Shape tunable synthesis of Eu- and Sm-doped ZnO microstructures: a morphological evaluation

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Abstract. Facile and low-cost aqueous chemical bath deposition route has been demonstrated to fabricate Eu- and Sm-doped ZnO microstructures. The effect of Eu and Sm ions on the morphology of the ZnO was investigated. The synthesized doped ZnO microstructures were systematically characterized by field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman and Fourier transform infrared spectra. FESEM images depicted the formation of Eu-doped ZnO microspheres and Sm-doped ZnO microplates. XRD spectra showed single crystalline nature of the undoped ZnO microdisks, whereas Eu- and Sm-doped ZnO exhibited the polycrystalline nature. The presence of Eu and Sm ions in the ZnO matrix was confirmed by XPS. This means that all the Eu ions substituted Zn^{2+} as Eu^{2+} into the ZnO matrix, whereas most of Sm ions were being in the trivalent state. This was probably due to the segregation of Sm_2O_3 species on the surface of ZnO microstructures.

Keywords. Zinc oxide; Eu and Sm ions doping; microstructures; chemical bath deposition.

1. Introduction

With the discovery of carbon nanotubes, the nanostructured materials have stimulated an increasing interest due to their importance in basic scientific research and potential technological applications. The key feature of these nanostructured materials is; tunable optical, electronic and magnetic properties which can easily be controlled by altering the size, shape and composition of the materials. In this connection, ZnO is considered as one of the most important nanostructured materials¹ in nanotechnology because of its structure richness and novel properties. To date, various morphologies of ZnO have been synthesized such as nanobelts,² nanocombs,³ nanosheets,⁴ nanocages,⁵ nanorings,⁶ needle-like nanowhiskers,⁷ nanorods^{8,9} and nanoforest.¹⁰ These morphologies have variety of practical applications which motivated the researchers towards controllable synthesis of ZnO nano-architectures.

ZnO is known to be a wide bandgap (3.37 eV), n-type semiconductor with a large free exciton binding energy of about 60 meV at room temperature.¹¹ It is an important technological material in material science due to its fascinating properties such as non-toxicity, high electron mobility, transparency in the visible range, resistivity of semiconductor (usually in the range of 10^{-3} – 10^5 Ω cm), electrochemical stability and low cost.¹² These remarkable properties of ZnO

make it suitable candidate for different applications like dye-sensitized solar cells,¹³ thin film transistor,¹⁴ piezoelectric devices,¹⁵ photocatalysis,¹⁶ antibacterial agent,¹⁷ etc. Beside the aforesaid properties, ZnO also acts as a good host lattice for most of the doping elements including rare earth (RE) metallic ions. Doping is referred as the most common technique to tailor the optical and electrical properties of semiconductor nanomaterials. RE-doped ZnO microstructures have attracted the researchers due to its applications in visible optoelectronic devices; hence most of the studies have been focused on the evaluation of its optical properties. However the effect of RE on the morphology of ZnO microstructures is an unexplored area of research which could restrict the application of these materials. Moreover, the doping of RE into the ZnO matrix is quite difficult because of the large difference in ionic radii between the host cations and RE ($\text{Zn}^{2+} = 0.074$ nm $\text{RE}^{3+} = 0.100$ – 0.120 nm)¹⁸ as well as large mismatches in regard of charge density and coordination environment between these two kinds of cations.

Various synthetic approaches have been made to synthesize RE-doped ZnO microstructures such as the hydrothermal route,¹⁹ electrodeposition,²⁰ rf magnetron,²¹ pulsed laser deposition,²² spray pyrolysis²³ and vapour transport method.²⁴ Most of these methods are based on expensive equipments, high temperature and vacuum conditions which increase the processing cost of the materials. In the search of low-cost synthesis procedure, chemical bath deposition is the solution-based (almost always aqueous) technique and suitable for large area of scientific and industrial applications due to its

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simplicity, requirement of inexpensive equipments, and low cost of the process. Moreover, this method allows growth of different microstructures material at relatively low temperature (below 100°C) hence defect caused by high temperature can be avoided. The properties of ZnO-based materials are largely affected by their morphologies.¹² In order to achieve the desired optical, electrical and magnetic properties of ZnO for the practical applications, the design and synthesis of controlled architectures in nanoregime is highly desirable. Hence, the change in morphology in the presence of RE doping element is an interesting topic to investigate.

The present study is focused on the fabrication of Eu-doped ZnO nano-sheet-based microspheres and Sm-doped ZnO micro-plates via a facile, low-temperature and low-cost chemical bath deposition route. We also studied the morphological changes in ZnO upon Eu and Sm ions doping, in comparison of undoped ZnO microdisks (synthesized by Self *et al*²⁵).

2. Experimental

2.1 Materials required

Zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich], hexamethylenetetramine [$\text{C}_6\text{H}_{12}\text{N}_4$, Alfa Aesar], trisodium citrate dihydrate [$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, Sigma Aldrich], europium oxide [Eu_2O_3 , Sigma Aldrich], samarium sulphate [$\text{Sm}_2(\text{SO}_4)_3$, Sigma Aldrich] were used as precursors. All the chemicals were of analytical reagent grade and were used without further purification. All the solutions were freshly prepared with Milli-Q water. The commercial microscopic glass slides were used as substrates. Before deposition, the substrates were boiled 2 h in chromic acid, cleaned with single distilled water (SD), double distilled water (DD), degreased with acetone, ultra-sonically cleaned by DD and finally dried in air.

2.2 Synthesis of ZnO microdisks

The procedure reported by Self *et al*²⁵ was followed. In brief, 0.356 g of zinc nitrate hexahydrate was added into aqueous solution of hexamethylenetetramine (HMT) prepared by adding 0.117 g in 60 ml of Milli-Q water in a vial, which was being stirred for 5 min and then 0.002 g of trisodium citrate (TSC) was added to the above mixture and stirred it for another 5 min. The pre-cleaned substrate was placed at an angle of 60° in a vial containing this solution; the vial was sealed and incubated at 60°C for 10 days. ZnO microstructures were expected to grow on the down faced surface of the glass slide, which was chosen for characterizations. After 10 days of incubation the substrate was removed, washed with Milli-Q water, and kept in room temperature for drying.

2.3 Synthesis of doped ZnO microstructures

Eu_2O_3 was dissolved in dilute nitric acid, heated to dryness at 120°C, and added with Milli-Q water to form 0.01 M

$\text{Eu}(\text{NO}_3)_3$ aqueous solution. For the preparation of doped ZnO microstructures, $[\text{Eu}^{3+}]$ and $[\text{Sm}^{3+}]$ solutions were added in $[\text{Zn}^{2+}] : [\text{Eu}^{3+}/\text{Sm}^{3+}] = 100 : 2$ M ratio in the same reaction bath as used for undoped ZnO.

2.4 Characterization techniques

Eu- and Sm-doped ZnO films were subjected to different characterization techniques. The phase purity and microstructure of films was studied by Bruker D-8 Advance X-ray diffractometer with Cu K α X-ray radiation (XRD) ($\lambda = 0.15496$ nm) operated at 40 kV and 40 mA in the 2θ range of 20–80° with a 2θ step size of 0.013° and step time of 13.6 s. Surface morphology was studied by Zeiss ultra plus field-emission scanning electron microscopy (FESEM) operated at 5 kV. The presence of doping elements, i.e., Eu and Sm in ZnO lattice was confirmed by KRATOS ESCA model AXIS 165 X-ray photoelectron spectroscopy (XPS) instrument. The binding energies were determined by fitting the XPS spectral line shapes with Lorentzian–Gaussian functions. Fourier transform infrared (FTIR) spectra were recorded using Thermo Nicolet Nexus 670 spectrometer with 4 cm^{-1} resolution. Micro-Raman scattering measurement was carried out on Horiba Jobin-Yvon HR800 Raman spectrometer equipped with a liquid-nitrogen cooled charge coupled device (CCD) detector and a confocal microscope. The emission line at 514 nm from an Ar^+ ion laser was focused on the sample under microscope with 0.3 cm^{-1} spectral resolution to investigate the effect of the Eu and Sm dopant on the microstructures and vibration properties of ZnO.

3. Results and discussion

Three typical samples and related morphological, structural, compositional and vibrational properties have been investigated in this work: namely ZO (ZnO microdisks), EZO (Eu-doped ZnO microspheres) and SZO (Sm-doped ZnO microplates).

3.1 Morphological analysis

Figure 1a and b depicts the morphology of undoped ZnO deposited on the glass surface. Here one could clearly observe

Figure 1. (a and b) FESEM images of undoped ZnO hexagonal microdisks grown on glass substrate.

the existence of hexagonal microdisks which was single crystalline in nature oriented along the (002) plane (single crystalline nature was also verified by XRD). The growth process of these ZnO microdisks was discussed in detail by Self *et al.*²⁵ The average diameter and thickness of ZnO microdisks were estimated using ImageJ software and found to be 8.29 and 1.42 μm , respectively. Figure 2a–h shows the FESEM pictures of Eu- and Sm-doped ZnO microstructures. The significant different morphologies (i.e., microspheres and microplates) were obtained by the incorporation of Eu and Sm ions into the ZnO matrix. The change in morphologies may arise from the presence of the foreign species (such as doping elements) which interrupt the nucleation and consequently the growth process. The effect of counter ions on the morphology of ZnO has been studied by

Alenezi *et al.*²⁶ The metal ion also affect the growth process either acting as nucleation centre itself or by altering the nucleation process. Wen *et al.*²⁷ demonstrated the formation of 3D self-assembled structure of ZnO in the presence of In and Sn metal ions. In recent times, Kim and Kwon²⁸ used Ag seeded substrate to control the morphology of ZnO. In the present investigation, the morphological changes of ZnO were observed due to the presence of Eu and Sm ions used as dopants. The absence of any doping element allowed ZnO to grow as single crystal microdisk (figure 1). But after adding Eu salt in the same reaction bath the morphology of the final product was changed, i.e., ZnO microsphere. The growth of the microspheres stated from the formation of nanoplate with the diameter of 75 nm which assembled as submicron triangles of the size *ca.* 534 nm. Finally these triangular-shaped particles were aggregated to form microsphere. The diameters of the Eu-doped ZnO microsphere was found to be $\sim 3.01 \mu\text{m}$. Meanwhile some spine-like structures also observed that was the outgrowth of these microspheres. These spine-like structures were formed by the layer to layer stacking of the nanosheets. The diameter of these nanosheets was radially reduced from bottom to top in the spine structures. This kind of growth has previously been observed for ZnO in the presence of citrate ions.²⁹ The presence of Sm ions in the reaction bath leads to the formation of microplates-like structures depicted in figure 2e–h. The entire surface of the substrate was covered by these microplates. The length and thickness were measured and found to be ~ 1.97 and $\sim 0.28 \mu\text{m}$, respectively. A closer examination indicated that these microplates were consisting of smaller nanoplates on the one surface while the other was being smooth. This observation revealed the textured growth of Sm-doped ZnO microplates. The detailed mechanism for the formation of Eu- and Sm-doped ZnO complex structures are still under investigation.

3.2 XRD analysis

The structural changes upon doping of Eu and Sm on ZnO lattice were investigated by the XRD technique. The XRD patterns of samples ZO, EZO, and SZO have been recorded in the 2θ range of $20\text{--}80^\circ$ as illustrated in figure 3. All the diffraction peaks were in good agreement with the Joint Committee of Powder Diffraction Standards data for ZnO (JCPDS card no. 89-0510) and could be indexed to hexagonal wurtzite structure. No other diffraction peaks related to Zn, $\text{Zn}(\text{OH})_2$, or other ZnO phases were detected indicating the pure single phase ZnO nanocrystals. In addition, sharp and high intensity of XRD peaks indicated the crystalline nature and excellent crystal quality without any amorphous phase. An interesting result on the crystal orientation has been observed. Sample ZO showed only a single diffraction peak corresponding to the (002) plane, indicating the monocrystalline nature of the material (this result also confirmed by SEM pictures). However, when doped with Eu and Sm ions, it exhibited the different crystallographic orientations of planes, i.e., (100), (002), (101), (102), (110) and

Figure 2. FESEM images of (a–d) Eu-doped ZnO microsphere, arrows and circle show the spine-like structures and triangle-shaped structures, respectively, (e–h) Sm-doped ZnO microplates at different magnifications grown on the glass substrate. Inset of g shows the enlarge view of microplates, arrow indicated the nanoplates on the surface of the microplates.

Figure 3. XRD patterns of undoped ZnO microdisks (ZO), Eu-doped ZnO microspheres (EZO) and Sm-doped ZnO microplates (SZO).

(103) suggested the polycrystalline nature of the samples, which means that the presence of Eu and Sm ions not only affected the morphology of ZnO but also altered the crystal orientation of ZnO-based materials. The incorporation of doping element also leads to shift in the diffraction angle especially for the (002) plane. The peak position of the (002) plane were found to be 34.39° , 34.35° , and 34.69° for the samples ZO, EZO, and SZO, respectively. A slight shift towards lower angle corresponds to the (002) plane was noticed for EZO as compared ZO indicating the increase in lattice parameters due to the fact that the ionic radius of Eu^{3+} (0.095 nm) or Eu^{2+} (0.125 nm) is higher than that of the Zn^{2+} (0.074 nm). This shift can also be attributed to successful substitution of Eu in Zn site, leading to expansion in ZnO lattice. In contrast, SZO showed peak shifting towards higher angle (ionic radius of Sm^{3+} is 0.096 nm) which is mainly due to beside the substitution of Sm ions into the ZnO lattice, most of the ions were aggregated as Sm_2O_3 on the surface of ZnO microstructure. These results were also verified by XPS analysis which has been discussed in next section.

3.3 XPS analysis

To investigate the chemical composition and valence state of doping elements, we carried out XPS measurement. Typical survey spectra of EZO and SZO are shown in figures 4a and 5. All the peaks were assigned to core levels of Zn 2p, Zn 3p, O 1s, Eu 3d, Sm 3d and C 1s. The binding energy scale was calibrated using carbon peak (C 1s) at 285 eV as reference. The XPS spectra of the Zn 2p core level region for EZO is presented in figure 4b, which showed the doublet

peaks at 1022.7 and 1045.8 eV, corresponds to the Zn 2p_{3/2} and 2p_{1/2} core levels, respectively.³⁰ The energy difference between these two spectral lines is 23.08 eV, which is in good agreement with the standard value *ca.* 22.97 eV,³¹ revealed the existence of Zn^{2+} in the form of oxide. The curve fitting in the O 1s region was contributed by two peaks, which showed the presence of two kinds of oxygen species near the surface of the doped nanocrystals. Peak at 531.8 eV is assigned to the metallic oxides. Peak at 533.3 eV corresponds to the hydroxyl species or adsorbed water on the surface of the doped nanocrystals.

The two peaks at 1125.8 and 1155.2 eV can be attributed to Eu 3d_{5/2} and Eu 3d_{3/2} core levels, respectively,^{32,33} as shown in figure 4d. The binding energy and peak position confirmed the existence of Eu ion mainly in divalent chemical state. No peaks were found related to Eu^{3+} ions which mean that all the Eu ions were incorporated into ZnO lattice without any segregation of Eu_2O_3 oxide phase. This result resembled with XRD analysis. Figure 5 depicted the XPS spectra of SZO. The peaks at 1084.5 and 1112.1 eV were corresponding to Sm 3d_{5/2} and Sm 3d_{3/2}, respectively, and the peak positions confirmed the existence of Sm in trivalent valence state, probably as Sm_2O_3 .^{34,35} This revealed that the most of the Sm ions were segregated as Sm_2O_3 on the surface of ZnO nanocrystals. It is well known that the RE ions have low solid solubility in ZnO lattice due to the large differences in ionic size and charge between RE ions and Zn^{2+} ions. So that, it is difficult to incorporate the RE ions in ZnO lattice completely via the low temperature method, hence the segregation of oxides phase on the surface of ZnO may result. Such a situation was also reported previously by Liu *et al.*³⁶ and Han *et al.*³⁷

All other peaks related to core levels of Zn 2p, Zn 3p, O 1s and C 1s were found same as in EZO.

3.4 Raman analysis

Micro-Raman scattering technique is sensitive to the microstructure of nanosized materials. It is used to probe the disorder, dopant-induced defects and crystalline phase through vibrational analysis. In the present work, micro-Raman measurement was carried out to investigate the quality and microstructure of Eu- and Sm-doped ZnO. The wurtzite ZnO belongs to the space group $\text{C}_{6v}^{4_6}$ with two molecules per primitive cell. On the basis of group theory, the optical Raman modes of ZnO can be categorized as³⁸ $1\text{A}_1 + 2\text{B}_1 + 1\text{E}_1 + 2\text{E}_2$, where A_1 , E_1 and E_2 modes are Raman active and B_1 is silent mode. A_1 and E_1 both modes are polar and split into transverse optical (TO) and longitudinal optical (LO) phonon modes. E_2 mode is non-polar and appeared at two frequencies, E_2^{high} which is associated with the motion of oxygen atom and E_2^{low} is associated with Zn sublattice. The representative Raman spectra of EZO and SZO are presented in figure 6. The deconvolution of the Raman spectra has been carried out by the multiple Gaussian peak fitting procedure using Origin 8.0 software, which gave the fundamental bands were roughly located at ~ 225 , ~ 272 , ~ 321 , ~ 373 , ~ 435 ,

Figure 4. (a) XPS survey spectra of Eu-doped ZnO microspheres, (b) Zn 2p, (c) O 1s and (d) Eu 3d signals recorded for Eu-doped ZnO microspheres.

Figure 5. XPS spectra of Sm-doped ZnO microplates. Inset showing the 3D signals for Sm³⁺ ions.

Figure 6. Micro-Raman spectra of Eu-doped ZnO microsphere (EZO) and Sm-doped ZnO microplates (SZO) recorded at room temperature.

Figure 7. FTIR spectra of Eu-doped ZnO microsphere (EZO) and Sm-doped ZnO microplates (SZO).

~ 580 , ~ 668 and ~ 750 cm^{-1} . The strongest peak centred at about ~ 435 cm^{-1} attributed to the E_2^{high} mode, which is the characteristic of the wurtzite ZnO.³⁹ The sharp and intense peak suggested the high crystalline nature of the synthesized materials, which again testified the result of XRD. One vibrational frequency at ~ 225 cm^{-1} was assigned for the defect-induced mode.⁴⁰ B1 (low) silent mode noticed at ~ 272 cm^{-1} vibrational frequency.⁴¹ The appearance of this mode can be explained as, the incorporation of dopants, induce the structural disorder which leads to the breakdown of the translational symmetry of the crystal lattice, resulting in the relaxation of the Raman selection rule. The Raman mode at ~ 321 cm^{-1} was assigned to the second-order scattering due to $E_2^{\text{high}} - E_2^{\text{low}}$ multiple scattering process. The similar result was also noticed previously.⁹ One weak peak located at ~ 373 cm^{-1} corresponds E_1 (TO) mode. A peak centred at ~ 580 cm^{-1} corresponds to E_1 (LO) mode, which is generally related to oxygen vacancies or Zn-interstitial defect states.⁴² The appearance of E_1 (LO) mode indicated the presence of oxygen vacancies or Zn interstitial defects in the Eu- and Sm-doped ZnO microstructures. Two peaks observed at ~ 668

and ~ 750 cm^{-1} attributed to multi-phonon processes or intrinsic host-lattice defects.^{43–45}

3.5 FTIR analysis

FTIR spectroscopy is widely used technique to analyse the nature of adsorbents present on the surface of nanostructured materials. FTIR measurements in the wavenumber range from 400 to 4000 cm^{-1} using the KBr method at room temperature were carried out and are shown in figure 7a and b for Eu- and Sm-doped ZnO microstructures, respectively. A series of infrared bands have been observed in both the samples. The broad band at 3436.59 cm^{-1} was assigned for O–H stretching vibration frequency, showing the presence of hydroxyl group which probably be adsorbed water on the surface of the nanocrystals. The 1558.95 cm^{-1} was associated with C=O stretching frequency of citrate ion. The 1384.14 and 1025.54 cm^{-1} peaks were assignable to the C–H bending and C–O stretching frequencies, respectively, for citrate ions.⁴⁶ A Peak located towards lower frequency region at about 471.00 cm^{-1} corresponds to Zn–O vibration.

4. Conclusion

In summary, Eu- and Sm-doped ZnO microspheres and microplates, respectively, were synthesized and the influence of Eu and Sm ions on the morphology of the ZnO was also demonstrated. XRD analysis suggested that the Eu and Sm both can alter the orientations of the crystal. XPS spectra confirmed the Eu ions completely dissolved into ZnO matrix, whereas most of the Sm ions were segregated as Sm₂O₃ on the surface of ZnO microstructures. It is believed that this study will be helpful to further design and fabricate ZnO-related different microstructures and even other important allied materials.

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