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Tuning the magnetic behavior and improving the antibacterial efficiency of ZnO nanopowders through Zr+Fe doping for biomedical applications

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Abstract

Zr and Zr+Fe co-doped ZnO nanopowders were synthesized using a simple soft chemical method keeping the doping level of Zr as constant (3 at%) and varying the doping level of Fe (1,5and 10 at%) in the precursor solution. The XRD studies reveal that the synthesized nanopowders exhibit hexagonal wurtzite structure of ZnO. The crystallite size of ZnO:Zr nanopowders is found to be 63 nm and then the size decreases gradually with the increase in the Fe doping level and attains a minimum of 28 nm at 10 at% of Fe doping level. The Zr doped ZnO nanopowders are found to have ferromagnetic property. The material exhibits paramagnetic nature up to 5 at% of Fe doping level. At 10 at% of Fe doping level superparamagnetic behavior is observed. The antibacterial efficiency against two different bacterial strains viz *Bacillus subtilis* and *Escherichia coli* is studied. The antibacterial efficiency is found to be the maximum at 10 at% of Fe doping level.

Keywords: A. Powders: chemical preparation; C. Grain size; D. Magnetic properties; E. Biomedical applications

1. Introduction

Semiconductor materials with desired magnetic properties as well as good antibacterial efficiency are much needed for use in biomedical applications because in a targeted drug delivery system, drug carrying magnetic nanoparticles (MNPs) with a suitable carrier system taken orally or injected through vein are directed to the diseased area by an external magnetic field [1–3].

Zinc oxide (ZnO) is one of the most promising multi-functional semiconductors which have potential applications in magnetically targeted drug delivery systems as its magnetic property can be tuned by the addition of suitable dopants [4,5]. It is biocompatible, biosafe and an antibacterial agent which is a promising material for the application in the field of biomedicine [6,7]. In our previous studies it was found that the simultaneous doping of some transition metal ions can enhance those properties further [8–11]. Hence in the present work, the magnetic and antibacterial properties of the ZnO nanoparticles are tuned by enhancing the carrier concentration with the help of simultaneous doping of zirconium (Zr) and iron (Fe) [12,13].

Various methods such as auto combustion [14], sol–gel [15], co-precipitation [16], hydrothermal [17], electrochemical [18] and soft chemical [19,20] have been employed to synthesize undoped and doped ZnO nanomaterials. Of these, the soft chemical method has been used as it is cost effective, requires low temperature and less processing time and enables easy doping [21,22].

In this work, Zr and Fe co-doped ZnO nanopowders were synthesized using simple soft chemical method. To the best of

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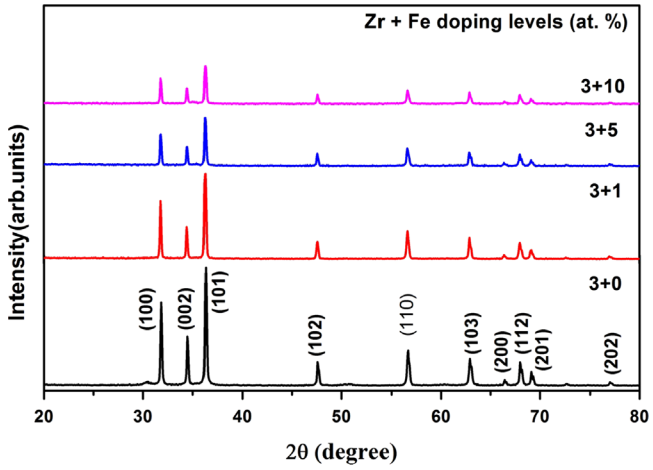

Fig. 1. XRD patterns of Zr and Zr+Fe doped ZnO nanopowders.

our knowledge, this is the first report on the Zr+Fe doped ZnO nanopowders prepared using the simple soft chemical method.

2. Materials and methods

2.1. Synthesis process

Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) (0.2 M) was used as a host precursor. Zirconyl nitrate ($ZrO(NO_3)_2 \cdot H_2O$) and ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) were used as dopant precursors for Zr (3 at%) and Fe (1, 5 and 10 at%), respectively. The precursors were dissolved in 200 mL of distilled water. The pH value was maintained at 7 by adding suitable amount of NaOH solution drop by drop with the starting solution. The prepared solution was stirred using magnetic stirrer for 2 h at a temperature of 85 °C and then allowed to cool to room temperature and kept undisturbed for 1 h to get the required precipitate. The precipitate was filtered and rinsed separately with water and ethanol several times and then dried in air at room temperature. Finally, the samples were calcined at 550 °C for 3 h to obtain the final product.

2.2. Characterization of ZnO:Zr:Fe nanopowders

The structural studies were carried out using X-ray diffractometer (XRD) (PANalytical-PW 340/60 X'pert PRO). Fourier transform infrared (FTIR) spectra were obtained using a Perkin–Elmer RX-I FTIR spectrophotometer. The surface morphology was studied using Field Effect Scanning Electron Microscope (FESEM, Hitachi SU8000) and Transition Electron Microscopy (TEM, Hitachi H-7100). The elemental analyses were made using energy dispersive X-ray analysis (EDAX) (Model: JEOL-JSM 6390 with attachment INCA-Penta FETX3 OXFORD). Photoluminescence (PL) spectra were observed using spectro-flurometer (Jobin Y Von _ FLUROLOG-FL3-11) with xenon lamp (450 W) as the excitation source of wavelength 325 nm. The room temperature magnetic properties were studied using a vibrating sample magnetometer (VSM, Lake Shore-7400, USA).

2.3. Evaluation of antibacterial activity

Antibacterial activitives of the synthesized ZnO:Zr:Fe nanopowders were tested against *Bacillus subtillis* (*B. subtillis*), and *Escherichia coli* (*E. coli*) bacteria using an agar well diffusion method. For bacterial growth Mueller Hinton Broth was used as nutrient agar medium. Four wells each of diameter 5 mm were made and 200 μg/mL of stock solution of the samples were poured into the wells. The plates were incubated at 37 °C for 24 h and the diameter of the inhibition zone was measured in mm. The dimethyl sulfoxide (DMSO) was used as the control.

3. Results and discussion

3.1. Structural studies

X-ray diffraction patterns of the Zr and Zr+Fe co-doped ZnO nanopowders are shown in Fig. 1. The peaks observed at Bragg's angles 31.82 °, 34.47 °, 36.30 °, 47.59 °, 56.64 °, 60.23 °, 62.91 °, 66.41 °, 67.99 ° and 77.02 ° are associated with the lattice planes (100), (002), (101), (102), (110), (103), (200), (112), (201) and (202), respectively. All the observed diffraction peaks are well matched with the standard JCPDS file (Card no: 36-1451) indicating that the synthesized samples have hexagonal wurtzite structure of ZnO. No other secondary phases related to either Zr or Fe are observed even at higher doping levels of Fe, which shows that the dopants are incorporated into the ZnO lattice.

The observed slight shift in the peaks towards lower angles may be due to the substitution of higher ionic radii dopant ions (Zr^{4+} (84 pm) and Fe^{2+} (77 pm)) in the regular sites of Zn^{2+} (74 pm) [23,24]. As the concentration of the Fe level increases, the intensities of the peaks decrease indicating a gradual degradation in the periodicity of the crystal lattice caused by excess Fe incorporation.

The crystallite size (D) and the lattice parameters 'a' and 'c' are calculated using the following formula [25]:

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

where 'λ' is the wavelength of the X-ray used, 'β' is the full-width at half-maximum (FWHM) and 'θ' is the Bragg's angle [3] and

$$1/d^2 = 4/3\left(h^2 + hk + k^2/a^2\right) + l^2/c^2 \quad (2)$$

where 'd' is the interplanar spacing and h, k and l are the Miller indices.

The micro strain (ε) along the c-axis is calculated using the formula [3]

$$\varepsilon = c - c_0/c_0 \quad (3)$$

where c and c_0 are the calculated and standard lattice constant values, respectively.

From Table 1 it is observed that the crystallite size decreases gradually from 63 to 28 nm as the Fe doping concentration increases from 1 to 10 at%. This decrease in the crystallite size may be due to the Zener pinning effect as explained in our