1. Introduction

Zinc Oxide (ZnO) represents an important semiconductor material due to its wide band gap (3.37eV at room temperature), large exciton binding energy (60meV), high optical gain, luminescence as well as piezo-electric properties [1]. From the 1960s ZnO thin films have been extensively studied because of their applications as sensors, transducers and catalysts. ZnO nanostructures have been becoming the focus point in nanoscience and nanotechnology in recent years. Nanostructures are considered to have unique physical, chemical, catalytic and optical properties that are profoundly different from their bulk counterparts. The change in the properties of nanoparticles is driven mainly by two factors, namely the increase in the surface to volume ratio and the change in the electronic structure of the material due to quantum confinement effect. Confinement of charge carriers in nanoscale materials leads to remarkable modification of their density of states. When the physical dimensions of matter become comparable or lower to exciton Bohr diameter ($2a_\varepsilon$), the functional properties of a semiconductor becomes sensitive to the size and shape due to confinement of excitons. Photoexcitation of a bulk semiconductor results in the transfer of an electron from valence band to conduction band creating an electron-hole pair, called ‘exciton’, bound by weak coulombic interaction. Excitons can be treated as hydrogen-like system and the spatial separation between the charge carrier pair is termed as exciton Bohr radius ($a_\varepsilon$) which can be deduced from Bohr approximation [2-5]. This phenomenon is often expressed as quantum size effect or quantum confinement effect. The quantum confinement effect is the phenomenon of nonzero lowest energy and the quantization of the allowed energy levels in low dimensional structures, arising from the confinement of the electrons within a limited space [6, 7]. The quantum confinement is responsible for the increase of energy difference between energy states and band gap. The minimum energy required to generate such an exciton is called the band gap energy [8]. Quantum confinement can be explained with the effective mass approximation. Quantum confinement yields a substantial density of states at the band edges and enhances radiative efficiency [9]. In general, the blue shift in quantum dots increases with the decrease in dimension of the crystallites whereas in a quantum well structure the quantum confinement becomes most effective when the well width becomes smaller than the de Broglie wavelength of the electron [10]. In this paper we report on the investigation of the quantum confinement effect of nanosized ZnO that was chemically synthesised in aqueous medium. UV, PL, XRD and HRTEM characterization techniques were employed for the necessary investigation.
2. Materials and Methods

2.1 Synthesis

A simple and inexpensive method i.e. chemical bath deposition (CBD) method was employed to synthesis zinc oxide (ZnO) nanostructures. ZnO was synthesized in a mixture of aqueous solutions of zinc sulphate (ZnSO₄) and sodium hydroxide (NaOH). A 3% Polyvinyl Alcohol (PVA) solution was added into the salt solution prior to mixing for the necessary capping effect. One solution of zinc sulphate (ZnSO₄) of 0.5 mol weighing 4.025g was mixed with sodium hydroxide (NaOH) of 0.5mol weighing 1g. The temperature of mixture solution was raised to 80°C and kept under constant stirring using magnetic stirrer for 3 hours to facilitate the reduction reaction to form ZnO nanostructures (sample 1). In an approach, the above mixture solution of PVA capped ZnSO₄ and NaOH was similarly kept at 80°C under constant stirring for 3 hours. After stirring a milky white colloidal solution was appeared that confirms the formation of ZnO nanoparticles. To this mixture solution of PVA capped ZnSO₄ and NaOH was similar to 80°C under constant stirring for another 1 hour and then collected on cooling (sample 2). Both the colloidal milky white solutions were poured over clean glass substrates to cast thin films needed for XRD measurements whereas the filtrated solutions were taken for optical measurements.

2.2 Characterization

The as-prepared samples of ZnO nanoparticles were characterized to investigate their optical and nanostructural properties. The thin films obtained were subjected to XRD study and the solutions were used for optical as well as HRTEM studies. The structural investigation of ZnO 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°-80°. The UV-Visible absorption of the samples was recorded using an automated spectrometer (Shimadzu, Model: UV-3101P) in the wavelength range 200nm-800nm. PL investigations were done using a He–Cd laser, a 1m Cerny–Turner spectrograph, and a photomultiplier [Thermospectronics, Model: AB2 (Aminco Bowman Series 2)]. The morphology of the nanoparticles were characterized by high resolution transmission electron microscope (HRTEM) [Model: JEM 2100, 200kV, Jeol].

3. Results and discussion

3.1 XRD Study

In order to get the fingerprint characterization of crystalline materials and to determine their structure XRD study has been made. The structure of the ZnO crystals has been examined by XRD using Cu Kα radiation (1.5406 Å). The intensity data were collected over the 2θ range from 30° to 75°. We obtained diffraction peaks at 2θ values of 31.15°, 33.73°, 35.53°, 46.5°, 56.65°, 63.3°, 65.2°, 67°, 69.2°, and 72.3° that correspond to (100), (002), (101), (102), (103), (200), (112), (201) and (004) planes of ZnO respectively. Thus the X-ray diffraction patterns in Figure 1 confirms the crystallinity and ZnO crystals obtained are of wurzite structure and all the diffraction peaks agreed with the reported JCPDS data [11]. XRD studies reveal most preferential orientation along the c-axis because the [002] reflection is greatly enhanced relative to the usual [101] maximum reflection [12]. The average particle size (D) of the sample was estimated to be 8.2 nm using Scherrer equation [13],

\[ D = \frac{0.9λ}{βCosθ} \]

Here β is the full width at half maximum (FWHM) of (002) peak corresponding to diffraction angle (2θ) of 33.75°. Using the usual Bragg’s law:

\[ nλ = 2d\sinθ \]

corresponding to that plane the value of lattice spacing ‘d’ was calculated and was found to be 0.265nm. The lattice parameter values of the hexagonal wurzite ZnO are estimated using the relation:

\[ \frac{1}{d^2} = \frac{4}{3} \left( \frac{n^2 + nk + k^2}{a^2} \right) + \frac{j^2}{c^2} \]

which gives the lattice constant ‘c’ as 0.513nm and for ‘a’ as 0.314nm. The calculated values are close to that of standard c=0.5206 nm and a=0.3249 nm. A small deviation however implies the creation of some native defects which are clearly reflected in our optical measurements.

P K Giri et al in their synthesis of ZnO nanostructure using acetic acid as a catalyst obtained zinc peroxide (ZnO₂) peaks of significant intensity in the XRD pattern of ZnO [14]. Thus the additional peaks in the XRD pattern of Figure 1 may be due to the existence of zinc peroxide (ZnO₂). The formation of ZnO₂ may be attributed to the additional oxidation reaction.

3.2 HRTEM Study

The structural morphology of synthesised ZnO was studied through the High Resolution Transmission Electron Microscopy (HRTEM). The HRTEM images exhibit formation of well defined spherical particles in large area together with some bigger structures dispersed in PVA matrix (sample 2). PVA is found to play a significant role in determination of quantum confinement in the samples. These bigger structures in fact results because of unwanted agglomeration of ZnO seed nanostructures in PVA matrix. Agglomeration causes likely to form rock shaped particle structure at few locations having average dimension of...
Figure 2. HRTEM images of (a) ZnO nanocrystal with the average diameter of 30nm, (b) ZnO quantum dots with the average diameter of 5.77nm, (c) the prime lattice spacing of 0.25nm and (d) SAED pattern of sample 2.

30nm (Figure 2a). Figure 2(b) shows the formation of large number of ZnO quantum dot, nearly spherical in shape with the average diameter of 5.77nm. The average particle size is in agreement with that of optical measurements. Close looks on the HRTEM images reveal that the bigger particles may actually exhibit the self assembled core/shell type nanostructures of ZnO/ZnO2. The outer layers around the bigger particles are expected as ZnO2. However ZnO2 were not formed in small size particle (5nm-7nm). In HRTEM images of the ZnO nanocrystals show lattice spacing of 0.25nm (Figure 2c). This is very close to the (002) plane d-spacing of hexagonal ZnO. The SAED pattern (Figure 2d) shows the synthesised ZnO nanoparticles possess polycrystalline hexagonal wurtzite type structure which is well agreement with that of XRD measurements. The wurtzite structure of ZnO crystal is formed by alternatively stacking Zn2+ and O2- along (001) direction resulting in positively and negatively charged top and bottom surfaces respectively. In ZnO nanostructures Zn-terminated (001) surface is chemically active and O-terminated surface is inert. The HRTEM images clearly indicate that the preferential growth direction of synthesised spherical ZnO nanocrystals in the present work is along (002).

3.3 UV-Visible study

UV-Visible spectroscopy was carried out to study the optical property of ZnO nanostructures. The UV absorption spectra of both the ZnO samples are shown in Figure 3. The spectra show a distinct exciton peak at 293nm which remain fixed for the both high temperature grown samples in PVA matrix. The band gap estimated for this sample is 4.24eV which is higher than that of bulk ZnO (3.37eV). Thus the clear blue shifting for a difference of band gap energy 0.87 eV is due to quantum confinement effect. By using polymer matrix, the excitonic absorption peak of UV-Vis absorption spectra of ZnO observed by Mazhdi et al at 310nm [15] and Soosen Samuel M et al obtained absorption peak of ZnO at 262nm at room temperature [16]. The particle size of strongly confined ZnO quantum dots can be estimated using effective mass approximation (EMA) method. Considering the parabolic band structure, the the band gap of ZnO quantum dots can be given as, 

\[ E = E_g + \left( \frac{\hbar^2 \pi^2}{2 \mu R^2} \right) \]

Where \( E_g \) is the bulk band gap of ZnO, \( \mu = \frac{m_e m_h}{m_e + m_h} \) being the effective reduced mass, \( m_e \) and \( m_h \) being the electron and the hole effective masses, respectively and \( R \) is the radius of the nanocrystalites. The diameter of the crystallites (2R) was found to be as 3.19nm. The HRTEM images show the formation of ZnO quantum dots with average size of 5.77nm.

Figure 3. UV Vis absorption spectra of (sample 1 and sample 2) ZnO nanostructures.

3.4 PL Study

Here we have studied the optical transitions in ZnO by photoluminescence method using the excitation wavelength 325nm. We tried to observe the luminescent properties of
ZnO nanostructures prepared with (sample 2) and without H$_2$O$_2$ (sample 1) at high temperature i.e. at 80°C. Figure 4 depicts the photoluminescence spectra of those nanosized ZnO synthesized in aqueous medium disperse in PVA matrix. The sample 1 shows a emission maximum at 396nm along with others at 360nm and 470nm. The UV emission at 396nm is originating from excitonic recombination corresponding to near band-gap emission, while the blue emission at 470nm is attributed to oxygen vacancies. Adding H$_2$O$_2$ into ZnO particles (sample 2), it is observed that UV emission at 360nm become prominent compared to that of at 388nm. PL enhancement may be attributed to the optical confinement effect via the formation of low dimensional structure. Strong symmetrical emission peak centered at 360nm may be an indication of uniform distribution of nanosized ZnO particles at high temperature bath. Apart from the confinement effect, the enhancement of PL intensity is attributed to the desorption of oxygen on the surface of ZnO nanoparticles. The interstitials oxygen ions (O$_{i}^-$ and O$_{i}^{2-}$) reacting with H$_2$O$_2$ provide surface states to trap photo generated holes and thus the electron-hole pairs recombine nonradiatively. As the oxygen is removed from the surface of the ZnO nanoparticles, fewer centers of nonradiative recombination lead to an increase in PL intensity. The band gap energy increases to 3.6eV owing to more blue shift which is also supported by absorption measurement. A close look on the PL curve of ZnO deposited at 80°C (sample 2) clearly exhibits several emissions in the visible region. It shows blue-green emissions at 420nm, 455nm, 470nm, 480nm and at 490nm while small traces of orange-red emissions at 600nm and at 720nm. These emission peaks are usually referred to as deep-level or trap- state emissions. Although the interpretation of deep-level emissions is still controversial because of complicated microscopic defects in ZnO, it is generally accepted that the deep- level emissions are closely related to the structural defects such as oxygen vacancies, Zn interstitials or impurities. The emission in the visible region may also be contributed by ZnO$_2$ formation. The blue-green emissions in ZnO might be associated to a transition with a self activated center formed by a doubly ionized Zn vacancy V$_{m}^{-}$ and the singly ionized interstitial Zn$^{+}$ at the one end or two nearest-neighbor interstitial sites [17, 18]. The orange-red emissions are often related to excess of oxygen. These emissions may result from the radiative recombination of photo-generated holes and electrons occupying the singly or doubly ionized oxygen interstitials (O$_{i}^{2-}$) and oxygen anti-sites (O$_{a}^{2-}$) [19]. In the present work the PL spectra however also reveals that the synthesised ZnO exhibit better quality in terms of nanostructure formation and composition as the band edge transition peak is intense and the sub-band transition peaks are suppressed and gets diffused. Those inherent native defects are expected at minimum in our samples. Majority workers found UV excitonic absorption and emission in ZnO nanostructures prepared through different techniques [20]. They also found additional emissions in the blue-green-yellow regions which are attributed to the quantity and nature of defects created in the samples corresponding to growth conditions [21].

4. Conclusion

ZnO has wide ranging application in nanoelectronics and optoelectronics. With the reduction in its size, the intriguing electrical and optical properties are manifested mainly due to effects of quantum confinement. The quantum confinement effect was found both for chemically synthesised with and without H$_2$O$_2$ induced ZnO nanostructures. PVA was expected a key role as a capping agent during synthesis. The XRD shows polycrystalline hexagonal type structure with the most preferential orientation along [002]. The UV absorption spectra show the absorption edge around 293 nm which clearly confirms the quantum confinement because of observed blue shift in the near UV emission. This excitonic emission significantly enhances the band gap energy upto 3.6eV. The particle size were also estimated using EMA method which are quite agreement with those measured from XRD and HRTEM. The additional peaks in the XRD pattern and the outer layer of the bigger NP from HRTEM images are attributed to ZnO$_2$. The photoluminescence spectra exhibit Strong emission peaks around 360-396 nm which is expected due to band to band transition. Hydrogen peroxide was found to modulate the PL properties. Additional small blue-green-orange emissions were also found which are attributed to the inherent native defects created in the samples. Quantum confinement yields a substantial density of states at the band edge and enhances radiative efficiency.

5. Acknowledgements

The authors gratefully acknowledge the Centre for Nanotechnology and the Department of Physics, Indian Institute of Technology, Guwahati and also the Sophisticated Analytic Instrument Facility (North Eastern Hill University), Shillong for providing necessary characterization facilities.

References

11. JCPDS Card No. 36-1451.
19. Li Li Yang, Synthesis and optical properties of ZnO Nanostructures, Thesis No. 1384, Linkoping University.

Source of support: Nil; Conflict of interest: None declared