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Room temperature ferromagnetism in chemically synthesized ZnO nanoparticles

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Abstract

Zinc Oxide (ZnO) is an intrinsic n-type metal oxide-based semiconductor with a wide bandgap and has attracted much attention of researchers due to its unique properties and applications in optoelectronic devices, ceramics, catalysis, pigments and many others. Herein, ZnO nanoparticles (NPs) have been successfully synthesised by a simple and cost-effective chemical co-precipitation method. The product is characterized by x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and UV-Vis absorption spectroscopy (UV-Vis), photoluminescence spectroscopy (PL) and vibrating sample magnetometer (VSM). The XRD pattern confirms the formation of the wurtzite phase ZnO nanoparticles. The structural information and composition were further confirmed by FTIR where the stretching vibration bands appeared at 493 cm^{-1} , 562 cm^{-1} and 831 cm^{-1} are due to the Zn-O bond. The absorption edge is observed at 359 nm which is due to its quantum confinement effect whereas the PL emission is observed in the range of 370 nm-600 nm. M-H loop shows the presence of room temperature ferromagnetism in ZnO nanoparticles possibly due to the presence of oxygen vacancies.

Key words : Co-precipitation, Diluted magnetic semiconductor, RTFM, Spintronics.

1. Introduction

The rapid development of nanotechnology and the advanced growth techniques make it

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possible to synthesize a variety of functional materials with desired properties at nanoscale level in a very controlled and effective manner. Nowadays, the nanostructured materials are being extensively reviewed to explore and investigate the novel phenomena occurring at the nanoscale. The uses of semiconductors as nanomaterials are developing for the future applications by their significantly atomic/molecular manipulations¹. In quantum confinement regime where the particle size becomes comparable to the radii of the Bohr excitons of the material, nanoparticles have diverse unique optical, electrical, chemical and magnetic properties. These enhanced properties of semiconductor nanoparticles are of particular importance for their better applications in various fields.

Zinc oxide (ZnO) is one among the II-VI semiconductors with wide bandgap (3.37 eV) and large exciton binding energy of 60 meV at room temperature and has been extensively studied with its unique physical and chemical properties. The high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photostability enable it to be used in variety of applications including varistors, piezoelectric devices, transparent ultraviolet (UV)-protection films, antibacterial activity, photoconductors, sensors, solar cells and so on²⁻¹⁵. Besides, ZnO is the most exploring materials for spintronic application, where the magnetic properties in materials are induced by the incorporation of certain percentage (usually <10%) of transition metal ion (impurity atoms) and such semiconductor materials are known as dilute magnetic semiconductor (DMS). R. Khan *et al.*, studied the structural and magnetic properties of (Co, Ce) co-doped ZnO-based diluted magnetic semiconductor nanoparticles¹⁶. Indeed the ferromagnetic feature may be induced in pure ZnO as the unique properties of ZnO nanoparticles are dependent upon the size and morphology of the synthesized nanoparticles^{17,18}. Most of the ZnO nanocrystals have been synthesized by high temperature solid state reactions which are both the expensive and energy consuming. The other drawback of these high temperature solid state method is the uncontrolled growth of the crystals during the synthesis and difficult to control the particle properties. ZnO nanoparticles can be synthesized by a number of methods including hydrothermal method, sol-gel, combustion and precipitation method¹⁹⁻²⁵. Among all, chemical co-precipitation method has several advantages over other growth processes such as the use of simple equipment, catalyst-free growth, low cost, environmental friendliness and less hazardous and very easy to control the size by adjusting the reaction parameters such as reaction temperature, time, pH and concentration of the precursors.

The present study focuses on the synthesis of ZnO nanoparticles by a simple cost-effective chemical co-precipitation method. The as synthesized ZnO nanoparticles were characterized by XRD, FT-IR, UV-Vis, PL and VSM measurements.

2. Experimental details

The synthesis of ZnO NPs has been carried out at room temperature by the chemical co-precipitation method. All the chemicals i.e. Zn(NO₃)₂(99.99%) and NaOH were of analytical grade purchased from Alfa Aesar and Thermo Fisher respectively and used without any further purification. Typical synthesis process of ZnO NPs involved preparation of fresh, homogeneous and clear solutions of 0.5 M Zn(NO₃)₂ and 0.9 M NaOH in ethanol by stirring magnetically for 1 h. Secondly, freshly

prepared solution of NaOH was injected dropwise into $\text{Zn}(\text{NO}_3)_2$ solution under constant stirring for further 1h and let the solution settled down for overnight. The solution was then centrifuged at 8000 rpm for 10 minutes. Finally, white precipitates were obtained indicating the formation of ZnO NPs. Precipitates were washed 3–4 times and dried at 60°C. The dried samples were crushed to obtain fine powders of ZnO NPs.

The structural analysis of the prepared sample is carried out by recording the X-ray diffraction pattern using the RigakuMiniflex X-ray Diffractometer with Cu-K α line ($\lambda=1.54\text{\AA}$) and Fourier transform infrared (FTIR) spectrum in the transmission mode using IRTracer-100 Shimadzu. The optical studies were performed by UV-Vis absorption spectroscopy (UV-VIS 2600 Shimadzu) and fluorescence spectrophotometer (RF-6000 Shimadzu) with an excitation wavelength of 357 nm. M-H curves were recorded using vibrating sample magnetometer (VSM) at 300 K in the applied field of $H = \pm 70$ kOe to study the magnetic behaviour of the synthesized material.

3. Results and Discussions

3.1 X-ray diffraction :

Fig. 1(a) shows the XRD pattern of ZnO nanoparticles over a 2θ range of 20–80° using Cu K α radiation. There exist diffraction peaks corresponding to the planes (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202) and well agreed with the PCPDFWIN No. 790208. Similar structure was also revealed by some other groups^{24,25}. All the diffraction peaks fit with the wurtzite phase of the ZnO nanoparticles which confirms the formation of ZnO with chemical co-precipitation method. No characteristic peaks were observed other than that for ZnO indicating the phase purity of the sample. A definite line broadening and high intensity of the diffraction peak is the indication of the nano range and high crystallinity respectively of the synthesized material.

3.2 FTIR analysis :

FTIR analysis helps to identify the functional groups present in the sample. FTIR spectrum of the ZnO nanoparticles exhibits peaks at $\sim 493\text{ cm}^{-1}$, 562 cm^{-1} , 702 cm^{-1} , 831 cm^{-1} , 1381 cm^{-1} , 1510 cm^{-1} , 1562 cm^{-1} , 1670 cm^{-1} and 3637 cm^{-1} as shown in the Fig. 1(b). These peaks indicate the corresponding characteristic functional groups present in the synthesized sample. The absorption peak at 493 cm^{-1} and 562 cm^{-1} corresponds to the metal-oxygen (ZnO stretching vibrations) vibration mode and absorption at 831 cm^{-1} is due to the formation of tetrahedral coordination of Zn^{26,27}. The bands centered at 1381 cm^{-1} and 1670 cm^{-1} are attributed to the C–O–H bending of carboxylic group and –C=C– aromatic stretching. The broad absorption in the frequency range $3750\text{--}3000\text{ cm}^{-1}$ is assigned to O–H stretching of residual alcohols, water and Zn–OH present in the sample²⁸.

3.3 UV-Vis absorption spectroscopy :

UV- Vis absorption spectroscopy was carried out to estimate the optical band gap of the synthesized nanoparticles. Fig. 2(a) shows the plot for the absorbance as a function of the wavelength.

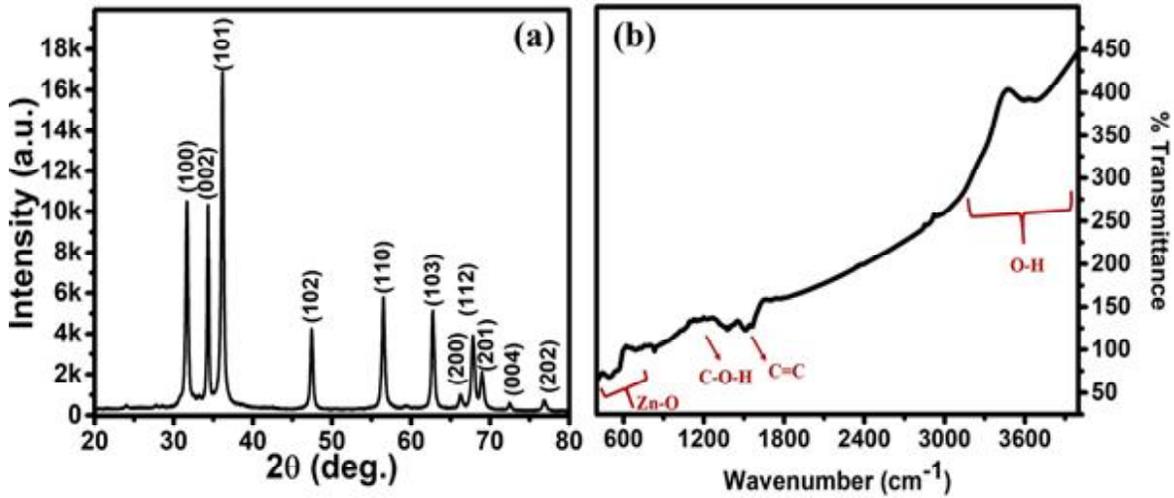


Fig. 1 (a) XRD scan, and (b) FTIR spectrum of ZnO nanoparticles

The absorption peak was recorded at 359 nm which is the characteristic of the pure ZnO. Herein also, the absence of any other peak confirms the formation of ZnO nanoparticles. The band gap of the sample has been calculated by using the equation:

$E_g = \frac{1243}{\lambda} eV$, where λ is the wavelength corresponding to the absorption edge or peak of the material and is estimated to be 3.42eV which is slightly higher than that of bulk ZnO (3.37eV). This blue shift may be attributed to the quantum confinement effects.

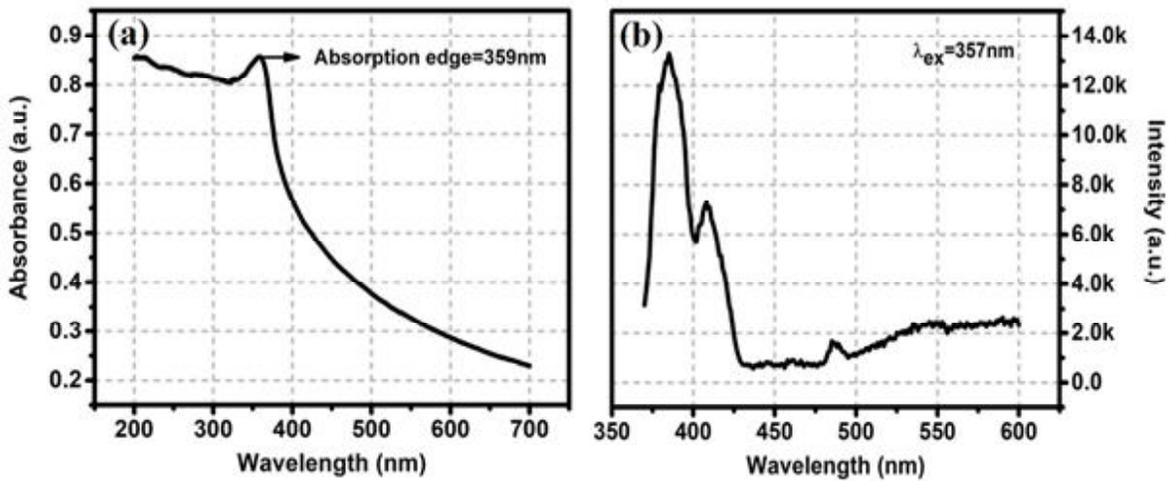


Fig. 2(a) UV-Vis Absorbance, and (b) Photoluminescence emission versus wavelength

3.4 Photoluminescence (PL) studies :

Photoluminescence spectroscopy was employed for the further investigation of the electronic

states accessible between the valence and conduction bands that are responsible for the radiative recombination of the ZnO nanoparticles. Fig. 2(b) shows the PL spectrum of pure ZnO which clearly indicates the presence of three peaks centred at 385 nm (3.22 eV), 407 nm (3.04 eV) and 486 nm (2.55 eV) with the excitation at 357 nm.

The narrow emission band appeared at 3.22 eV is attributed to the quantum confinement effect and can be explained by a near band edge transition of ZnO NPs i.e. the recombination of free excitons through an exciton–exciton collision process²⁹. The generation of other emission peak gives violet emission centered at 407 nm for ZnO NPs. This may be due to the reason that if the electrons are excited to a sub-band of the conduction band, they can first relax to Zn_1 state through a non-radiative transition, and then transit to the valence band³⁰. It is probable that some electrons jump from the conduction band to the defects level of the valence band of Zn and give rise to the violet emission at 407 nm as reported by Xingping Peng *et al.*³¹⁻³³. The blue-green emission band at 486 nm is possibly due to the surface defects in the ZnO NPs corresponding to the transition between oxygen vacancy and oxygen interstitial defect³⁴.

3.5 VSM :

Fig. 3 shows the magnetization (M) versus the applied magnetic field (H) curves. The magnetic parameters such as the saturation magnetization (M_s), coercivity (H_c), remnant magnetization (M_r) and aspect ratio (M_r/M_s) *etc.* are shown in Table 1. It is clear from the figure that the sample exhibit non-saturating hysteresis loops with certain loop width. This indicates the presence of magnetic ordering in ZnO NPs at the room temperature. The observed room temperature ferromagnetism in ZnO NPs may be due to the presence of defects like oxygen vacancy and oxygen interstitials. The results observed here are in line with many reports which suggest that the oxygen vacancies play an important role in introducing ferromagnetism for the ZnO nanoparticles at room temperature³⁵⁻³⁷.

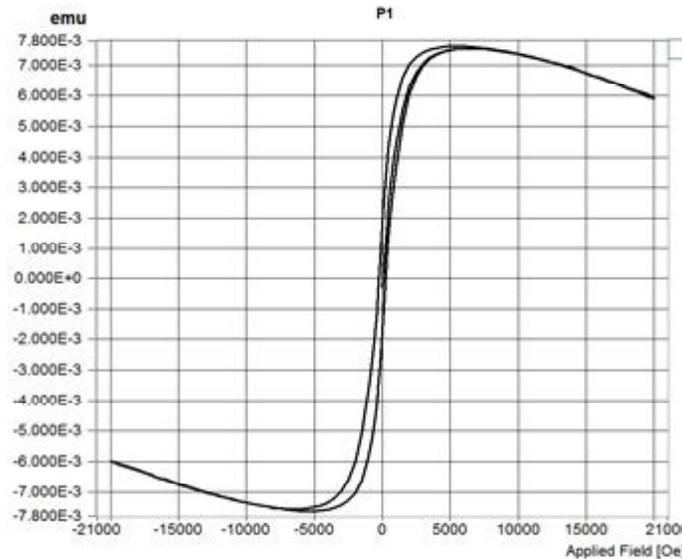


Fig.3 M-H loop for ZnO nanoparticles

Table 1: Parameters for Magnetic behaviour of ZnO nanoparticles at room temperature

	Upward Part	Downward part	Average	Parameter 'definition'
Hysteresis Loop				Hysteresis Parameters
Hc Oe	230.490	-234.206	232.348	Coercive Field: Field at which M/H changes sign
Mr emu	-1.765E-3	1.803E-3	1.784E-3	Remanent Magnetization: M at H=0
S	0.231	0.236	0.234	Squareness: Mr/Ms
S*	0.126	0.102	0.114	1-(Mr/Hc)(1/slope at Hc)
Ms emu	7.630E-3	-7.646E-3	7.638E-3	Saturation Magnetization: maximum M measured
M at H max emu	5.921E-3	-5.985E-3	5.953E-3	M at the maximum field

4. Conclusions

The structural, optical and magnetic properties of chemically synthesized ZnO NPs are studied. Our studies established the successful synthesis of the wurtzite phase of the ZnO nanoparticles as confirmed by XRD studies and further supported by the presence of Zn-O stretching vibration modes peak at 493 cm^{-1} and 562 cm^{-1} . The band gap of the synthesized ZnO NPs is estimated to be 3.42 eV by the absorption peak present in the absorption spectra. The presence of oxygen vacancies confirmed via observation of dip in the FTIR spectra at 831 cm^{-1} corresponding to the formation of tetrahedral coordination of Zn and is further supported by the observation of emission peak at 486 nm. These oxygen vacancies are the cause of observed room temperature ferromagnetism in ZnO NPs.

The exhaustive studies regarding the role played by the oxygen vacancies in inducing RTFM in chemically synthesized transition metal (TM) doped/co-doped DMS ZnO nanoparticles may be carried out in future towards spintronic applications of such materials.

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