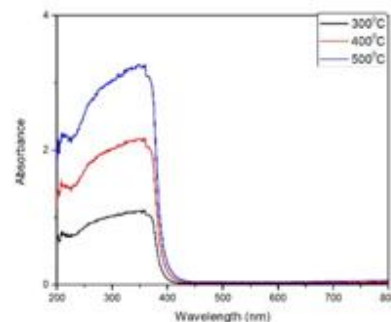


Fig 3: Absorption Spectra of ZnO nanoparticle annealed at (a) 300°C (b) 400°C and (c) 500°C.

Photoluminescence spectra:

The semiconductor ZnO nanoparticles, with sizes comparable to or below their exciton Bohr radius, have distinctive electronic and optical behaviors due to exciton quantum confinement phenomena [12]. Figure 4 shows the room temperature photoluminescence spectrum for ZnO nanoparticles. The PL spectra of the products possess one obvious intrinsic emission peak of the range of 380 nm to 390 nm, which corresponds to the exciton recombination related to the near-band edge emission. Clearly, the intensity of emission peaks (around 385) increased as the annealing temperature increases from 300°C to 500°C. This behavior indicates the improvement in the crystalline nature of the samples [12]. The spectrum of the sample annealed at 500°C, exhibits the strongest PL peak (95 Int. %) at 380 nm while the sample annealed at 400°C, has a PL peak (50 Int. %) at 382 nm. Both of these peaks value are close to the theoretical energy band-gap of ZnO (3.37 eV). Therefore, the relative luminescent intensities of the UV emission peaks showed a dependence on preparation conditions. The blue shift in the bandgap of ZnO

nanoparticles is confirmed by these excitation peaks which correspond to the transition from band to band [13]. This result may be ascribable to the fact that the products have a good crystallinity and a less amount of impurity due to the relatively high temperature.

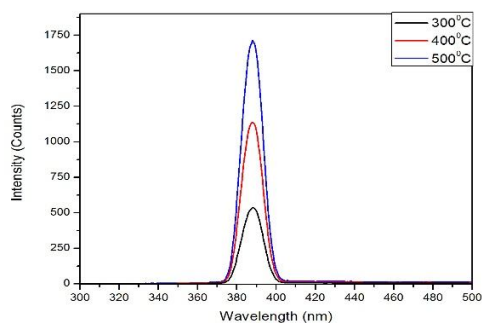


Fig 4. Photoluminescence spectrum of CdO nanoparticle(0.5 M) annealed at (a) 300°C (b) 400°C and (c) 500°C.

FTIR Studies:

The peak at low wave number regions of 576 cm^{-1} is assigned to ZnO group [14, 15]. It was reported that the broad bands between 500 and 800 cm^{-1} were attributed to vibration of Zn-O bond [16]. The sharp peak at 1123 cm^{-1} is due to C-H plane bending vibration [17]. The band appears at 1619 cm^{-1} may be attributed to C=C Stretching mode of quinoid ring [18]. whereas the two prominent signals at 1430 cm^{-1} and 1545 cm^{-1} are caused by a symmetric and asymmetric (COO⁻) stretching vibration. These two bands are typically observed for metals which are complex by acetate [19, 20]. A similar pattern was found for the synthesized nanoparticles at slightly higher wavenumbers. This suggests that the acetate is also bound to the particle surface. Analogous results from ZnO particles derived from zinc acetate have already been reported on literature [19–25]. For the annealed nanoparticles, neither the water signal nor the hydroxyl peaks could be found within the spectrum.

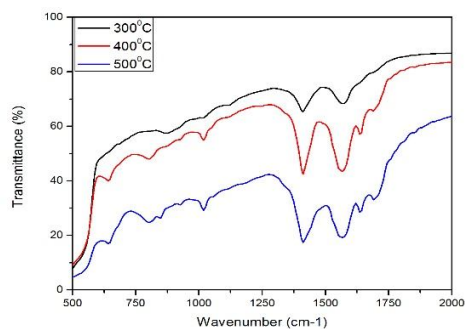


Fig 6: FTIR Spectra of CdO nanoparticle at 300°C, 400°C & 500°C

V. CONCLUSIONS

The ZnO nanoparticles were synthesized through the annealing the precursor of different temperatures ranging from 300°C to 550°C . XRD results confirmed that the mean crystalline size of the ZnO nanoparticles increased with increasing annealing temperature. From SEM images, it is clear that with increasing temperature the morphology of the particles changes in shape and nanopowders were closely agglomerate. The energy band gap between as synthesized nanoparticles was obtained to be equal to 3.37 eV . The room temperature photoluminescence (PL) spectra of the products shown intrinsic UV emission peaks at a range of 380 to 390 nm , which is attributed to a near-band edge transition. FT-IR analysis also confirmed the formation of Zinc Oxide nanoparticles. From the above analysis data's, when annealing the nanoparticles was exhibiting appreciable variation in structural and optical defects.

REFERENCES

- [1] C. Ma, D. Moore, Y. Ding, J. Li and Z. L. Wang, *Int. J. Nanotechnol.* 1,431,2004.
- [2] S. Mondal, P. Kanta, and P. Mitra, *J. Phys. Sci.* 12, 221,2008.
- [3] D. Sridevi and K. V. Rajendran, *Int. J. Nanotechnol. App.* 3, 43,2009.
- [4] N. F. Hamedania and F. Farzaneh, *J. Sci.* 17, 231,2006.
- [5] Z. Wang, H. Zhang, L. Zhang, J. Yuan, S. Yan, and C. Wang, *Nanotechnol.* 14, 11, 2003.
- [6] Q. G. Al-zaidi, A. M. Suhail, and W. R. Al-azawi, *App. Phys. Res.* 3, 89, 2011.
- [7] G. Jia, Y. Wang, and J. Yao, *J. Ovonic Res.* 6, 303 (2010).
- [8] Sivakumar S, Venkateswarlu P, Rao VR, Rao GN. Synthesis, characterization and optical properties of zinc oxide nanoparticles. *International Nano Letters*, 3(30):1–6, 2013
- [9] Cullity. B. D, "Elements of X-Ray Diffraction," Addison - Wesley, Reading, 2005.
- [10] Rejani.P, Asha radhakrishnan and Beena, Structural, optical and dielectric studies in nano rods by microwave assisted method, *Int. J. Nano Dimens.* 5 (5): 497-503, 2014.
- [11] Oladiran AA, Olabisi IA. Synthesis and Characterization of ZnO nanoparticles with Zinc Chloride as Zinc source. *Asian Journal of Natural and Applied Sciences.* 2:41.
- [12] Anisimkin VI, Penza M, Valentini A. Detection of combustible gases by means of a ZnO-on-Si surface acoustic wave (SAW) delay line. *Sensor Actuat B: Chem* 23:197 -201, 1995.

- [13] Aneesh PM, Vanaja KA, Jayaraj MK, Synthesis of ZnO nanoparticles by hydrothermal method. Proceedings of SPIE, India.; 66390J:1–9, 2007
- [14] Shukla, S. K, A. Tiwari, Advanced Materials Research, 306-307, 82, 2011,
- [15] Tiwari, A, R.Kumar, M.Prabaharan,R.R. Pandey, P. Kumari, A.Chaturvedi, A.K. Mishra, Polymers for Advanced Technologies, 21, 615, 2010.
- [16] J. Wang, L. Gao, Inorg. Chem. Commun. 6, 877,2003.
- [17] Ansari, S. P, F. Mohammad, “Electrical studies on the composite of polyaniline with Zinc oxide nanoparticles,” The IUP Journal of Chemistry, vol. 4, pp. 7–18, 2010
- [18] Shahid Pervez Ansari and Faiz Mohammad, ISRN Materials Science, Vol 129869 7pages, 2012
- [19] A. Lenz, L. Selegård, F. Söderlind,A. Larsson, P. O. Holtz, K. Uvdal, L. Ojamaäe,P.-O. Käll, The Journal of Physical Chemistry C, 113, 17332– 17341, 2009
- [20] S. Sakohara, M. Ishida, M. A. Anderson, The Journal of Physical Chemistry B,102, 10169–10175, 1998.
- [21] E. M.Wong, P. G. Hoertz, C. J. Liang, B.-M. Shi, G. J. Meyer, P. C. Searson, Langmuir, 17, 8362–8367, 2001
- [22] R. N. Spitz, J. Barton, M. Barteau, R. Staley, A. Sleight, The Journal of Physical Chemistry B, 90, 4067, 1986
- [23] S. Pawsey, K. Yach, J. Halla, L. Reven, Langmuir, 16, 3294–3303, 2000.
- [24] R. Marczak, F. Werner, J.-F. Gnichwitz, A. Hirsch, D. M. Guldi, W. Peukert, The Journal of Physical Chemistry C, 113, 4669–4678, 2009
- [25] M. Voigt, M. Klaumünzer, H. Thiem,W. Peukert, The Journal of Physical Chemistry C, 114, 6243–6249, 2010