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IMPROVED AND UNUSUAL MAGNETIC PROPERTIES OF ZnO NANORINGS

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We report the novel result regarding the observation of unusual magnetic behavior with high magnetic moment (higher than reported so far) at room temperature in highly pure ZnO nanorings synthesized by a simple chemical route using cetyltrimethyl ammonium bromide. The enhanced magnetization is attributed to the huge number of surface spins associated with defects created due to the larger surface to volume ratio of nanorings. The present study demonstrates that ZnO samples can be made highly magnetic just by tailoring the nanostructure even without doping transition-metal. Some new magnetic features have been observed and possible explanations are delineated here.

Keywords: ZnO nanorings; chemical route; magnetization.

Magnetic semiconducting materials are efficient in continuous transfer of information between semiconductors (microprocessors) and magnetic materials (memories), leading to faster and cheaper devices.[1–4] In this context, one of the most versatile systems is zinc oxide, ZnO. The novel magnetic, electronic, optical and electromechanical properties of ZnO offer the unique possibility to multifunctionally create integrated devices for practical applications.[5–10] In particular, recent experimental results on ZnO nanoparticles have revealed ferromagnetism even in the absence of magnetic impurities.[11–14] 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 have been reported[15–18] which affects the properties. Also surface defect is a very important factor of the origin of the ferromagnetism in ZnO, especially for nanoparticles.[19–21]

In this paper, we experimentally demonstrate for the first time that ZnO nanorings show 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).

ZnO nanorings were synthesized by precipitation of 50 ml $Zn(NO_3)_2$ solution (0.05 M) with 50 ml NaOH solution (0.1 M). Initially, 0.01 M cetyltrimethyl ammonium bromide (CTAB) was added to both the solutions. The white precipitate formed by addition of NaOH solution to the salt

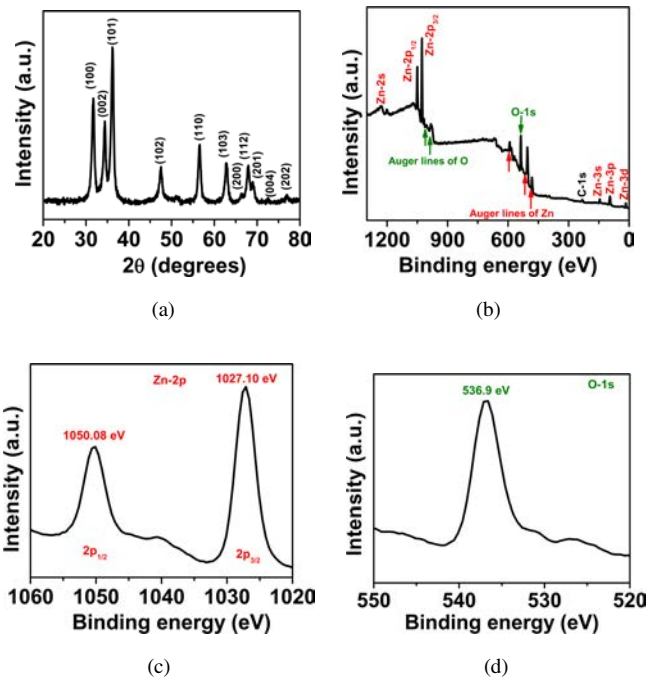

Fig. 1. (a) XRD pattern of the as-synthesized ZnO sample, (b) XPS survey scan spectrum, high resolution scan of (c) Zn 2p, (d) O 1s, for ZnO sample.

solution, was filtered, washed several times with water and then dried at 333 K for three days.

The crystal structure and morphology of the sample was determined using Rich Seifert X-Ray diffractometer (XRD) 300P and JEOL 2010 transmission electron microscope (TEM) operated at 200 kV and equipped with a detector for energy dispersive X-ray spectroscopy (EDS) study. The X-ray photoelectron spectrum (XPS) of the sample was recorded on Specs (Germany) spectrometer. The magnetic measurements were performed on a Quantum Design SQUID MPMS VSM. The hysteresis loops and field cooled (FC) — zero field cooled (ZFC) curves were measured within temperature range 4−300 K.

Figure 1(a) presents a typical XRD pattern of the as prepared ZnO sample. The peaks can be well indexed to hexagonal ZnO, consistent with standard data [JCPDS no. 36-1451]. No peaks corresponding to any impurities are present which suggests that the synthesized product is pure ZnO. The lattice parameters as obtained using TREOR analysis are $a = 0.3254$ nm and $c = 0.5210$ nm. The average crystallite size of the sample was determined using standard Debye-Scherrer formula. The average crystallite size is calculated to be 12 nm within an error of ±1 nm.

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 Fig. 1(b). 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 any ferromagnetic impurities like Mn, Fe, Co or Ni. Figure 1(c) 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 Fig. 1(d) and the peak at 536.9 eV is assigned to O^{2-} ion in wurtzite structure of ZnO.

The morphology of the synthesized sample was investigated using transmission electron micrographs. The typical electron micrograph confirms the presence of irregular shaped annular ring like structures of ZnO as can be seen from Fig. 2(a) (marked with red lines). The sample exhibited a wide distribution of size of nanorings with average diameter 14 nm. The high resolution transmission electron micrograph (HRTEM) of the nanoring is presented in Fig. 2(b). The nanorings are formed by coalescence of ultrafine crystalline nanoparticles with average size ∼ 4 nm. The d-spacing as observed from HRTEM image is 0.24 nm which corresponds to (101) plane of hexagonal ZnO. The hexagonal structure is further examined from the fast Fourier transformation (FFT) pattern [shown in the inset of Fig. 2(a)]. The hexagon is drawn just to give a better presentation. We have also explored EDS facility attached to TEM to check the presence of different elements. EDS spectrum of the nanorings are

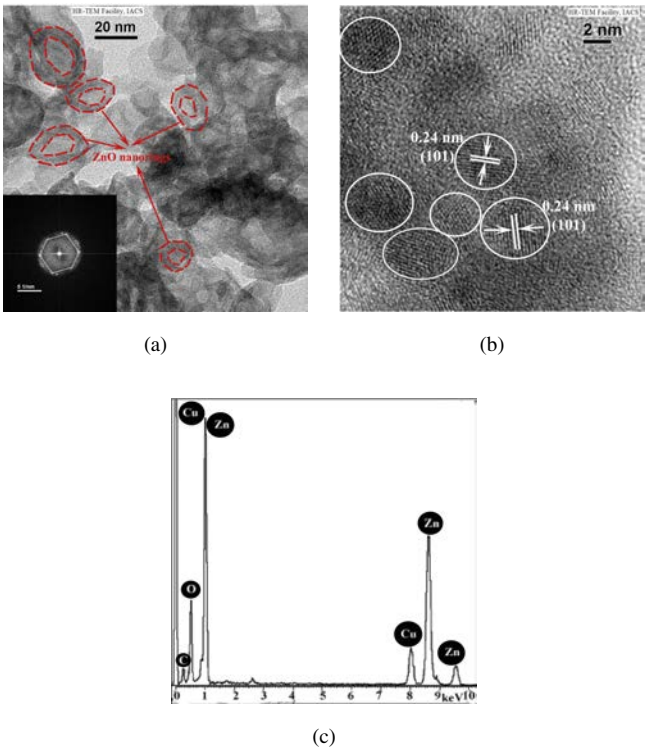

Fig. 2. (a) Transmission electron micrograph of the ZnO nanorings. Inset: FFT showing hexagonal ZnO structure. (b) HRTEM of ZnO nanorings. (c) EDS spectrum of the nanorings.

presented in Fig. 2(c) which confirms the presence of the element Zn and O. The element C comes from the carbon coated copper grid on which a drop of ethanol containing the sample was cast. The EDS spectrum strengthens our arguments that no other magnetic impurities are present in the sample. Together with XRD and XPS study, HRTEM analysis also confirms that the prepared sample is pure, single phase ZnO and nanocrystalline in nature.

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. 3. 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.[22] Further, we observe that the magnetic moments are almost thermally independent beyond the hump as illustrated in Fig. 3.

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.[11] 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 EDS also confirms the absence of any ferromagnetic impurities. The appearance of magnetization can

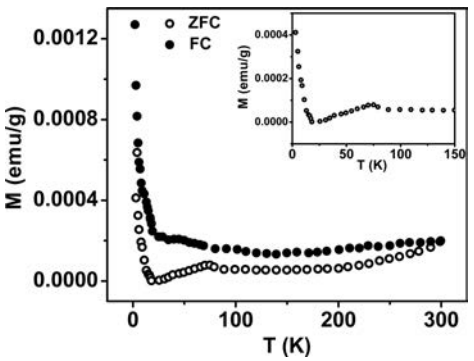

Fig. 3. ZFC−FC curve of ZnO nanorings at 100 Oe magnetic field. Inset: ZFC curve up to 150 K.

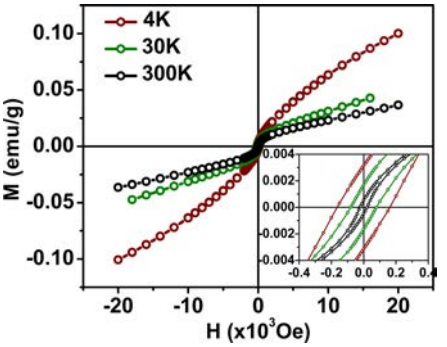

Fig. 4. Hysteresis loops of ZnO nanorings at different temperatures.

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.[11]

Figure 4 presents the 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 expanded portion of the Fig. 4 is placed in inset to visualize the coercive field. The values of the coercive field (H_c) and maximum magnetization (M_{max}) obtained at the applied magnetic field of 2 T at different temperatures are presented in Table 1. 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/g),[11] PVP capped ZnO nanocrystals (∼0.007 emu/g),[13] ZnO nanorods (∼0.004 emu/g).[21] 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 induce the magnetic property of the ZnO nanorings. The modification of electronic structure is further proved from the room temperature photoluminescence spectrum of the sample.[23]

Table 1. Datas extracted from magnetic measurements.

T(K)	H_c(Oe)	M_{max}(emu/g)
4	163.2	0.100
30	80.6	0.049
300	23.1	0.036

To summarize, we are able to prepare ZnO nanorings through a simple chemical route in the presence of CTAB. An unusual magnetic behavior is observed indicating the presence of both ferromagnetic and antiferromagnetic order. We also observe highest magnetic moment in pure ZnO nanoparticles reported so far. 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. Observed high magnetic moment may find some possibility of creating room temperature magnetic semiconductor for spintronics applications.

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