Chapter 6

Optical and Magnetic properties of ring shaped ZnO nanocrystals

This Chapter focusses on the synthesis of ring shaped ZnO nanocrystals, using precipitation technique. Characterization of the samples using i) XRD, ii) TEM, iii) UV-Vis spectroscopy, iv) FTIR spectroscopy and v) XPS spectroscopy are discussed in details. The growth kinetics of ring shaped nanocrystals is discussed in details. The photoluminescence and magnetic properties of the samples are studied in details. Also a possible mechanism to explain its unusual luminescence property is briefly discussed with the help of a band model proposed on the basis of experimental results.

6.1 Introduction

In recent years, research on semiconducting nanocrystals has been extensively focused due to their exceptional properties, which are different from bulk materials [1-5]. Among the semiconductors, ZnO is one of the most promising material due to its wide band gap (3.37 eV) and high excitonic binding energy (60 MeV), unique acoustic and electronic properties [6-8]. As a result of its unique properties ZnO is extensively used in luminescence, solar cells, phosphors, piezoelectric transducers and actuators, gas sensors, surface acoustic coatings, varistors, photocatalysts, decontamination agents, fluorescent biological labelling [9-16]. The properties of the nanocrystals are determined by the size, shape and crystalline structure, thus rational control over these factors is a topic of immense interest. Various structures of ZnO such as nanowires, nanorods [17, 18], nanosheets [19], nanosprings [20],
nanobroom [21], nanobelts, nanobridges, nanonails [22], brush like hierarchical structure [23] have been synthesized using different routes. Among the various methods, wet chemical route can be exploited to achieve more precise control over composition, shape and size of the products. The numerous advantages of this process are cost efficient, easy handling of precursors, non-hazardous to environment also can be scaled up to any amount.

Interestingly, ZnO produces very bright luminescence in ultraviolet region. The UV emission is usually attributed to the interband transition or the exciton combination in ZnO. In addition, very strong green emission peaked at around 510 nm [24, 25], orange luminescence around 630 nm [26], yellow luminescence at around 570 nm [27] has been observed. The origin of the visible emission has been investigated for a long time. Various proposed mechanisms are transitions between defect states mainly donor to acceptor level [26], oxygen vacancy [28], zinc interstitials [29], oxide antiside defect [30]. As proposed by Vanhausden, the green luminescence originates from transition between the photoexcited holes and singly ionized oxygen vacancy [31].

In particular, recent experimental results on ZnO nanoparticles have revealed ferromagnetism even in the absence of magnetic impurities [32-35]. This finding is remarkable due to possible technological applications both in information storage and processing devices. However, one of the main obstacles in realizing the full potential of ZnO materials is lack of a perfect understanding of the role of intrinsic and extrinsic lattice defects, which largely affect the magnetic, electronic and optical properties. In ZnO, existence of various kinds of defects like O vacancy, Zn vacancy, interstitial Zn, n-type doping and p-type doping and surface defects affects the properties [36-38].

Manipulation of structure of nanoparticles is always fascinating which may produce some remarkable properties also. Though very rare, weak blue emission is also reported for nanocrystalline ZnO having typical microstructure [39]. The origin of blue emission is much obscured till date and demand more work on this line. In this chapter, we present a water based chemical route to synthesize cetyltrimethylammonium bromide (CTAB) capped annular ring shaped ZnO nanostructures formed by assembly of ultrafine particles. We have observed strong unusual violet and blue emission in addition to ultraviolet emission in the as synthesized nanocrystalline ZnO nanorings. Also we observed ferromagnetic-like behavior up to 300 K having enhanced magnetic moment. Though the origin of ferromagnetism in this system is still poorly understood yet, this result can help to understand the current controversy about the origin of magnetic properties in dilute magnetic system (DMS).
6.2 Experimental Section

6.2.1 Materials

The precursors, Zinc Nitrate \([\text{Zn(NO}_3\text{)}_2\cdot 6\text{H}_2\text{O}]\), Sodium Hydroxide \([\text{NaOH}]\) and cationic surfactant CTAB \([(\text{C}_{16}\text{H}_{33})\text{N(CH}_3\text{)}_3\text{Br}]\) were procured from Merck. All the reagents were analytical grade and used without further purification.

6.2.2 Methods

In a typical synthesis of annular ring shaped ZnO by water based wet chemical route, 50 ml aqueous solution of \(\text{Zn(NO}_3\text{)}_2\) (0.05M) and \(\text{NaOH}\) solution (0.1M) were prepared. The two solutions were separately stirred till they became clear. Calculated amount of CTAB (0.01M) was then added to both the solutions and continued the stirring. \(\text{NaOH}\) solution was then added drop wise to the salt solution under continuous stirring till white precipitate was formed. The precipitate was then filtered out and washed several times with water to remove any un-reacted ions present. The white precipitate was left to dry at 60°C for 3 days. A schematic flowchart for the preparation technique is presented in Fig. 6.1 for more clarity.

![Flowchart of synthesis technique.](image)

6.2.3 Characterization

Characterization of the dried product was carried out by different techniques. X-Ray diffraction pattern of the powder sample was obtained using a Rich Seifert X-Ray
diffactometer. The morphology of the sample was visualized using transmission electron microscope (JEOL 2010) operated at 200 kV and equipped with a detector for energy dispersive X-ray spectroscopy study. The UV-Vis absorbance spectrum was recorded on Varian Cary 5000 UV-Vis-NIR spectrometer. FTIR spectrum was recorded with Shimadzu FTIR 8400S spectrometer. Photoluminescence measurement was carried out on F-2500 FL spectrometer, Hitachi. The magnetic measurements were performed on a Quantum Design SQUID MPMS VSM. The hysteresis loops and FC-ZFC curves were measured within temperature range 4 K-300 K.

6.3 Results and Discussion

6.3.1 X-ray diffraction study

The XRD measurements were performed to assess the overall structure and phase purity. A typical XRD pattern of ZnO nanorings is shown in Fig. 6.2. The peaks can be well indexed to wurtzite structure of ZnO [JCPDS No. 36-1451].

![XRD pattern of ZnO nanorings](image)

**Fig. 6.2. XRD pattern of ZnO nanorings.**

No peaks corresponding to any impurities are present which suggests that the synthesized product is pure ZnO. The lattice constants of synthesized ZnO, as obtained from Rietveld refinement of XRD data using MAUD software, is \( a = 0.3254 \) nm and \( c = 0.5213 \) nm.
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nm which are very close to that of bulk ZnO (a = 0.3249 nm and c = 0.52066 nm). An appropriate fit was observed with the goodness of fit (GOF) value 1.8. The average particle size and lattice strain as determined from Rietveld fit is 11 nm and 0.0034. The average crystallite size of the sample was also determined using Debye-Scherrer formula by considering two most intense peaks

\[
a = \frac{0.89 \lambda}{\beta \cos \theta}
\]  

(6.1)

where, a is the crystallite size, \( \lambda \) is the wavelength of the X-ray used, \( \beta \) is FWHM of the concerned peaks and \( \theta \) is the grazing angle. The average crystallite size calculated to be 12 nm.

6.3.2 Morphological Study

The morphology of the synthesized sample was investigated using Transmission electron micrographs. The typical electron micrograph confirms the presence of particles with annular ring like structure as can be seen in Fig. 6.3(a). It is clear from micrographs that the outer peripheries of nanostructures are dark compared to the central portion confirming the presence of high electron density along the peripheries. The ultrafine ZnO particles assemble to form annular structure (marked in Fig. 6.3(b)).

\[\text{Fig. 6.3. Transmission electron micrograph (a) ZnO nanorings (b) marked rings of ZnO.}\]

High resolution TEM image of the arc of a ring is shown in Fig. 6.4(a) which exhibits the presence of particles assembly. The average size of the ultrafine particles forming the nanoring as estimated from TEM is 4 ±1.3 nm (Fig 6.4(b)). The d-spacing as calculated from
high resolution TEM images is 0.24 nm which corresponds to (101) plane of ZnO. Further the lattice fringes in the image also depict the high crystallinity of nanocrystalline ZnO.

Fig. 6.4. (a) High resolution transmission electron micrograph of an arc of ZnO nanoring, (b) particle size distribution.

The rings of SAED pattern in Fig. 6.5(a) consists of bright spot which indicates the presence of polycrystallinity. The rings can be indexed to diffractions from the planes of the hexagonal ZnO. The typical EDAX spectrum of the sample presented in Fig. 6.5(b) confirms the presence of the element Zn and O. The element Cu and C comes from the carbon coated copper grid on which a drop of ethanol containing the sample was cast. Further the presence of Br or N of capping agent CTAB is not reflected in the EDX spectrum.

Fig. 6.5. (a) SAED pattern, (b) EDX spectrum, of ZnO nanorings.
6.3.3 Growth Mechanism

Effort has been made to understand the growth of nanorings. Actually, during synthesis, the reactions taking place are as follows

\[
\begin{align*}
\text{Zn(NO}_3\text{)}_2 & \rightarrow \text{Zn}^{2+} + \text{NO}_3^{2-} \\
\text{NaOH} & \rightarrow \text{Na}^+ + \text{OH}^- \\
\text{Zn}^{2+} + 4\text{OH}^- & \rightarrow [\text{Zn(OH)}_4]^{2-} \\
[\text{Zn(OH)}_4]^{2-} & \rightarrow \text{Zn(OH)}_2 + 2\text{OH}^- \\
\text{Zn(OH)}_2 & \rightarrow \text{ZnO} + \text{H}_2\text{O}
\end{align*}
\]

CTAB comprises of hydrophobic tail and hydrophilic head which favours formation of bilayer in water [40]. Due to Coulomb attraction, \([\text{Zn(OH)}_4]^{2-}\) attaches to head of CTAB molecules which on further reaction allows the assembly of ZnO nanoparticles to form ring like structure. The schematic presentation of the reaction mechanism is presented in Fig. 6.6.

![Fig. 6.6. Schematic presentation of formation of ZnO nanoring.](image)

6.3.4 UV-Vis absorbance study

The UV-Vis spectroscopy was employed to study the effect of morphology on the optical properties of ZnO nanorings. Fig. 6.7 depicts the corresponding absorption spectra of ZnO nanorings. The absorbance edge onset is at around 323 nm which corresponds to the
intrinsic band gap of ZnO [41]. For interband transition in direct band gap semiconductors, the equation obeyed is

$$a h \nu = \left( h \nu - E_g \right)^{1/2}$$

(6.2)

where, $\alpha$ is absorption co-efficient, $h\nu$ is photon energy and $E_g$ is band gap in eV. The band gap of ZnO is determined by plotting photon energy vs $(a h \nu)^2$ curve and extrapolating the linear region for $\alpha=0$. The band gap thus calculated is 3.9 eV which is blue shifted corresponding to bulk ZnO. This is ascribed to the quantum confinement effect of synthesized particles having average diameter less than 10 nm.

![Fig. 6.7. UV-Vis absorbance spectrum of ZnO nanorings.](image)

The average particle size can also be estimated from the absorbance spectra according to the effective mass model [42-44] using the formula

$$E^* = E_g + \frac{\hbar^2}{8 \pi^2 r^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8 e^2}{4 \pi \varepsilon_0 r} - \frac{4 \times 0.124 e^2}{\hbar^2 (4 \pi \varepsilon_0 r)^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right)^{-1}$$

(6.3)

where, $E^*$ is the observed band gap of ZnO nanoparticles, $E_g$ is the band of bulk ZnO (3.4 eV), $h$ is Planck’s constant, $e$ is electronic charge, $r$ is the particle radius, $m_e^*$ is effective mass of electrons (0.24 $m_0$), $m_h^*$ is holes effective mass (0.45 $m_0$), $\varepsilon_0$ is the permittivity of free space, $\varepsilon$ is the relative permittivity (3.7), $m_0$ is rest mass of electrons. The diameter of the particles comprising the nanorings as estimated from equation (6.3) is found to be 3.4 nm.
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The result is consistent with our TEM study. The particle sizes computed from different characterization techniques are presented in table 6.1.

The average particle size estimated from XRD measurement is quite different than other measurement techniques. A possible explanation is that the result obtained from XRD measurements gives an idea of the diameter of the rings rather than the ultra fine particle size. The result is in good agreement with the diameter of the nanorings as observed from transmission electron micrograph (Fig. 6.4(a)).

<table>
<thead>
<tr>
<th></th>
<th>Particle size from XRD (nm)</th>
<th>Particle size from TEM (nm)</th>
<th>Particle size from UV-Vis spectra (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rietveld analysis</td>
<td>11</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>Debye Scherrer formula</td>
<td></td>
<td></td>
<td>3.4</td>
</tr>
</tbody>
</table>

6.3.5 FTIR Spectroscopy

To analyze the chemical structure of the surface, FTIR spectroscopy was employed. Fig. 6.8 shows the FTIR spectrum of the synthesized ZnO nanorings. The broad hump around 3300 cm\(^{-1}\) corresponds to stretching vibrations of O-H bonds of adsorbed water. The absorbance band at 2918 cm\(^{-1}\) and 2852 cm\(^{-1}\) can be assigned to asymmetric and symmetric stretching vibrations of \(-\text{CH}_2\)-bond. The peak at 1502 cm\(^{-1}\) and 1385 cm\(^{-1}\) is attributed to \(-\text{CH}_3\) anti-symmetric and symmetric bending vibrations, respectively. The above peaks confirm the presence of CTAB on the surface of the particles [45]. The broad band at 424 cm\(^{-1}\) corresponds to stretching frequency of ZnO [34]. Different bands corresponding to ammonia ligand (~1615, 1220, 797 cm\(^{-1}\)) is not detected in the spectrum confirming the non-hazardousness of the synthesized product [46].
6.3.6 XPS Spectroscopy

XPS is an efficient technique to determine the chemical states of the sample and to investigate the presence of any undesirable impurity phase on the sample surface. A representative XPS spectrum of ring-shaped ZnO nanostructures is presented in figure 6.9(a).

Fig. 6.9. (a) XPS survey scan spectrum, high resolution scan of (b) Zn 2p, (c) O 1s, for ZnO sample.
Evidently, the spectrum reveals the presence of only the elements Zn, C and O. The absence of any peak in the range 640-780 eV in the spectrum confirms the absence of other ferromagnetic elements like Mn, Fe, Co or Ni. Figure 6.9(b) presents the XPS spectrum of Zn 2p core level and the peaks at binding energies 1027.1 and 1050.1 eV corresponds to Zn \(2p_{3/2}\) and Zn \(2p_{1/2}\) respectively. A spin-orbit splitting of 23 eV confirms the presence of Zn as Zn\(^{2+}\) bound to oxygen in ZnO. The XPS spectrum of O 1s core level is illustrated in figure 6.9(c) and the peak at 536.9 eV is assigned to O\(^{2-}\) ion in wurtzite structure of ZnO.

### 6.3.7 Photoluminescence Study

Photoluminescence (PL) spectroscopy is a powerful technique for revealing the energy band structure of materials. Fig. 6.10 shows the room temperature PL spectra of ZnO nanorings within the range 325-575 nm after exciting the system with 300 nm.

![Photoluminescence spectrum of ZnO nanorings at room temperature.](image)

The PL spectrum is quite unusual and consists of four overlapping peaks. We have deconvolute the peaks with the help of Lorentzian functions. The peak positions as estimated are 376, 410, 431 and 463 nm. The broad neck at 376 nm originated from excitonic recombination corresponding to the near band-edge emission of ZnO. The strong violet emission at 410 nm originates from recombination of an electron in the defect state of Zn...
interstitial (Zn\textsubscript{i}) with a hole in the valence band [47]. The strong blue emission about 431 nm is ascribed to transition from a state (S\textsubscript{s}) created due to ZnO/CTAB interface to the valence band [48]. This is consistent with the FTIR spectrum which confirmed the presence of CTAB on the surface of ZnO. The hump at 463 nm is attributed to transition from conduction band to defect state of zinc vacancy (V\textsubscript{Zn}) [49].

Fu and co-workers [47] have calculated the energy level of various defect centres, such as vacancies of oxygen and zinc, interstitial oxygen and zinc, and antisite oxygen in bulk ZnO (band gap 3.36 eV). The gap between conduction band and level of oxygen vacancies is 2.28 eV (about 540 nm) and that from interstitial zinc level to valence band is 2.9 eV (about 425 nm). The former was well consistent with the normal green emission of ZnO. Though not clear, the weak blue emission in their study could be attributed to interstitial zinc in ZnO nanoparticles. It implies that the visible emission from ZnO cannot be fully explained by a single type of defect. A schematic energy band diagram is presented in Fig. 6.11 to explain the observed emission spectra. The broad peak at 530 nm, which is normally observable in ZnO is absent here. This green luminescence is caused due recombination of a photogenerated hole with singly ionized oxygen vacancies [31] and excess oxygen on the surface, which might be in the form of OH\textsuperscript{-} ions. The absence of green emission in the ring shaped ZnO confirms the almost absence of oxygen vacancy [50]. We describe the origin of blue emission as the surface states due to presence of CTAB and the violet emission originates from donor level of Zn interstitial. The synthesized product can be useful for biological fluorescence labelling and full-colour display.

**Fig. 6.11. Schematic band diagram of ZnO nanorings.**
6.3.8 Magnetic Property

In order to illustrate the magnetic ordering in these nanorings, the temperature dependence of zero field-cooled (ZFC) and field-cooled (FC) magnetization (with 100 Oe magnetic field) has been studied and curves are presented in fig. 6.12. Bifurcation of ZFC and FC is observed in the whole temperature range measured from 4-300 K suggesting the presence of unblocked ferromagnetic state in this temperature range. In addition, the variation of magnetic moment with temperature indicates that at lower temperatures the ZFC and FC curves are not reflective of simple paramagnetism or superparamagnetism. The most interesting phenomenon is the observation of an anomalous temperature dependence of magnetization, such as a sharp minimum in magnetization at around 20 K accompanied by a small hump at about 70 K. Such an unusual magnetic behavior is believed to appear when a combination of ferromagnetic and antiferromagnetic order compete with each other [51]. Further, we observe that the magnetic moments are almost thermally independent beyond the hump as illustrated in fig. 6.12(a).

![Fig. 6.12. ZFC- FC curve of ZnO nanorings at 100 Oe magnetic field. Inset: ZFC curve upto 150 K.](image)

For magnetic impurities dispersed in diamagnetic matrix, the magnetization is found to decrease with temperature and the system behaves paramagnetically. In our case, the thermal independence of magnetization strongly suggests that the magnetic impurities are not
responsible for the ferromagnetic behavior of ZnO [32]. It is worthy to be mentioned here that the precursor used in this experiment is nitrate salt of Zn which is non-magnetic and the microstructural characterization using XRD, XPS, HRTEM and EDX also confirms the absence of any ferromagnetic impurities. The appearance of magnetization can be attributed to the formation of a large amount of surface defects due to the distorted ring shape and not due to any magnetic impurities. Our experimental result suggested that the magnetic moments arising from these defects are ordered both ferromagnetically and antiferromagnetically in places. Different types of magnetic order may appear due to different morphology and size of nanorings. Therefore, the magnetic property of the ZnO nanorings has a very different behavior compared with the magnetic property of bulk ZnO [32].

Fig. 6.13 presents magnetization as a function of field measured within the temperature range 4-300 K. The sample exhibits various features of the ferromagnetic material as can be seen from hysteresis loops. We observe high value of coercivity up to room temperature though saturation was not achieved even at a field of 2 T. The extended portion of the fig. 6.13 is placed in inset to visualize the coercive field. The values of the coercive field (Hc) and maximum magnetization (M\text{max}) obtained at the applied magnetic field of 2 T at different temperatures are presented in table 6.2.

![Fig. 6.13. Hysteresis loops of ZnO nanorings at different temperatures.](image-url)
Table 6.2. Datas extracted from magnetic measurements.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$H_c$ (Oe)</th>
<th>$M_{max}$ (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>163.2</td>
<td>0.100</td>
</tr>
<tr>
<td>30</td>
<td>80.6</td>
<td>0.049</td>
</tr>
<tr>
<td>300</td>
<td>23.1</td>
<td>0.036</td>
</tr>
</tbody>
</table>

It is to be noted here that the observed magnetization $M_{max}$ is one order of magnitude higher than the reported values of thiol capped ZnO nanoparticles (~0.002 emu/gm) [32], PVP capped ZnO nanocrystals (~0.007 emu/gm) [34], ZnO nanorods (~0.004 emu/gm) [38]. Enhancement of magnetization could be attributed to the huge number of surface defects created by virtue of large surface area of nanorings. Further, the morphology of ZnO along with the capping agent CTAB modifies the electronic structure which may also induces the magnetic property of the ZnO nanorings. The modification of electronic structure is further proved from the room temperature photoluminescence spectrum of the sample.

### 6.4 Conclusions

In summary, we report a simple, novel way to prepare ZnO nanorings through chemical route by introducing CTAB. The synthesis route is easily controllable, well reproducible and may be feasible to develop into scale-up production. In addition, it does not need any template to grow the nanorings. Both XRD and HRTEM indicate that ultrafine ZnO nanoparticles coalesce into the nanorings which are crystalline in nature and oriented along (101) direction. Quantum size effects are evident from the optical absorption spectra, which showed prominent blue shifts. The strong blue emission about 431 nm is ascribed to transition from a state ($S_s$) created due to ZnO/CTAB interface to the valence band. The violet-blue emission was significantly enhanced at the expense of the near band-edge luminescence. On the basis of experimental results, we propose a plausible band structure to explain the unusual blue – violet emission. Additionally, an unusual magnetic behavior is observed indicating the presence of both ferromagnetic and antiferromagnetic order. It is not
possible to exactly pin down the reason of enhanced magnetization yet the huge number of surface defects created due to the larger surface to volume ratio of nanorings is likely to play a major role. The present study demonstrates that ZnO samples can be made highly magnetic just by tailoring the microstructure. These ZnO nanorings with high surface may have immense potential for application in catalysis, drug delivery, sensor devices and spintronics applications also.
References