Materials Letters 142 (2015) 30–34

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

A novel one-pot synthesis of hierarchical europium doped ZnO nanoflowers

Amit Panwar [a], K.L. Yadav [a,b,*]

[a] Centre for Nanotechnology, Indian Institute of Technology Roorkee, Roorkee 247667, India
[b] Department of Physics, Indian Institute of Technology Roorkee, Roorkee 247667, India

ARTICLE INFO

Article history:
Received 28 October 2014
Accepted 27 November 2014
Available online 3 December 2014

Keywords:
Nanocrystalline materials
Nanosize particles

ABSTRACT

The effect of dopant concentration on the morphology of ZnO nanostructures was investigated. This study demonstrated morphological changes in ZnO nanostructures from spherical to flower-shaped on increasing dopant concentration. The structural and morphological changes in europium doped ZnO nanostructures are validated by SEM and TEM results, clearly indicating the formation of hierarchical ZnO nanoflowers as the dopant concentration is increased to 5%. The phenomenal morphological and optical emission characteristic of europium doped ZnO nanoflowers may serve as a potential material in materials science and other fields of technology.

1. Introduction

Zinc oxide (ZnO) is a potential material with huge number of researchers around the world exploring its wide range applications as UV laser devices [1], biomedical labels [2], solar cells [3], chemical sensors [4], electronics [5], acoustic and luminescent devices [6]. Being a wide direct band gap semiconductor, with band gap of 3.37 eV [7,8] makes it a material with promising photonic properties in UV or blue spectral range [9]. The band gap and optical properties of ZnO nanostructures can be tailored by changing the shape and size of the particles [10], as well as, by doping ZnO structures with different elements. The wide band gap energy of ZnO presents it as a versatile host lattice for doping different elements [11].

The dopant influences the size and morphology of the ZnO nanocrystal by participating in growth pattern of nanocrystal [12]. The striking effect on the shape and morphology of ZnO nanocrystals with the nature of dopant ion, e.g. ionic radius and electronic configuration has been investigated in various studies [1,3]. Morphological changes from spherical particles to flowers by Na doping [13], change in the nanorod morphology of pure ZnO to nanoparticles by Cu^{2+} doping [14], as well as ZnO nanoparticles with tetrapod morphologies by Co doping have been observed [15].

The optical properties of ZnO nanostructures have also been altered by doping them with rare earth metals. The high fluorescence efficiency of rare earth metal doped nanostructures has been of key interest in development of next-generation photonic devices and biolabels. Among the various rare earth metals, europium is one of the most eligible elements which can be acclaimed for its ability to tailor the optical properties of ZnO nanostructures. Trivalent europium ion is a common dopant of different compounds, showing red emission, with the emission mechanism depending upon energy of 4f emitting level [16].

Various nanostructure forms of europium doped ZnO have been demonstrated by following different synthesis methodologies, like, vapor deposition method [17], hydrothermal method [18], solution combustion method [19] and sol–gel method [20]. In this study, a novel facile method for synthesis of europium doped ZnO nanostructures has been demonstrated. The study follows to pay emphasis on development of esthetic morphological and optical changes in ZnO nanostructures on doping with europium.

2. Materials and methods

Zinc nitrate ($Zn(NO_3)_2$) and europium oxide (Eu_2O_3) were purchased from HiMedia, India. Triethanolamine ($C_6H_{15}NO_3$) was used as a capping agent and was obtained from Rankem, India. All the chemicals were of analytical grade and were used as received without further purification. The solutions were prepared using Millipore water.

The structural and crystal phases of nanostructures were determined by powder XRD patterns recorded using a Bruker AXS D8-Advance powder X-ray diffractometer (CuKα) at a scan speed of 1°/min. IR spectra of the ZnO nanostructures were recorded using a Thermo Nicolet FT-IR spectrometer in the range 4000–400 cm^{-1}

---

[*] Corresponding author at: Department of Physics, Indian Institute of Technology Roorkee, Roorkee 247667, India. Tel.: +91 1332 285744.
E-mail address: klalyfph@iitr.ernet.in (K.L. Yadav).

http://dx.doi.org/10.1016/j.matlet.2014.11.143
0167-577X/

using KBr pellets. The thermal gravimetric analysis (TGA) was carried out, in air, using a PerkinElmer Pyris Diamond instrument with a heating rate of 10 °C/min. Field emission scanning electron microscopy (FE-SEM) images along with energy dispersive X-ray (EDX) analysis were recorded using a FEI Quanta 200F microscope operating at an accelerating voltage of 20 kV. A TECNAI G2 transmission electron microscope (TEM) operating at 200 kV was used for the identification of morphology and size of the nanoparticles. Photoluminescent studies were carried out using a Hitachi F-4600 fluorescence spectrophotometer.

The typical procedure for synthesis of pure ZnO nanostructures was as in an earlier report [21]. The europium doped ZnO (Eu–ZnO) nanoparticles were synthesized by a one-pot chemical method using zinc nitrate hexahydrate and europium oxide as zinc and Eu^{3+} sources, respectively. Before starting the reaction, europium oxide was converted into europium nitrate with the use of 10% HNO$_3$ solution. In a typical synthesis, a combined solution of Eu(NO$_3$)$_3$ and Zn(NO$_3$)$_2 \cdot$6H$_2$O was made with an atomic ratio of Eu/(Eu+Zn)=0%, 2%, 5% and 8%. The final molar ratio of the solution was 0.48 M in 25 ml. Another solution of 1.07 M triethanolamine in 25 ml was also prepared, where TEA acted as a capping agent during the synthesis of ZnO nanoparticles. The above solutions were mixed at 25 °C under continuous stirring. The pH of the reaction was adjusted to 8, using ammonia, to obtain a clear solution. The mixture was stirred continuously for 3 h at 80 °C. The clear solution gradually became colloidal during the increase in temperature. The sample was then centrifuged at 1500 rpm for 10 min to discard the supernatant. The ZnO precipitate was washed with absolute ethanol and water, successively, and then air-dried in an oven at 40 °C.

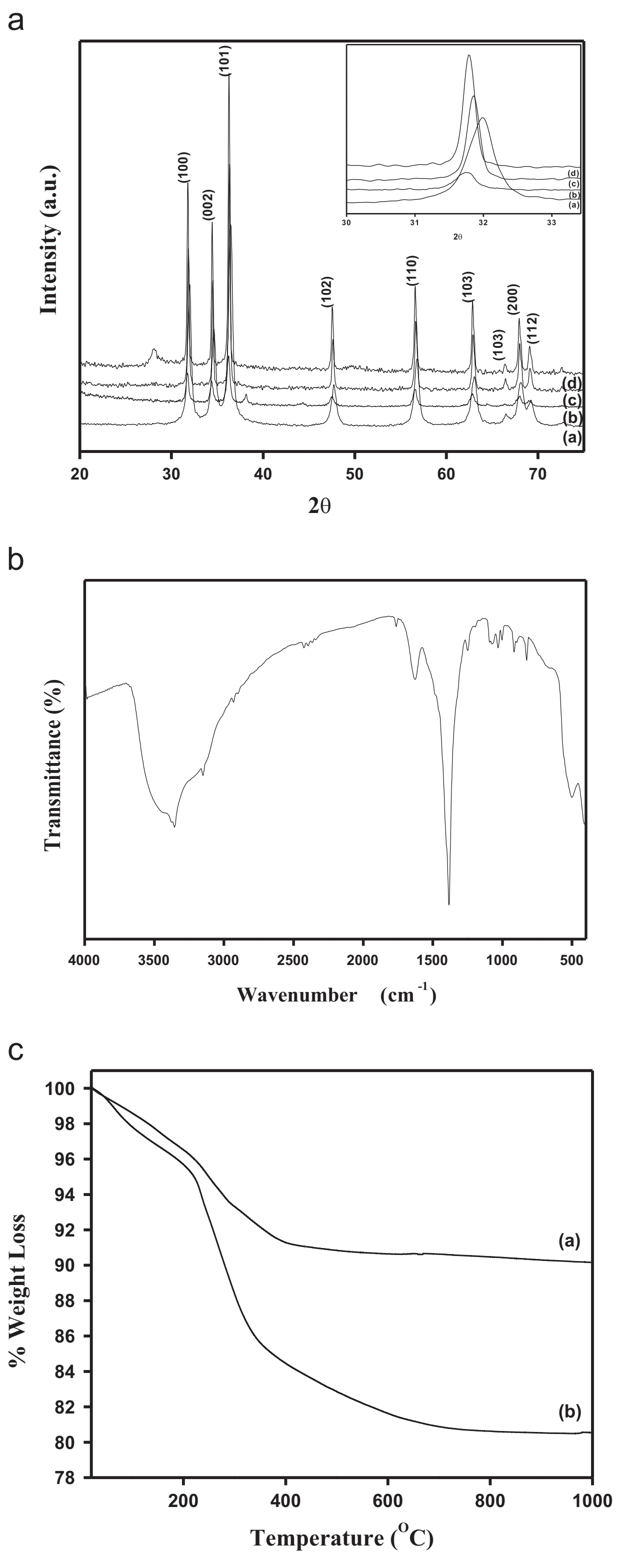

Fig. 1. (A) The XRD patterns of (a) pure ZnO and (b)–(d) Eu–ZnO nanostructures prepared using different doping percentages, 2%, 5% and 8%. Inset shows magnified image of peak corresponding to (100). (B) The FTIR spectra of Eu–ZnO nanostructure at europium doping percentage of 5%. (C) TGA analysis of (a) pure zinc oxide and (b) 5% Eu–ZnO nanoparticles.

3. Results and discussion

Europium doped ZnO nanostructures were synthesized by a wet chemical method. First, ZnO nanostructures were synthesized and characterized for their structure. Further, ZnO nanostructures were doped with europium and its effect on morphology and optical properties was analyzed. The XRD patterns of pure ZnO and Eu doped ZnO nanostructures prepared by using different doping percentages (2%, 5% and 8%) are shown in Fig. 1(a). The patterns show sharp characteristic peaks corresponding to perfect Wurtzite structure of ZnO (JCPDS data card no: 05-0664) for all the samples. A shift in all the peaks of the doped sample was observed towards a lower 2θ value. The shift in (100) peak can be clearly observed in the inset of Fig. 1. The shift in the diffraction peaks towards a lower 2θ corresponds to increase in the lattice parameters of the ZnO crystal structure due to doping of the bigger size Eu^{3+} cations (effective ionic radii r=0.947 Å) in place of comparatively smaller Zn^{2+} (r=0.74 Å) [17]. The shift in peak is observed to increase with increase in doping concentration. The peak shift, therefore, indicates successful doping of Eu in the ZnO nanostructures. The FTIR spectra of Eu–ZnO nanostructures (Eu=5%) displayed characteristic bands at 1013, 1071, 1631, 1710 and 2840–2960 cm^{-1} corresponding to ν (C–N), ν (C–O), ν_s (N–H), ν_a (N–H) and ν_a–ν_s (N–H), respectively (Fig. 1(b)). The presence of these bands in the FTIR spectra confirmed the capping of Eu doped nanostructures with protonated triethanolamine. Additional bands at 3434 and 420 cm^{-1} were representation, respectively, of–OH stretching originated from the water molecules adsorbed on the ZnO surface and ν (Zn–O) bond in the nanostructures [21]. Thermal Gravimetric Analysis (TGA) of pure zinc oxide and 5% Eu–ZnO nanoparticles is shown in Fig. 1(c). TGA analysis shows two steps weight loss due to dehydration and evaporation of triethanolamine (TEA). The first weight loss step that lies between 20 and 170 °C is due to dehydration of water and second major step that lies between 200 and 400 °C due to evaporation of triethanolamine. The weight loss due to evaporation of triethanolamine is 20% in 5% Eu–ZnO nanoparticles, whereas, the weight loss at the same step was 5% in pure ZnO nanoparticles. This indicates a significant change in size or shape of ZnO nanoparticles after doping with 5% europium (Fig. 2).