Structural and optical properties of Yb doped ZnO nanorods synthesized via a green process

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Abstract. Recently, ZnO Nanostructures have attracted considerable attention due to their various morphologies, easy synthesis and excellent physical properties for fabricating optoelectronic devices. In this study, we report the synthesis of Yb doped ZnO nanorods via a green process using plant extracts. Their morphology, structural and optical properties were characterized by different techniques. The obtained materials show promising properties and remarkable effects of the dopant. Our investigations and discussions were conducted to reveal our synthesized materials ability for optoelectronic applications such as solar cell and light emitting diodes devices.

1. Introduction

ZnO is a natural n-type semiconductor with a direct wide band gap (3.37 eV) and large exciton binding energy (60meV). Its optical and electrical properties make it useful as an attractive and promising material for optoelectronic and photonic applications such as solar cells, lasers, light emitting diodes, photodetectors [1-2]. In addition, ZnO is a material easily synthesized under several morphologies such as quantum dots [3], nanorods [4], nanowires [5], nanobelts [6], nanoflowers [7], etc. So far, various methods have been used to synthesis ZnO nanostructures, such methods include green synthesis [8], hydrothermal [9], sol-gel [10], chemical vapor deposition [11] and microwave assisted [12]. The green synthesis of ZnO nanorods makes use of economical and safe reagents, non-toxic, environmental friendly methods that have attracted much attention recently.

Structural and optical properties of ZnO nanostructures can be modified and improved by doping/co-doping processes using metallic dopants such as Al [13], Ga [14], Na [15], etc. In recent years rare earth doped ZnO nanomaterials have attracted the attention of scientist researches since they are useful and
better luminescent materials owing to their 4f intra shell transitions [16]. In the literature, studies of rare earth doped ZnO are scarce, we find among them for example, the study conducted by Senol [17] which reported the synthesis of rare earth (Er-Yb) doped ZnO nanostructures using the hydrothermal method. Zamiri et al [18], have also synthesized rare earth (Er, La, Yb) doped ZnO nanostructures through wet precipitation method and studied their structural and optical properties. Soumahoro et al [19] have reported the structural, optical and electrical properties of Yb-doped ZnO thin films synthesized by the spray pyrolysis method in order to investigate the effect of Yb ion in the ZnO matrix and the related optical properties of the films. Kumar et al [20] have also prepared Nd-doped ZnO thin films deposited on a glass substrate by sol-gel. 

In our work, we report the structural and optical properties of pure and Yb doped ZnO nanorods; samples have been synthesized by hydrothermal method for pure ZnO and green hydrothermal method for Yb doped ZnO and their structural and optical properties were studied by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Photoluminescence (PL). The aim of this study was to investigate the effect of Yb dopant on the optoelectronic properties of ZnO nanorods.

2. Experimental details 
ZnO precursors used in this work were purchased from Sigma-Aldrich. To synthesize ZnO nanorods, an equi-molar aqueous solution of 0.1 M zinc nitrate (Zn(NO₃)₂) and hexamethylenetetramine (C₆H₁₂N₄, HMT) was prepared using deionized water. This mixture was heated at a constant temperature of 90°C in an oven for 24 h. The doping process followed the same steps with the addition of 10% of ytterbium chloride and 10 ml of tea leaves extract. Dry green tea leaves were purchased from Lipton company. In this setup, 0.1 g of these leaves were boiled at 70°C in a volume of 200 ml of de-ionized water for 40 min. A brown solution of in, brown colored extract of pH=5 was obtained. The brown solution was filtered 3 times to eliminate residual solids. Determined volumes were taken from this extract rich in polyphenols and used in the synthesis of our nanomaterials. The obtained materials were deposited on Si (100) substrates and dried at 50°C for 2 hours in air.

Results and discussion

2.1. X-ray diffraction 
Figure 1 shows the X-ray diffraction pattern of pure and Yb-doped ZnO nanorods. As can be seen from the spectra, the analysis of diffraction peaks of both pure and Yb doped ZnO reveals the presence of hexagonal wurtzite structure without any diffraction peaks of Yb related impurities. Results showed that the intensity of (002) peak and (101) peak decreases with the addition of ytterbium, while the intensity of (100) peak does not change; it means that the growth in the case of pure ZnO was in the three principal directions (reflections (100), (002), (101)), although for Yb-doped ZnO the direction (100) is the preferred one for growth (because the addition of Yb causes notable decrease in both (002) and (101) peak intensities), the growth in directions (002) and (101) is limited after doping which means that doping has an effect on crystallinity.
Figure 1. X-ray diffraction spectrum of pure and Yb doped ZnO nanorods.

2.2. Scanning electron microscopy
Morphological characterization of pure and Yb doped ZnO nanorods was performed by SEM observation, Figure 2 shows typical SEM image of ZnO nanorods prepared via a green process. As clearly shown in the Figure 2(a), the ZnO nanorods have an hexagonal shape, the average diameter and the length are about 500 nm and several micrometres (~4µm) respectively. ZnO nanorods were relatively grown vertically with a coexistence of two different sizes and high density (an average of 11 nanorods/10µm2). The graph at the top of the figure presents the distribution of nanorods taken from different areas of 10 µm2. The image of Yb doped ZnO in the Figure 2(b) indicates the formation of a bulk material with rarely located nanorods with different sizes in the edges, which means that both the nucleation and the growth were affected due to the dopant.
2.3. Photoluminescence

Room temperature photoluminescence study has been performed for investigating the optical properties and the effect of Yb doping ZnO. It was known that the luminescence of ZnO largely depends on the synthesis method and most importantly the defects concentration in the bulk and on the surface of material. Figure 3 shows the obtained PL spectra of pure and Yb doped ZnO with 10% concentration of doping prepared respectively by hydrothermal and green hydrothermal method. It is clearly remarkable that pure ZnO peak is more intense than that Yb doped ZnO. A number of hypotheses have been proposed to explain this strong decrease in intensity, such as an increase in non-radiative recombination process [21], a higher concentration of Yb (10%) (because when the doping exceeds a given concentration the intensity decreases in the visible region [22]), the compensation of ions introduced by the Yb doping into the ZnO lattice or to bioactive molecules of tea introduced during the preparation which occupy the intrinsic defect of ZnO.

To better understand the nature and the origin of emissions, Figure 4 illustrates the normalized spectra of photoluminescence. The two samples exhibit two peaks in the visible region; the peak of pure ZnO was observed approximately at 560 nm (yellow emission). In general, oxygen vacancy (\(V_O\)) is the most widely accepted mechanism for the visible emission of ZnO; thus, the peak of pure ZnO is usually attributed to the doubly ionized oxygen vacancy (\(V_O^{2-}\)) [23]. In the PL spectra of Yb doped ZnO nanorods, the peak is approximately located at 545 nm (green and yellow emission), which can be attributed to the decrease of number of oxygen vacancies and interstitial oxygen and this emission comes from the recombination of the holes and the interstitial oxygen ions when electrons occupy the singly ionized oxygen vacancy (\(V_O^+\)) [24]. Therefore, after doping with ytterbium, there is a slight shift of the observed peak to high energies; this effect could be attributed to the decrease of structures defects which were responsible of the emission in this region (520-620), this decrease may be due to the occupation of the Yb atoms, i.e. the creation of a level which limits the emission in this region.
**Conclusion**

This present study is focused on the study of structural and optical properties of Yb doped ZnO nanorods able to enhance their performance in the optoelectronic devices. Pure and Yb doped ZnO nanorods were prepared respectively via hydrothermal and green hydrothermal methods; the Yb concentration of doped
ZnO nanorods was 10%. Structural, morphological and optical properties have been studied, and the results revealed that both pure and Yb doped ZnO have the hexagonal wurtzite structure, with (100) as a preferred orientation for the growth of the Yb-doped ZnO. The doping conducted to a bulk material with rarely located nanorods with different sizes. The PL spectra show a strong decrease in intensity after doping with Yb and a slight shift to high energies.

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