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Research Paper

Synthesis and Characterisation Of ZnO Nanoparticles Embedded in Glucose and PVA Matrix

Physics

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ABSTRACT

Zinc oxide (ZnO) nanoparticles have been synthesised through chemical bath deposition(CBD) method using glucose and poly vinyl alcohol (PVA) respectively as capping agent. The XRD, HRTEM and UV-Visible characterisation techniques were employed. Tauc's plot of PVA capped sample yield direct band gap of 5.72eV. Blue shifting observed in the absorption edge of the UV-Visible spectra confirms quantum confinement. Good crystallinity has been inferred from XRD spectra. In the XRD spectra of PVA capped sample of 0.5M molarity of nano ZnO synthesised at a temperature of 80^{0}C. Crystallite size calculated using Scherrer formula was found to be of 2.08nm. HRTEM images show nanocrystals and quantum dots of ZnO.

Introduction

Synthesis, characterisation along with the extensive investigation of the diverse aspects of Zinc oxide (ZnO) nanoparticle still remains at the forefront of present day research. The multifunctional properties of ZnO like electrical, optoelectonic, photochemical, catalytic, wide and direct band gap, large exciton binding energy, etc. have made it a promising material in applied fields of which device fabrication is one important part. For the synthesis of ZnO nanoparticle various methods such as sol-gel method, chemical vapour deposition method, microwave assisted combustion methods, etc. have been employed [1]. In recent years, extensive research work is going on in the field of ZnO quantum dots (QD). Efforts are being made to realise single photon source using ZnO quantum dots in micro cavities. ZnO QDs are heterostructures of nearly thousand atoms whose excitons are confined in all three spatial dimension. An exciton behaviour is somewhat similar to that of a hydrogen atom whose positive-negative charge being separated. Most of the electrons in QD remain bound to its nuclei except few one to hundred free electrons. The de Broglie wavelength of the electrons is nearly equal to the size of the dots. The electrons occupy discrete quantum level and thereby exhibit discrete excitation spectrum. Band gap splitting into energy levels, band gap variation resulting in blue shift and red shift and enhancement of surface area compared to its volume in nanomaterial due to quantum confinement introduce complete different material properties of QD in comparison to the bulk. [2] Quantum confinement can be explained with the effective mass approximation.

In this paper we report our investigation on ZnO nanoparticles as well as its quantum dots. We synthesised nano ZnO chemically in aqueous medium and the characterization processes employed for the investigation were XRD, HRTEM and UV-Vis. The sample 1 was obtained by synthesising nano ZnO at room temperature using poly vinyl alcohol (PVA) as capping agent. Sample 2 of nano ZnO was synthesised at a temperature of 80^{0}C using PVA. Sample 3 of nano ZnO was synthesised in glucose matrix maintaining a temperature of 80^{0}C. The samples 1, 2 and 3 are being named as S1, S2 and S3 in subsequent discussions in this paper. Molarity of PVA capped sample is 0.5M and that of glucose capped being 0.1M.

Materials and methods

Synthesis

We employ chemical bath deposition (CBD) method in synthesising zinc oxide (ZnO) nanostructure. An aqueous solution of the 0.5 mol of zinc sulphate ($ZnSO_4$) and sodium hydroxide (NaOH) with 3% polyvinyl alcohol (PVA) were prepared. The mixture was magnetically stirred for a period of 3 hours at constant temperature of 80^{0}C. In the process a milky white colloidal solution was obtained. In another process, a 3% aqueous solution of glucose of 200ml was poured into the aqueous solution of zinc chloride ($ZnCl_2$) of 0.1M weighing 2.7256gm. The resultant solution was heated maintaining a constant temperature of 80^{0}C and is constantly stirred using magnetic stirrer. At the same time another 200ml solution of 0.1M of NaOH weighing 0.8gm was added drop by drop to the said mixed solution at 80^{0}C. The stirring of the solution was carried up to 3 hours duration. Finally as earlier, a milky white colloidal solution was obtained.

Characterisation

In order to investigate structural and optical properties of the ZnO nanoparticles in glucose as well as in PVA matrix, the necessary characterisations were made. The structural investigation of ZnO nanoparticles embedded in PVA matrix was carried out using X-ray powder diffractometer (Model: Seifert XRD 3003 T/T) with CuKα radiation (λ= 0.15406nm) scanning 2θ" in the range 20^0-80^0. For those ZnO nanoparticles embedded in glucose matrix the corresponding structural investigation was carried out using X-ray powder diffractometer with MoKα radiation (λ = 0.0709nm) and scanning of 2θ was done in the range 3^0-40^0 operating at 40kV/30mA. The morphology of ZnO nanostructures were characterised by HRTEM (JEM 2100, 200kV, Jeol). The UV-Visible absorption spectra of the samples were obtained in the wavelength range 200nm-800nm with the help of automated spectrophotometer (Shimadzu, UV-3101P).

Results and discussion:

XRD Study:

In figure 1 and 2 the XRD pattern of the S1 and S2 respectively are shown. More intensity in the XRD pattern of S2 is noticed in comparison to the S1. Figure 3 represents XRD pattern of S3. The diffraction peaks support hexagonal wurtzite crystal structure of ZnO and establish the crystallinity . The intensity data were collected over the 2θ range from 30^0 to 75^0 for S1 and S2. The intensity data for the S3 were collected over the 2θ range from 3^0 to 35^0 for being exposed to MoKa radiation (λ = 0.0709nm). Peak broadening observed in XRD spectra of S1 and S3 may be attributed to micro-straining arising out of defects.

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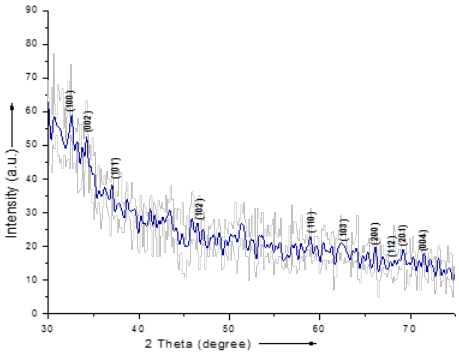


Figure1. Room temperature XRD pattern of nano ZnO embedded in PVA matrix

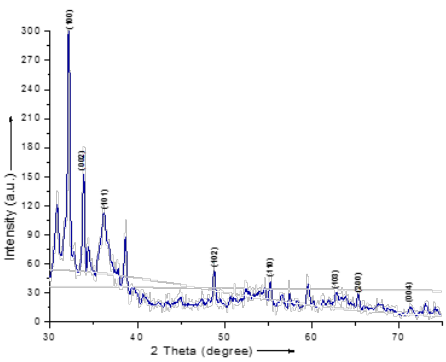


Figure2. XRD pattern of nano ZnO embedded in PVA matrix obtained at 80^{0}C

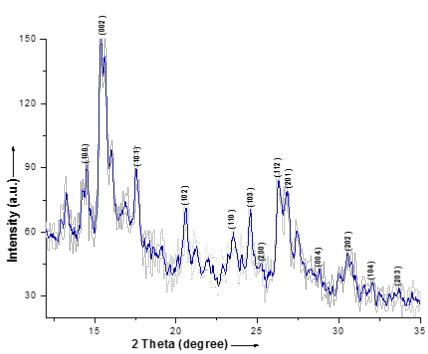
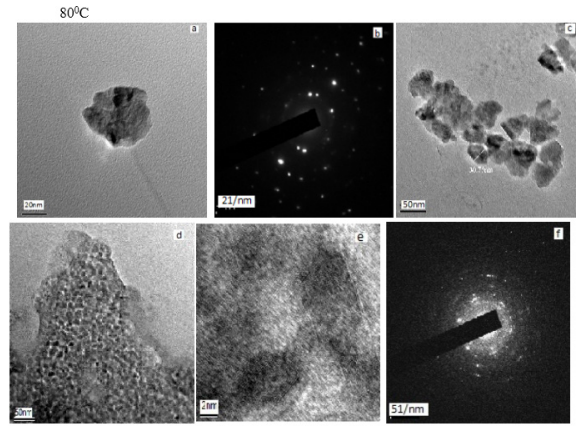


Figure3. XRD pattern of nano ZnO embedded in glucose matrix obtained at 80^{0}C

Good crystallinity of the S2 and S3 can be inferred from the strong and narrow peaks of the diffraction pattern. The diffraction peaks are found to support the JCPDS data. Using Scherrer formula $D = 0.89\lambda/\beta \cos\theta$ for a diffraction angle 2θ for a diffraction angle $2q = 33.91^0$ with FWHM (β) of 0.3949018^0 for (002) peak, the average particle size (D) for the S2 is found to be 2.08nm. Thus XRD pattern study of S2 ascertains the formation of ZnO QDs.

HRTEM Study

Figure 4. (a), (b), (c), (d), (e) and (f) HRTEM images of samples of nano ZnO



The HRTEM images shown in Figures 4. (a), (b) and (c) reveal the characteristic image of the sample of ZnO embedded in PVA matrix and figures 4(d), (e) and (f) yield the pattern of image formed due to nano ZnO embedded in glucose matrix.

In order to see the grain size distinctly, HRTEM was used to characterise the samples [3]. The selected area diffraction (SAED) pattern of PVA capped ZnO is shown in figure (b) and that of glucose capped sample is shown in figure (f). SAED pattern indicate polycrystalline nature of the samples. Figure (d) exhibits glucose capped nano crystals and figure 3 (e) ensures quantum dot formation of S3.

UV-Visible study

UV-visible absorption spectra of the as-prepared samples are shown in figure 5. The UV absorption peak of S3 is 280nm and that of S2 is 290nm. Thus the estimated band gaps for these two samples are respectively of 4.44eV and 4.29eV. Comparing these with 3.37eV band gap of bulk ZnO we find significant blue shifting of 1.07eV for S2 and 0.92eV for S3.In other words, quantum confinement is confirmed from the blue shifting of the absorption peaks[4].

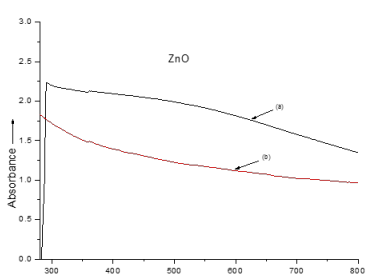


Figure 5. UV-visible spectra of (a) PVA capped and (b) glucose capped ZnO.

In order to determine optical band gap the absorption co-efficient (α) was calculated using the relation $\alpha = 2.303\ A/t$ where A is the optical absorbance and t is the thickness of the cuvette. Optical band gap was calculated by using Tauc relation

$(ah\nu)^2 = B\ (h\nu - E_g)^n$

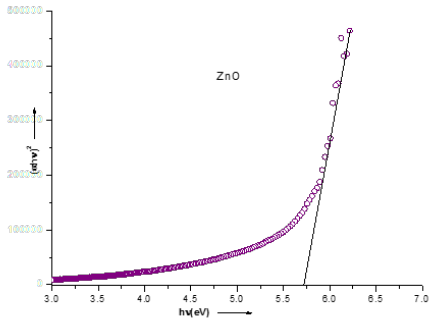


Figure 6. Plot of $(ah\nu)^2$ vs. Photon energy of PVA capped ZnO sample

where B is constant and n value is respectively ½ and 2 for direct and indirect transition. The intercept of the linear portion of $(ah\nu)^2$ on the energy axis gives the energy band gap [5]. Thus the direct band gap of the S2 was found to be 5.72eV. The band gap enhancement is due to the decrease in particle size because of quantum size effect [6, 7].

Conclusion

We have synthesised nanocrystal and QDs of ZnO of which sample 1 and 2 are being PVA capped of 0.5M in molarity and the sample 3 being glucose capped with 0.1M in molarity. Significant blue shifts have been observed in the absorption peaks of UV-Vis spectra. Thus quantum confinement is confirmed which is also seen in HRTEM image. In as-prepared samples, bigger nanocrystals of 30nm average size were also obtained along with quantum dots. The technique employed is the chemical bath deposition (CBD) method which is a cost-effective one.

Acknowledgements

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