Hydrothermal synthesis and properties of hierarchical ZnO and Eu-doped ZnO 3D structures

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ABSTRACT

Zinc oxide is a very interesting material for several technological applications. The properties of ZnO materials have been investigated and the influence of the 3D structure has been evaluated. Controlling experimental parameters is possible to obtain branched structures, which results in the preparation of materials presenting high surface area. Herein, we present a hydrothermal procedure to synthesize flower-like ZnO materials. In this work, the introduction of a rare earth metal in the ZnO structure resulted in the formation of a hierarchical Eu-doped ZnO material presenting branched morphology. SEM and TEM images, Raman spectroscopy and PL measurements were used to characterize undoped and Eu-doped ZnO 3D structures.

Keywords: zinc oxide, flower-like morphology, branched structures

1 INTRODUCTION

Hierarchical oxide nanostructures are very promising materials for different applications, such as gas sensing, due to their high surface area. Literature shows that hierarchical nanostructures improve gas sensing response and response speed. This effect is due to the effective gas diffusion toward the sensing surfaces [1].

Gas sensing properties of ZnO materials have been investigated and the influence of the 3D structure has been evaluated. Yangang Sun et al. [2] showed a response improvement in the gas sensing for ZnO flower-like microstructures. This behavior has being attributed to more active centers that are obtained from the enhanced oxygen vacancy defects on the junctions within the ZnO flower-like 3D structures.

In this work, we present a hydrothermal procedure to synthesize ZnO with flower-like morphology. Controlling experimental parameters is possible to obtain branched structures, which results in the preparation of materials presenting even higher surface area. Different reaction mediums have being tested in our experiments, such as water, water/glycerol, and deuterium solutions. Moreover, several polymers have being investigated as shape driving molecules. Rare earth metals have also being employed in the synthesis of doped ZnO materials and their influence in the final morphology and material structure has being evaluated. Herein, the addition of Eu^{3+} ions during the synthesis of flower-like ZnO resulted in the formation of a branched morphology as clearly observed by high-resolution SEM images. Raman spectroscopy and PL measurements have been used for characterization and showed different features for both undoped and Eu-doped ZnO materials.

2 EXPERIMENTAL

Zn-01 sample: An aqueous solution of a zinc precursor (0.045 $mol.L^{-1}$) was mixed to a NaOH solution and transferred to an autoclave system. A hydrothermal treatment was performed at 120 ^{o}C for 12 hours. The final material was isolated by centrifugation, washed with water and dried at 60 ^{o}C overnight.

Zn-02 sample: An aqueous solution of a zinc precursor (0.1 $mol.L^{-1}$) was mixed to a NaOH solution containing poly(acrylic acid) (PAA) 0.05 wt% and transferred to an autoclave system. A hydrothermal treatment was performed at 90 ^{o}C for 30 minutes. The final material was isolated by centrifugation, washed with water and dried at 60 ^{o}C overnight.

Eu-Zn-01 sample: An aqueous solution of a zinc precursor (0.045 $mol.L^{-1}$) containing Eu^{+3} ions (Zn:Eu molar ratio = 5:1) was mixed to a NaOH solution and transferred to an autoclave system. A hydrothermal treatment was performed at 120 ^{o}C for 12 hours. The final material was isolated by centrifugation, washed with water and dried at 60 ^{o}C overnight.

Eu-Zn-02 sample: An aqueous solution of a zinc precursor (0.1 $mol.L^{-1}$) containing Eu^{+3} ions (Zn:Eu molar ratio = 5:1) was mixed to a NaOH solution containing poly(acrylic acid) (PAA) 0.05 wt% and transferred to an autoclave system. A hydrothermal treatment was performed at 90 ^{o}C for 30 minutes. The final material was isolated by centrifugation, washed with water and dried at 60 ^{o}C overnight.

Samples were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), Raman spectroscopy and Photoluminescence (PL) measurements using 325 nm excitation line.

3 RESULTS AND DISCUSSION

Figure 1a shows the flower-like morphology obtained for sample Zn-01 presenting structures larger than 10 µm in diameter. In the case of sample Zn-02 (Fig. 1b) flowers presented diameters up to 4 µm. Besides the size of the microstructured flowers, changes in experimental conditions also were responsible for differences in the shape of the sticks forming the flower-like materials as can be observed in the micrographs.

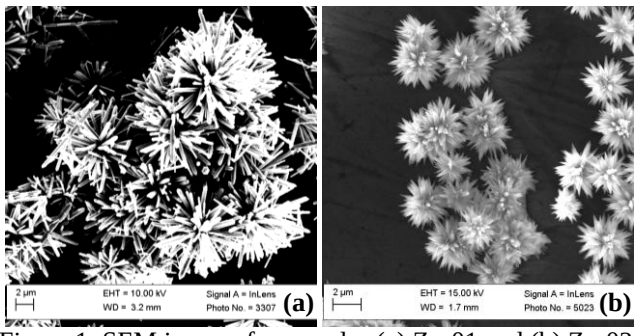

Figure 1: SEM images for samples (a) Zn-01 and (b) Zn-02.

XRD measurements for samples Zn-01 and Zn-02 (Fig. 2) are characteristic of crystalline hexagonal würtzite-type ZnO [3], showing preferential growth in the (100) direction for sample Zn-01.

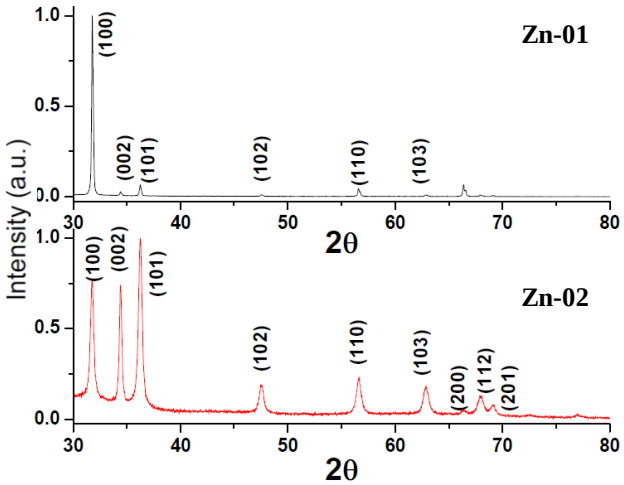

Figure 2: XRD patterns for samples Zn-01 and Zn-02.

When Eu^{+3} ions were added to the syntheses of sample Zn-01, leading to the preparation of sample Eu-Zn-01, no changes were observed in the ZnO flowers morphology. However, nanobars were grown attached on the surface of the ZnO flowers, probably related to the segregation of Eu^{+3} precursor resulting in europium oxide nanobars synthesis (Fig. 3a). In the case of sample Eu-Zn-02, the addition of Eu^{+3} ions was responsible for changes in the 3D structure, leading to the formation of a branched flower-like morphology (Fig. 3b).

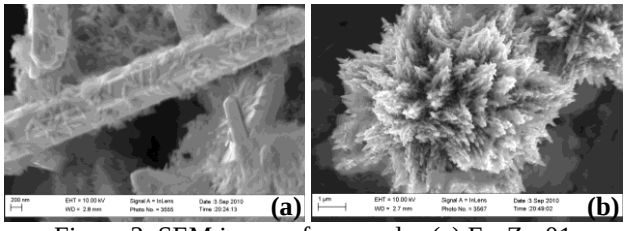

Figure 3: SEM images for samples (a) Eu-Zn-01 and (b) Eu-Zn-02.

Figure 4 shows EDS analysis for samples Eu-Zn-01 and Eu-Zn-02. It is possible to observe the presence of Eu for both samples. However, the Eu signal for sample Eu-Zn-02 (Fig. 4c) is more concentrated on the region where the material is located whereas this signal is spread in the case of sample Eu-Zn-01 (Fig. 4g). This observation suggests the Eu^{+3} could be into the structure of sample Eu-Zn-02.

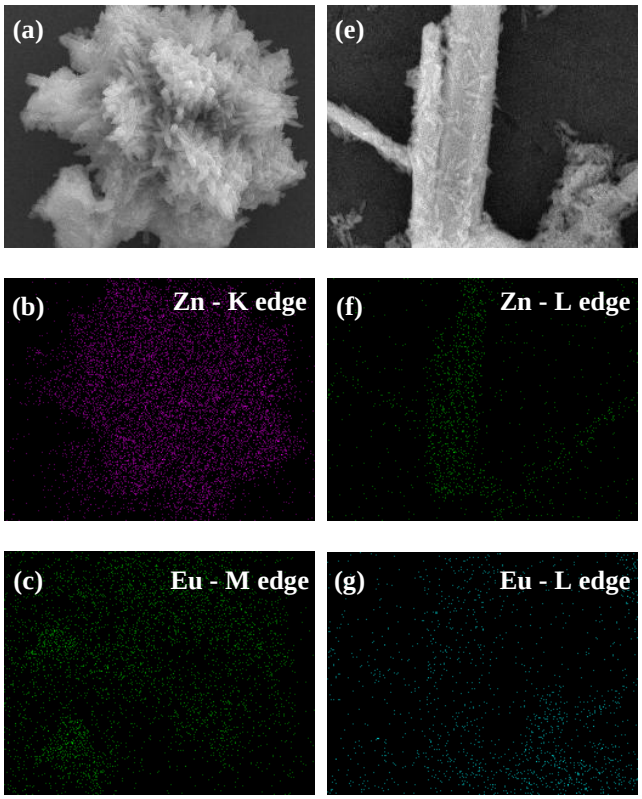

Figure 4: EDS analysis for samples (a, b, c) Eu-Zn-02 and (d, e, f) Eu-Zn-01. Images (b) and (f) are related with the presence of Zn whereas images (c) and (g) are related to the presence of Eu.

A closer observation in SEM images suggests the flower-like material in samples Zn-01 and Eu-Zn-01 could be originated from ordered aggregation of previously

formed ZnO microrods. On the other hand, sample Eu-Zn-02 seems to be formed according to a different growth mechanism (under investigation).

Raman (Figure 5) and PL (Figure 6) characterization show different features for samples Zn-02 and Eu-Zn-02. For both samples Raman spectra show a peak at 430 cm^{-1} related to the würtzite structure which corroborates with XRD patterns [3]. The occurrence of the peak around 565 cm^{-1} suggests structural defects like oxygen deficiency for both undoped and Eu-doped ZnO samples.

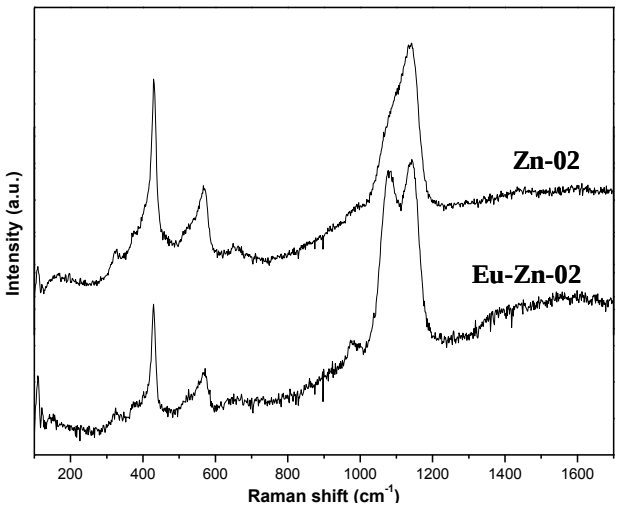

Figure 5: Raman spectra for samples Zn-02 and Eu-Zn-02.

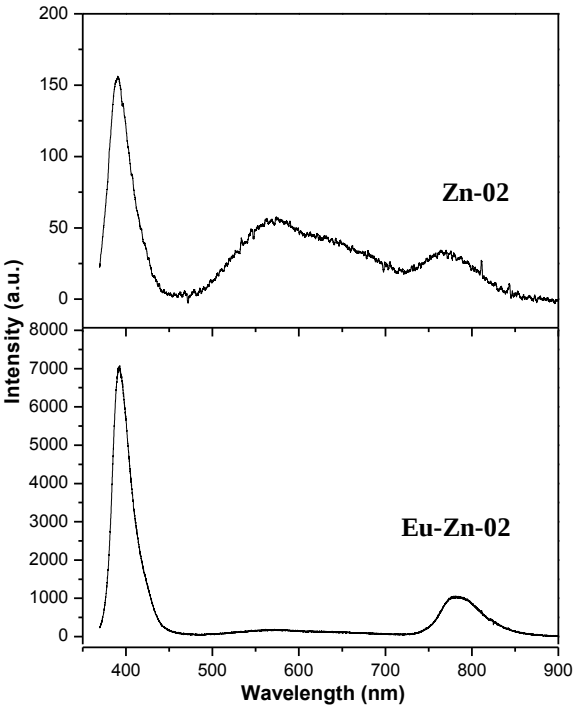

Figure 6: Room temperature PL spectra for samples Zn-02 and Eu-Zn-02.

PL spectra displays a peak at 390 nm attributed to the near band edge emission of ZnO and a broad peak from 500 to 750 nm related to defects in the ZnO structure [4]. Despite the energy laser in 325 nm is not in resonance with Eu^{+3} ions transitions, intensification in PL response in the case of Eu-doped sample is observed in Fig. 6, which suggests that Eu^{+3} ions are influencing in the optical characteristics of the material.

4 CONCLUSION

In this work, Eu^{+3} ions employed under specific experimental conditions led to the formation of Eu-doped ZnO presenting hierarchical structure.

The preparation of these branched structures is of great interest for applications in technologies like gas sensing. The occurrence of defects in the oxide structure is also interesting for more reactive materials aiming sensing applications.

REFERENCES

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