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Structural, morphological and optical properties of Eu-N co-doped zinc oxide nanoparticles synthesized using co-precipitation technique

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ABSTRACT

The doping of metal oxides with rare-earth element is an effective way of enhancing the optical properties of ZnO nanoparticles. The ZnO nanoparticles were prepared using co-precipitation method with different concentrations of Eu, constant N doping and characterized through X-ray diffraction, scanning electron microscopy, Raman spectroscopy and UV-visible spectroscopy. The Rietveld refined XRD of ZnO nanoparticles confirms the hexagonal wurtzite structure. The XRD results indicated that crystallite size increases with doping and found in the range of 37–52 nm. Scanning electron microscopy illustrated that ZnO nanoparticles were less agglomerated and the average size of nanoparticles was found to increase from 62 to 90 nm with doping. Raman spectrum also confirmed hexagonal wurtzite arrangement of all samples. The band gap of pristine ZnO nanoparticles was found 3.18 eV as confirmed by UV-visible spectroscopy. The red shift (3.14 eV & 3.16 eV) in band gap was observed at 2 & 3 mol% of Eu, while blue shift (3.20 eV & 3.23 eV) in band gap was observed at 1 & 4 mol% of Eu respectively. This modification in the band gap makes ZnO nanoparticles an appropriate electrode material for dye-sensitized solar cells and optoelectronic devices.

1. Introduction

In recent years, metal oxide semiconductors are a subject of active research owing to developing optoelectronic and electronic devices for the immensely market demands. Among different metal oxides, Zinc oxide (ZnO) is paramount n-type inorganic semiconductor material with wide direct band gap 3.37 eV and high exciton binding energy 60 meV [1]. These interesting properties make ZnO as an appropriate candidate in several applications viz. optoelectronic devices, spintronic devices, solar cells, light emitting diodes, photocatalysts and gas sensors [2–7]. It is more stable in hexagonal wurtzite arrangement at room temperature rather than zinc blende and rock salt structure [8]. The intrinsic and extrinsic defects such as zinc interstitials and oxygen vacancies affect the structural and optical behavior of ZnO. The control of defects and charge carriers improve the performance of various applications of ZnO based on the structural and optical properties [9–11]. Wang and Zhang studied photoluminescence property of ZnO nanowires and investigated that oxygen antisite and oxygen vacancy coexists in ZnO and induces visible light emission [12].

The control of size and morphology is the major problem for preparing ZnO nanoparticles which effect the performance of various potential applications. Pu et al. fabricated organic light emitting device by controlling the size and shape of ZnO nanoparticles [13]. Wang et al. prepared ZnO nanostructures by controlling morphology and also improve the performance of DSSC [14]. Therefore, many synthesis techniques have been reported in the literature to prepare ZnO nanoparticles such as hydrothermal method, sol-gel method, pulsed laser deposition (PLD) technique, chemical vapor deposition (CVD) technique, electro-deposition technique [15–19]. The co-precipitation technique is the finest technique as compared to other techniques because of its some advantages: easy to control temperature, pH of solution, dopant concentrations and mixing rate. By controlling these parameters, this technique produces nanoparticles with high purity and fine size [20]. Swaroop and Somashekarappa prepared ZnO nanoparticles using co-precipitation method by varying pH value. They investigated that the average grain size decreased with increase of pH [21]. Kumar et al. synthesized ZnO nanoparticles at different calcination temperature. They obtained ZnO nanoparticles in the nanorange and demonstrated that band gap of ZnO nanoparticles decreases with the increase of calcination temperature [22].

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The band gap engineering and size of particle is essential for the fabrication of highly efficient solar cells and optoelectronic devices [23]. Band gap of semiconductors can be tuned by altering the size, shape of the materials and doping. The third generation of solar cell namely dye-sensitized solar cell (DSSC) uses ZnO nanoparticles as electrode material. In DSSC, smaller particles will increase the surface area for the absorption of dye. The narrow band gap causes photo-excitation which leads to an increase in electron hole pairs and electrons can directly move from valence band to conduction and thus, the performance of DSSC can be improved [24,25]. In optoelectronic devices, the ZnO nanoparticles have been exploited as an electron injection layer in light emitting diodes (LEDs) [26]. The intensity of emitted light is also depending on the energy gap among the conduction band and the valence band.

Doped ZnO nanoparticles considered as a potential candidates as conductors with high transparency in the visible light range. Rare earth (RE) ions doping in ZnO have generate a great significance because of their f → f or f → d internal orbital transitions, which have the ability to absorb light and thus gives very strong emission lines in the ultraviolet (UV), visible and infrared regions. Various rare earth elements like La, Ce, Pr, Gd, etc. have been doped in ZnO which prove useful application in optoelectronic devices because they provide numerous interesting optical properties including efficient modulation of the emission in the visible region [27–31]. Europium (Eu) is most interesting among other rare earth elements which can facilitate to separate the photo generated electron-hole pairs resulting in enhancement of optical properties [32]. Ivetic et al. reported Eu doped ZnO nanoparticles by ball milling method and combustion reaction method. They reported that small amount of Eu ions were well incorporated into ZnO lattice and found red shift in band gap due to $^5D_0$-$^7F_2$ transition ions [33]. Koao et al. synthesized ZnO nanostructures using chemical bath deposition method. They demonstrated that the solubility of Eu ions in ZnO is upto 3 mol%. After that the large amount of Eu ions exists as interstitial ions or enters into vacancies and found optical absorption was enhanced with increasing of Eu ions [34].

On the other hand, research on the incorporation of non-metals in ZnO especially nitrogen (N) has increased since few years. Several researchers demonstrated that mixing of N (2p) and O (2p) states help narrowing of band gap and also enhance the optical properties [35–37]. Since single dopant element may originate compensating defects in ZnO, while co-doping has been proposed to conquer these constraints in ZnO [38–40]. Zhang et al. studied rare earth (Pr) and non metal (N) co-doped ZnO nanoparticles and found red shift in absorption band edge which leads to improving energy conversion efficiency of dye-sensitized solar cell [41]. Therefore, the structural and optical properties of Eu and N doped ZnO nanoparticles have been reported by many researchers. Yet, the study of Eu-N co-doped ZnO nanoparticles via co-precipitation technique is scarce. This aggravated the authors to examine the effect of Eu-N co-doped on structural, morphological and optical properties of ZnO nanoparticles via co-precipitation technique.

In this work, we synthesized $Zn_{1\text{-}x}Eu_xN_yO_{1\text{-}y}$ (x = 0, 1, 2, 3, 4 mol% & y = 0, 0.3 mol%) nanoparticles and results of this work find the potential application in dye-sensitized solar cell and optoelectronic devices. The structural, morphological and optical properties of Eu-N co-doped ZnO nanoparticles have been examined in detail by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy and UV-visible spectroscopy.

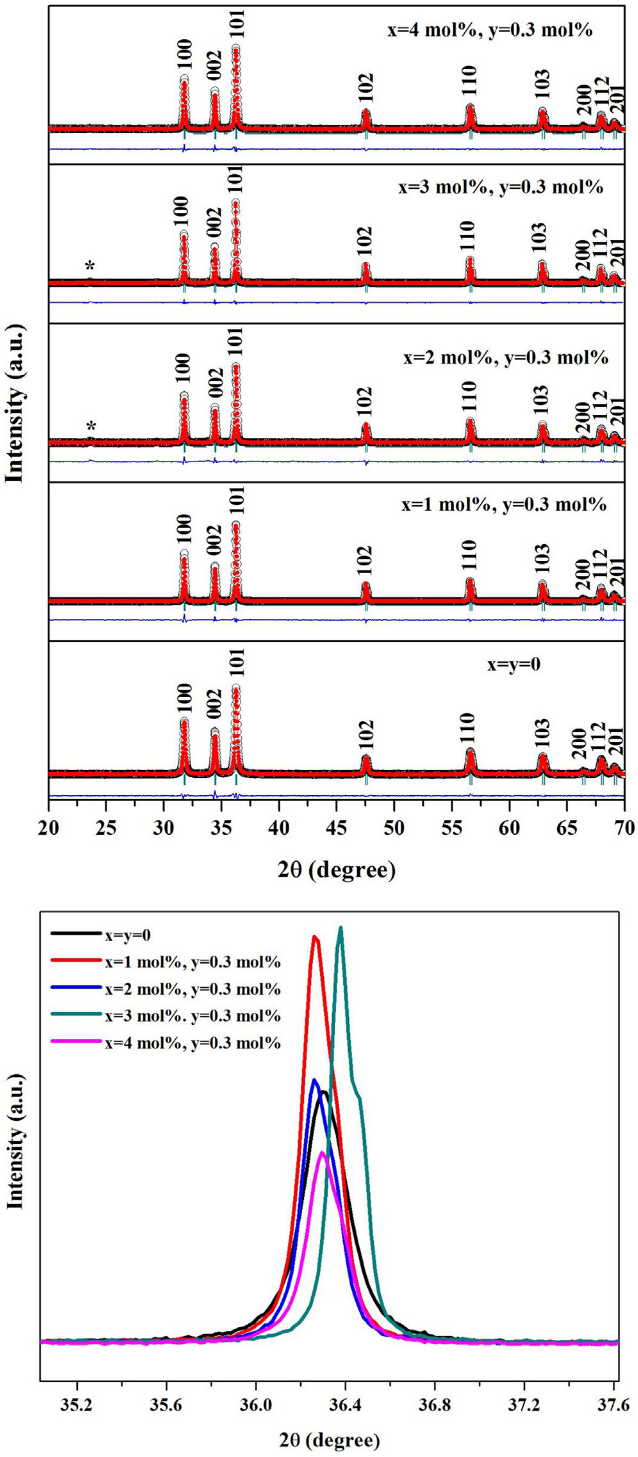

Fig. 1. (a): XRD pattern of $Zn_{1\text{-}x}Eu_xN_yO_{1\text{-}y}$ (x = 0, 1, 2, 3, 4 mol% & y = 0, 0.3 mol%) nanoparticles along with Rietveld refinement.
(b): Variation in peak position along (101) plane of XRD.

2. Experimental detail

2.1. Synthesis of undoped and Eu-N co-doped ZnO nanoparticles

$Zn_{1\text{-}x}Eu_xN_yO_{1\text{-}y}$ (x = 0, 1, 2, 3, 4 mol% & y = 0, 0.3 mol%) nanoparticles were synthesized via co-precipitation method. The pure reagents like zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) (CDH 96%), europium (III) acetate hydrate ($Cu(NO_3)_2.3H_2O$) (Sigma Aldrich, 99%) and urea (NH_2CONH_2) (Himedia 99%) were used as precursors. For preparing pure ZnO nanoparticles (5 g), 18.278 g m of zinc nitrate hexahydrate was first dissolved in double distilled water. The solution was continuously stirred on magnetic stirrer at 100 RPM speed for 2 h to completely dissolve all reagents. Then 1 M solution of potassium hydroxide (KOH) was added drop by drop into the solution till pH becomes 7 and white precipitates were formed. The white precipitates were washed by double distilled water for 5–6 times and then kept in hot air oven at 120 °C for 2 h. The dried precipitates were crushed to