Sonochemically synthesized iron-doped zinc oxide nanoparticles: Influence of precursor composition on characteristics

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ABSTRACT

Iron-doped zinc oxide nanoparticles have been synthesized sonochemically from aqueous acetyl acetonate precursors of different proportions. Synthesized nanoparticles were characterized with UV–vis spectroscopy, X-ray diffraction and microscopy. Influences of precursor mixture on the characteristics have been examined and modeled. Linear correlations have been proposed between dopant dosing, extent of doping and band gap energy. Experimental data corroborated with the proposed models.

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1. Introduction

ZnO is a widely studied chemically stable and biocompatible n-type semiconductor material having a wide band gap of 3.2 eV with a large binding energy of 60 meV at room temperature [1–4]. The range of application of zinc oxide nanoparticles are wider compared to the bulk counterpart [5]. The optical and electronic properties of semiconductor nanocrystals can be 'engineered' for its practical applications by doping with transition metals (TM) [6–10]. Generally, the metal sites are considered to act as trapping sites by accepting the photogenerated electrons from the ZnO, restraining recombination of the hole–electron pair, and thus improving the photo catalytic activity of the material by decreasing its band gap energy [11]. Doping or surface modification is a possible way to shift the photo response of ZnO into the visible light region. Therefore, many efforts have been made to modify ZnO by introducing various TM cations into its lattice.

There are several methods of introducing dopant into a ZnO lattice. Chemical method [12,13], sol–gel technique [14], solid-state reactions [15,16], co-precipitation [17] and pulsed laser deposition [18,19] are a few of them. Iron oxide is the most popular dopant for ZnO owing to its compatibility with Zn^{2+} ion as per Hume-Rothery rule, due to its abundance and low cost, as well as its non-toxicity, which maintains the biocompatibility of ZnO particles [20]. It can impart ferrimagnetism to the semiconductor as well [21,22]. In addition of being a sunlight-efficient photo-catalyst, Fe-doped ZnO nanoparticle can have its application in the fields of human-diagnosis and spintronics.

The use of ultrasound is an important tool to enhance chemical reactivity of the synthesized nanostructures for the energy efficiency and environment–friendliness [23]. Advantages of sonochemical synthesis are summarized by Manickam and Rana [24]. The most significant ones are decrease in reaction time, mild reaction conditions, versatility with solvents, avoidance of toxic solvents and high annealing temperature. Ultrasound can be induced into a solution directly or indirectly by using probe or bath type sonicators respectively. Direct ultrasound is more powerful and requires less reaction time [25]. Ultrasound, when passed through a liquid reaction mixture, propagates through a series of rarefaction and compression waves. Cavitation bubbles are formed when the rarefaction cycle exceeds the attractive forces of the liquid molecules. Implosions of collapsing bubbles generate energy for mechanical and chemical effects [26]. Reports are available on the sonochemical synthesis of different nanomaterials. Bang and Suslick [27] reviewed applications of ultrasound in the synthesis of

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nanomaterials. Very few reports are available on sonochemical synthesis of doped ZnO nanoparticles. Khataee et al. [28] sonochemically prepared $Pr_xZn_{1−x}O$ ($x = 0–0.05$) nanoparticles from $ZnCl_2$ (99.5%) and $Pr(NO_3)_3$, $6H_2O$ (99.99%). Synthesized nanoparticles were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) techniques. SEM images revealed that incorporation of Pr into ZnO structure restrains the aggregation phenomenon. XPS spectra verified the presence of Pr in the doped samples. Phuruangrat et al. [29] also synthesized ZnO and Ho-doped ZnO samples by sonochemical method. They used $(Zn(NO_3)_2, 6H_2O)$ and $(Ho(NO_3)_3, H_2O)$ as zinc and holmium source respectively and NaOH as hydrolyser. Morphologies and structures of the nanoparticles were characterized by XRD, SEM and TEM. The SEM and TEM revealed a flower-like structure composed of numerous one-dimensional hexagonal nanoprisms ZnO and Ho doped ZnO growing along [0 0 2] direction. Chakma et al. [30] reported ultrasound assisted impregnation method for synthesis of Fe^{3+} doped ZnO from a mixture of calcined ZnO and aqueous solution of $Fe_2(SO_4)_3, H_2O$ by sonicating for 2 h. Nanoparticles thus synthesized were characterized by XRD, FTIR, zeta potential, DelsaNano particle size analyzer (PSA), vibrating sample magnetometer analysis (VSM) and field emission scanning electron microscopy (FE-SEM). Pure ZnO and Fe-doped ZnO both were characterized to compare BET surface area which was reduced in case of doped ZnO. Doped ZnO particles were much monodispersed than undoped one. Nanostructures of ZnO doped with Sb^{3+} ions with dopant content ranging from $x = 0.00$ to 0.15 were prepared by Omidi et al. [31] in water under ultrasonic irradiation for 60 min. Zinc acetate and antimony chloride were used as precursors. The nanostructures were characterized by XRD, FTIR, SEM and DRS techniques. XRD results showed that the particles were in wurtzite hexagonal crystalline phase and the mean particle size decreased with increasing doping concentration due to formation of Sb—O—Zn bonds on the surface of the doped nanostructures. SEM structures revealed the particles were mainly plates with different sizes.

This paper aims at describing the ultrasound assisted synthesis of Fe-doped ZnO nanoparticles from organic precursors, acetyl acetonates of zinc and iron. Nanoparticles thus synthesized were characterized by DLS, FESEM, EDX, XRD, UV–vis spectroscopy and SQUID. Influence of the precursor-composition on the characteristics was examined. Similar studies were done by Chakrabarti et al. [32] earlier. They obtained correlations between dopant-concentration and grain size as well as between temperature and grain size and extent of doping. Here correlations have been obtained between dopant concentration and band gap as well as between dopant concentration and extent of doping. A particular pattern was observed for the dimensions along [1 0 0], [1 0 1] and [0 0 1] with dopant concentrations.

2. Materials and methods

2.1. Chemicals

(a) Zinc acetyl acetonate, $Zn(acac)_2$ (A.R., MP Biomedicals, LLC, France; M.wt. 263.6082) (b) Ferric acetyl acetonate, $Fe(acac)_3$ (A.R., Spectrochem Pvt. Ltd., Mumbai (India); M.Wt. 353.18) (c) Ethanol (A.R) and (d) single distilled water as solvent.

2.2. Preparation of iron-doped zinc oxide nanoparticles

For the preparation of iron-doped zinc oxide nanoparticles two precursors were taken with 20 ml of ethanol and it was shaken thoroughly until the solutes were dissolved completely. After that water was added to make the total volume to 230 ml for exposing to ultrasound using $30 ± 3$ kHz frequency ultrasonic probe (Trans-O-Sonic, Model: D-120/P) for a period of 40 s. The pulse mode used was '1 s on and 1 s off' for optimum use of ultrasonic power. After sonication, the content became slightly turbid. The turbid solution was poured onto a petri dish of 6 in. diameter and dried in a vacuum oven at 700–750 mm Hg vacuum at 65–100 °C temperature to drive off the solvents. The dry powder obtained was repeatedly washed with a mixture of 1:1 distilled water and ethanol, centrifuged using a REMI R-24 research centrifuge, followed by drying again under vacuum till constant weight and stored in a dessicator.

2.3. Characterization of the nanoparticles

The nanoparticles were characterized by DLS (dynamic light scattering), XRD (X-ray diffraction spectroscopy), FESEM (field emission scanning electron microscopy), EDX (energy dispersive X-ray spectroscopy), UV–vis spectroscopy and SQUID-VSM (superconducting quantum interference device-vibrating sample magnetometer) instrument. Z-average size and particle size distribution analysis was evaluated using a Zetasizer Nano-ZS90 System (Malvern Inc.). Structural characterization was performed with X-PERT-PRO PANalytical instrument diffractometer using Cu Kα ($λ = 1.5406$) at a scanning rate of 1°/min and generator voltage of 40 kV and current of 30 mA in the range from 10° to 90°. The X-ray diffraction (XRD) patterns of the nanoparticles were verified by comparison with the JCPDS data (No. 36-1451). Sizes of the nanoparticles have been calculated using the well known Scherrer equation [33].

$$t = \frac{0.9λ}{B\cos θ} \tag{1}$$

where t is the grain thickness, $λ$ is the wavelength of the X-ray, B is FWHM value of the XRD peaks and $θ$ is the diffraction angle. Cell volume and lattice parameters (a and c) were calculated by UnitCellWin software. Optical characterization has been performed using a HITACHI U-4100 spectrophotometer with a photon wavelength range 200–800 nm. Size and surface morphology of ZnO was analyzed using FESEM (JEOL-SEM/Carl Zeiss, Germany, Supra 35VP). The samples for FESEM were prepared on glass slides. Elemental analysis of the samples was done by energy dispersive X-ray spectroscopy (EDX) using Oxford Link Isis (UK) instrument that was fitted with a scanning electron microscope. MPMS SQUID VSM (Quantum design) instrument was used for analysis of magnetic properties of the nanoparticles.
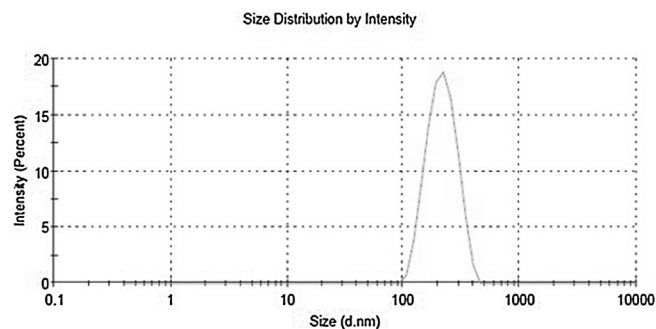

Fig. 1. Particle size distribution of Fe doped ZnO (0.053 mmol Fe/mmol Zn precursor composition).