1. Introduction

ZnO is a promising wide band semiconductor for ultraviolet (UV) and visible light optoelectronics. Because of the band gap tunability and low production cost, ZnO nanoparticles have a lot of potentials for applications in the field of light emitting diodes (LEDs) and laser diodes (LDs). However, their potential for UV devices is impaired because of the reduction of UV luminescence (UVL) yield due to the presence of a large density of unintentional defect states emitting a broad band of green luminescence (GL) [1–3]. The latter, though can be utilized effectively for the visible light optoelectronic devices, the UV devices would require its complete suppression. Both the UV and the visible luminescence can potentially be utilized to fabricate optoelectronic devices using ZnO nanoparticles; a control over their relative intensities is imperative. In order to achieve such a control, the understanding of the origin of the GL emission is foremost important. Even though a large volume of research has been devoted along that direction, the origin of green luminescence still remains controversial. In case of ZnO thin films GL has been assigned to various types of defects such as oxygen vacancies (V\text{O}), oxygen antisites (O\text{Zn}) [4–6], Zn vacancies (V\text{Zn}) [7] and Zn interstitials (Zni) giving rise to red, orange, yellow, and green luminescence [8–10]. Many reports also suggest extrinsic impurities such as Cu to be the likely cause for the origin of green luminescence (GL) band [11,12]. In case of ZnO nanoparticles, GL is often believed to be stemming from the surface [13–15]. However, the precise origin of this feature is yet to be understood. Role of the surface becomes more crucial for the smaller particles as the surface to volume ratio increases with the decrease of the particle size. In order to exploit the advantages of quantum confinement effect, which results in an enhancement of the band gap with the reduction of the particle size, the particle radius has to be comparable or smaller than the excitonic Bohr radius of ZnO that is only ~2.5 nm. Therefore, it is a challenge to enhance both the energy and the relative intensity of the UVL emission with respect to the GL emission at the same time.

Here, we have performed a comparative study of the optical and the structural properties of ZnO nanoparticles before and after their surroundings are evacuated. Our study reveals that certain groups that are physically adsorbed on the surface of the nanoparticles are responsible for the GL emission. The study further suggests that out of the two
most probable candidates, namely the hydroxyl groups and the acetate
acetate groups, the hydroxyl groups are likely to be responsible for the
GL emission observed in our ZnO nanoparticle samples.

2. Experimental

ZnO nanoparticles are synthesized by a sol–gel technique [16]. In
this process Zn-acetate powder is used as Zn precursor. This powder
is mixed to obtain 0.16 mM solution in 100 ml ethanol at room tempera-
ture. The solution initially forms a white color suspension. The mixture
is then transferred into a distillation apparatus and boiled under vigor-
ous stirring at 70 °C for 1 hour (Sol. A). 7 mM of LiOH·2H₂O powder is
mixed in 50 ml of ethanol. The suspension is kept in an ultrasonic bath
at room temperature for 20 minutes to obtain a homogeneous so-
lution (Sol. B). The hydroxide containing solution (Sol. B) is added drop
wise at a rate of 5 ml/min to the Sol. A under vigorous stirring main-
tained at 70 °C and then placed in an ultrasonic bath for 1 hour at
room temperature. In order to separate ZnO nanoparticles from the so-
lution, the following decantation procedure is implied. Hexane is added
to the mixture until a turbid solution is formed. Hexane dissolves all the
by-products of the process and ZnO nanoparticles segregate from the
solution as precipitate. The precipitate is then collected and redissolved
in methanol and casted on Cu-grids for HRTEM study. Powder samples
are used for XRD, Raman and XPS studies. Optical properties are inves-
tigated through photoluminescence (PL) and absorption spectroscopy.

3. Results and discussion

3.1. Structural properties

Fig. 1(a) shows the HRTEM image of a ZnO nanoparticle. The
size of the particle visible in this image is ~5.5 nm. Fast Fourier
transform (FFT) of the image shown in the inset of Fig. 1(a) confirms
the formation of ZnO in hexagonal wurtzite structure. The lattice
parameters calculated from the FFT pattern matches very well with
that of ZnO. Fig. 1(b) shows a TEM image of these ZnO nanoparticles.
The histogram plot describing the particle size distribution is shown
in the inset. This distribution is obtained by analyzing the size of
about 300 particles from several such TEM images.

Fig. 2 shows the absorption spectra taken for suspended ZnO nano-
particles. The profile resembles the absorption spectra typically found
for ZnO nanoparticles suspended in alcohol solutions featuring a sharp
on-set followed by a peak at higher energy. The energy E (λ₁/₂) is the
energy position at which the absorption is half of its peak value, is usu-
ally considered as the average band-gap of the nanoparticles. E (λ₁/₂)
for our ZnO nanoparticles (≈3.65 eV) is found to be higher than the
band gap (Eg) energy (≈3.32 eV) of bulk ZnO that confirms the quan-
tum confinement effect. The average particle diameter can be obtained
from E (λ₁/₂) using tight binding model (TBM) [17].

\[ \Delta E_g = 100 \times \left( \frac{18.1d^2 + 14.4d - 0.8}{3.32} \right) \]

(1)

where, \( \Delta E_g = E(\lambda_{1/2}) - E_g \) and d is the mean diameter for the nanopar-
ticles. In this case d is estimated to be ~5.2 nm, which matches well
with the mean diameter obtained from the particle size distribution shown
in the inset of Fig. 1(b).

Fig. 3 represents the wide angle X-ray diffraction (XRD) profiles for
the ZnO nanoparticles. All the peaks can easily be identified as (100),
(002), (101), (102), (110), (103) and (112) reflections associated
with wurtzite phase of ZnO. No additional feature related to impurity
phase can be seen in the XRD profile. Average diameter of the nano-
particles is estimated to be 6 nm from the full width at the half maxi-
mum (FWHM) of (101) peak using Debye-Scherrer formula [18]. Both
a and c-lattice constants are estimated to be 3.23 and 5.20 Å, respec-
tively from these peak positions. Interestingly, both the parameters

![Fig. 1. (a), HRTEM image of a ZnO nanoparticle. Inset shows the Fast Fourier Transform (FFT) of the image. (b) TEM overview image of the ZnO nanoparticles. Inset shows the particle size distribution. Bar shows the number of particles and the thick line is the gaussian fit used to calculate mean diameter of the nanoparticle.](image-url)
are found to be little less than those obtained for bulk ZnO samples \((a = 3.25 \text{ Å} \text{ and } c = 5.21 \text{ Å})\) [19].

Fig. 4 compares the FTIR spectra recorded for samples under the atmospheric and vacuum conditions. Clearly, certain absorption features are visible in both the conditions. For example, the feature appearing between 1400 and 1600 cm\(^{-1}\), which comprises of several peaks, are attributed to the stretching modes (symmetric and asymmetric) of the acetate group (-COOH) [20]. These groups are believed to be adsorbed on the surface of the nanoparticles during the synthesis process. The absorption peak appearing at 1000 cm\(^{-1}\) is due to C≡O deformation mode of the acetate groups. Few narrow peaks appearing around 2830 cm\(^{-1}\) and 2920 cm\(^{-1}\) due to C-H bond can also be seen [21]. The broad feature appearing around 3400 cm\(^{-1}\) is resulting from the hydroxyl (-OH) group [20, 21]. It is noticeable that the intensity of all these features decreases upon evacuation. Since the same amount of material is used for the FTIR studies carried out both in the vacuum and the atmospheric conditions, our FTIR results indicate that the density of the hydroxyl and the acetate groups decreases when the surroundings of the nanoparticles are evacuated, which further implies that these groups are physisorbed on the surface (but not chemically bonded) of the ZnO nanoparticles such that they can be removed upon evacuation.

Fig. 5 represents the Raman spectra for the ZnO nanoparticles. Raman features in ZnO powder are ascribed to Raman active modes of the ZnO wurtzite crystal [22]. Wurtzite-type ZnO belongs to the space group \(P_6_{3}mc\), with two formula units per primitive cell. The zone center optical phonons can be classified according to the following irreducible representation: \(\Gamma_{opt} = A_1 + E_1 + 2E_2 + 2B_1\), where \(B_1\) modes are silent, \(A_1\) and \(E_1\) are polar modes, both Raman and infrared active, while \(E_2\) modes (\(E_2\) low and \(E_2\) high) are non polar and Raman active only. The \(E_2\) (high) Raman mode observed at 437 cm\(^{-1}\) is dominantly assigned to the oxygen vibration [22, 23]. The \(E_1\) (LO) mode present at 578 cm\(^{-1}\) usually originates from second-order Raman scattering.

Although the presence of impurities and/or defects can also influence these modes, the \(E_1\) (LO) mode is more strongly affected by these effects [23]. The peak at 332 cm\(^{-1}\) is assigned to the second-order Raman process [22]. Other vibrational peaks, which originated from acetate group are assigned in Fig. 5. The acetate ligand can be in the forms of free zinc acetate or potassium acetate (KAc). Some of this ligand is also believed to be attached to the ZnO surfaces. As the vibration frequencies of the functional groups are sensitive to the chemical environment, the Raman spectra can help in identifying the chemical forms of the acetate ligand. However, the C-O stretch and O-C-O bend modes are much more sensitive to the surrounding environment. The C-O stretch of acetate is red-shifted by 5 cm\(^{-1}\) compared to that of KAc and 24 cm\(^{-1}\) to free zinc acetate [24]. This result shows the absence of free acetate group or potassium acetate present in the powder. Instead, they are bound to ZnO surfaces as has been clearly observed in our FTIR results [25].

XPS is used to investigate the chemical composition of ZnO nanoparticles. The survey scan (not shown here) of the ZnO nanoparticles shows the presence of different peaks that can be attributed to Zn, O, and C elements. No impure feature is observed in these samples. Fig. 6 shows (a) O 1s core level (b) Zn2p\(_{3/2}\) core level XPS spectra for ZnO nanoparticles. It has to be clearly mentioned that binding energies are calibrated by taking the carbon C1s peak (285.0 eV) as reference in these spectra. In the XPS spectra, the open circles denote the experimental data, thick solid line represents the fitted curve and the deconvoluted individual peaks are depicted by thin solid lines. In Fig. 6(a), the deconvolutions show the presence of five different O1s peaks in the ZnO nanoparticles. The peak located at 529.8 eV (curve 1) is attributed to the H bonds attached to the ZnO surface [26]. The peak centered at 531.2 eV (curve 2) is associated to the O\(_{2}^{2-}\) ions in the wurtzite structure surrounded by the Zn atoms [27]. The peaks at 531.96 (curve 3) and 532.67 eV (curve 4) are attributed to the presence of –OH bonds attached to Zn ions on the surface of ZnO nanoparticles [28]. The
3.2. Optical properties

Fig. 7 shows room temperature PL spectra recorded at the atmospheric condition and at the vacuum. The figure compares the room temperature PL spectra obtained in the atmospheric (thin solid line) and the vacuum (dashed line) conditions for ZnO nanoparticle sample. The curve 3 shown in the form of thick solid line represents the PL spectra when the experiment is performed again in the atmospheric condition. In all cases, an ultra violet luminescence (UVL) band centered at 3.3 eV, resulting from the transition between the conduction and the valance band states can be seen. In addition to that, a broad green luminescence (GL) band is also observed. The GL emission is centered at 2.09 eV for PL performed under atmospheric condition. The GL intensity dominates the UVL intensity when the PL spectra are obtained in the atmospheric conditions. On the other hand, the GL emission intensity is much less than that of the UVL emission in vacuum. Note that the green luminescence peak position is slightly blue shifted to 2.35 eV when PL is performed under vacuum condition. This finding clearly suggests that the green emission must be linked to certain groups which are present on the surface of the nanoparticles in a way that they can be easily removed by evacuation. It is also clear from our FTIR study that hydroxyl and the acetate groups can be easily removed from the surface of the nanoparticles upon evacuation. This indicates that either the hydroxyl or the acetate groups or both are responsible for the GL emission. However, it has to be noted that when the PL spectrum is recorded again at the atmospheric condition, the GL intensity recovers almost up to its original value. This observation suggests that the hydroxyl groups rather than the acetate groups are the likely cause for the GL emission observed in this system because there are plentiful of water molecules in air, which can source the hydroxyl groups. While, the acetate groups are not expected to be abundant in air. The results of Fig. 7 also show that the GL band is not only suppressed but also blue shifted to 2.35 eV under the vacuum condition, which suggests that the origin of GL in the vacuum condition may not be the hydroxyl groups. Here, the native defects such as Zn interstitial or oxygen vacancies could be the possible reason for the residual GL emission. We believe that the GL emission peaking at 2.09 eV, which is observed when the PL is performed under the atmospheric condition, is originating from the hydroxyl groups attached to the ZnO nanoparticles. When these groups are removed upon evacuation, the blue shifted GL band (peaking at 2.35 eV) is most likely resulting from certain native defects or groups, which are chemically bonded to the surface of the nanoparticles and therefore difficult to be removed upon evacuation. It should be noted that our experimental observations show that the presence of surface complexes seems to have a more pronounced effect on the origin of green luminescence from the photoluminescence studies.

4. Conclusions

We have done a comparative study of the structural and optical properties of ZnO nanoparticles of diameter ~5 nm synthesized by a sol–gel technique. The optical studies have been performed in the atmospheric and vacuum conditions. Our study reveals that certain chemical species, which are physically adsorbed (but not chemically bonded) at the surface of the nanoparticles, are responsible for the GL emission. The study also indicates that the hydroxyl groups are the likely candidate, responsible for the GL emission observed in this system.
Acknowledgment

We would like to acknowledge Nanoelectronics Centre, Electrical Engineering department, IIT—Bombay and Department of Science and Technology (DST) for financial support.

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