Structural and optical characterization of Holmium coated ZnO nanorods

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Abstract. One-dimensional ZnO nanostructures have been attracting growing research effort worldwide over the last few years due to their various morphologies, easy synthesis and excellent physical properties for fabricating optoelectronic devices. In this study, we have reported the synthesis of Holmium coated ZnO nanostructures. The structural, morphological and optical properties of our materials were studied using different techniques. The obtained materials show promising properties and the remarkable effects of the coated material. The experimental results obtained for our material exhibit significant enhancement in properties, which is suitable for the optoelectronic applications.

1. Introduction

Zinc Oxide (ZnO) is considered as a very promising semi-conductor for optoelectronic and photonic applications such as solar cells, light emitting diodes, laser diodes and photodetectors due to its wide band gap (3.37eV), large exciton binding (60meV) and high electron mobility [1-3]. Pure ZnO has transmittance of more than 75% and low absorption and scattering values at high wavelengths, making it transparent over the visible range [4]. The variety of nanostructures of ZnO makes it as an attractive and new material with potential applications in many fields of nanotechnology. One-dimensional structures are considered the largest group of ZnO nanostructures including nanorods [5], nanowires [6], nanobelts [7] and nanotubes [8]. Various methods have been developed during several years for the synthesis of one-dimensional ZnO that have included hydrothermal method [9], chemical vapor deposition [10], green synthesis [11], sol-gel method [12] and electrochemical technique [13]. However, the hydrothermal method is very simple, easy and low-cost method used for obtaining nanostructures in a specific shape and size at lower temperature (lower than 100°C) [14].

Optoelectronic properties of ZnO nanostructures can be modified and improved by doping and coating processes with other materials; As known ZnO have been heavily doped and co-doped with...
metals such as Al [15], Ga [16], and Fe [17]. Therefore, rare earth doped materials exhibit very good luminescent properties owing to their 4f intra shell transition [18]. Among the Rare Earth (RE), holmium (Ho) is a promising element for applications with good luminescent properties because it exhibits fluorescence in the visible and near infrared region [19]. In the recent years, ZnO nanostructures have been doped by Rare earths (Ytterbium (Yb), Erbium(Er) and Holmium (Ho)); the study conducted by Zamiri et al [20] reported the synthesis of rare earth (Er, La, Yb) doped ZnO nanostructures through wet precipitation method and studied their structural and optical properties. Senol [21] have also studied the structural, optical and electrical properties of rare earth (Er, Yb)-doped ZnO using hydrothermal method. The study was carried out by Soumahoro et al [22] have reported the structural, optical and electrical properties of Yb-doped ZnO thin film 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. Khataee et al [23] synthesized Holmium doped ZnO nanoparticles using sonochemical technique. Singh et al [24] have synthesized Ho and Y-doped ZnO nanoparticles using wet chemical synthesis technique, the optical studies reveal that the near band edge position shifts towards the lower wavelength side for the as synthesized nanoparticles. Franco et al [25] have also reported the optical and dielectric properties of Ho doped ZnO synthesized by the combustion reaction method.

Coating ZnO nanostructures could be one of the most effective approaches, which used to improve its properties. In spite of that, the studies on the coated ZnO nanostructures are relatively poor in literature; Li et al [26] have investigated the micro-structure and optical performance of Ag-coated ZnO nano-needles. Chen et al [27] have reported the characterization of freestanding graphene coated ZnO nanowires for optical waveguiding. To the best of our knowledge, the synthesis and characterization of ZnO nanorods coated with holmium have not been previously reported in literature.

In this present work, we report the synthesis and the structural characterization of pure and Holmium coated ZnO nanorods; hydrothermal method has been applied to synthesize uncoated and Ho-coated ZnO nanorods. X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Fourier-transfer infrared spectroscopy (FTIR) were used to characterize the structural modifications induced by Holmium into the surface of ZnO and to survey the change in the morphology of samples. UV-visible spectroscopy was performed to study the absorbance properties of Ho coated ZnO nanorods. Hence, the fundamental aim of this current work is to investigate the effect of holmium on the structural and optical properties of ZnO nanorods.

2. Experimental details
In the hydrothermal process, ZnO precursors were purchased from Sigma-Aldrich. To synthesize ZnO nanorods, an equi-molar aqueous solution of 0.1 M zinc nitrate (Zn(NO$_3$)$_2$) and hexamethylenetetramine (C$_6$H$_{12}$N$_4$, HMT) was prepared using deionized water. This mixture was heated at a constant temperature of 90°C in an oven for 24 h. The coated material followed the same steps, then the surface of ZnO nanorods was coated with holmium using the drop coating. The obtained materials were deposited on Si (100) substrates and dried at 50°C for 2 hours.

3. Results and discussion
3.1. X-Ray diffraction
Figure 1 shows the X-ray diffraction pattern of pure and Ho coated ZnO nanorods. As can be seen from the spectra, the analysis of the diffraction peaks of pure ZnO reveals the presence of hexagonal wurtzite structure with no other peaks of impurities. Moreover, it shows that the growth was in the three principal directions (reflections (100), (002), (101)). For Ho coated ZnO, results showed that (002) and (101) peaks of ZnO have been disappeared, while the corresponding diffraction peak (100) of ZnO still exist, but its intensity have been decreased. Intense diffraction peaks corresponding to holmium emerged at
$2\theta = 8.32^\circ$, $2\theta = 9.38^\circ$ and $2\theta = 18.51^\circ$. This indicates that the ZnO nanorods were coated with Ho by using drop coating technique.

![X-ray diffraction spectrum of pure and Ho coated ZnO nanorods.](image)

**Figure 1.** X-ray diffraction spectrum of pure and Ho coated ZnO nanorods.

### 3.2. Scanning electron microscopy

Morphological characterization of pure and Ho coated ZnO nanorods was studied using scanning electron microscopy (SEM) observation. Figure 2 illustrates typical SEM of ZnO nanorods prepared via hydrothermal method. As clearly shown in the Figure 2(a), pure ZnO nanorods were relatively grown vertically, nanorods having hexagonal shape with average diameter and length are about 500 nm and several micrometres (~4µm) respectively. For the coated material shown in the figure (b), ZnO nanorods grown with different sizes and different diameters. In addition, it is clear to see that the nanorods are coated tightly by the holmium with a few wrinkles and higher defect density on surface of nanorods, which indicates that the surface morphology of ZnO nanorods is influenced by coating with holmium.

![SEM images of pure ZnO nanorods and Ho coated ZnO nanorods.](image)

**Figure 2.** SEM images of pure ZnO nanorods and Ho coated ZnO nanorods.
3.3. Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy is an important technique, which reveals information about the structure orientation; chemical compositions of a compound and identification of impurities mainly exist near samples surface. ZnO coated with holmium were characterized by FTIR spectroscopy shown in the Figure 3. The coated material exhibits characteristic absorption peaks at 475 cm\(^{-1}\) and 674 cm\(^{-1}\) which could be assigned to Metal-Oxygen (Zn-O or Ho-O) stretching vibration. The peak located at 674 cm\(^{-1}\) is more intense which is may be correspond to Zn-bending vibration mode of ZnO; the typical characteristic band of the wurtzite hexagonal phase of pure ZnO, normally the region band of 400-700 cm\(^{-1}\) corresponds to the metal-oxygen band [28]. The band observed at around 1050 cm\(^{-1}\) may be ascribed to the bending vibration of nitrate [29]. The two peaks located at 1460 cm\(^{-1}\) and 1660 cm\(^{-1}\) that may be assigned to the symmetric and asymmetrical stretching of Zinc carboxylate respectively; probably from the small residue of zinc acetate used in reaction [30]. The absorption peak around 2920 cm\(^{-1}\) is due to C-H (acetate) stretching mode of alkane groups and the peak around 3734 cm\(^{-1}\) is due to O-H stretching vibrations of hydroxyl group on the surface of the material [31]. However, the origin vibration of the strongest peak located at 2350 cm\(^{-1}\) can be assigned to adsorbed CO\(_2\) molecules on the surface of the sample [32]. Comparing our measurements with the results of pure ZnO nanorods synthesized via hydrothermal method reported by Soni et al [30], there is a shift of the all bands in addition to the presence of strongest band at 2350 cm\(^{-1}\) indicating a strong interaction between ZnO and holmium.

![FTIR spectra of Ho coated ZnO nanorods.](image)

3.4. UV-Visible spectroscopy

The optical absorption spectra of Holmium coated ZnO was explored by UV-Vis spectrometer in the wavelength range (280-400nm) shown in the Figure 4. The three absorption bands at 314, 356 and 382 nm were blue shifted as compared with bulk absorption band of ZnO; band gap emission of ZnO originates from the recombination of the free exciton [33]. The band located at 382 nm may be attributed to \(\pi \rightarrow \pi^*\) transitions of ZnO; from the valence band to the conduction band (O\(_{2p}\)→Zn\(_{3d}\)) as shown in the schematic diagram (Figure 5). The Two other bands located at 356 nm and 314 nm may be assigned to
4f→4f transitions (n→π* and π→π* transitions) of Ho that are located at the surface of the ZnO nanorods, which give rise to the energy transfer from photon generated electron-hole pair in the ZnO nanorods to Ho in the surface of the ZnO nanorods [34]. The schematic diagram in figure 5 illustrates different transitions and absorption mechanisms indicated in the UV-Vis spectra. The blue shift may be ascribed to the nano size effect of the synthesized ZnO or may be attributed to the higher defect density on the surface of nanorods as shown in the SEM images, which may be expected to provide new bound excitons with new binding energies, which gave rise to the appearance of new absorption peaks [30]. Or maybe ascribed to the combination of optical transition to the excitonic state of ZnO nanorods and electronic transitions involving the 4f levels in Ho substituting the Zn ions [35].

Figure 4. UV-Vis spectra of Ho coated ZnO nanorods.

Figure 5. Schematic transitions diagram of ZnO and Holmium.
Conclusion
To summarize, to the best of our knowledge, the present study explores, for the first time, the synthesis and characterization of ZnO nanorods coated with Holmium. ZnO nanorods were prepared using hydrothermal method, the surface of ZnO nanorods was coated with Holmium by drop coating. Structural and morphological properties have been performed. The results revealed that both pure and Ho coated ZnO have the hexagonal wurtzite structure, nanorods were grown with different sizes and coated tightly with holmium. UV-Vis spectra measurements demonstrated that the coated material exhibits blue shifted absorptions peaks. This study was focused to reveal information about the structural and optical properties of Yb doped ZnO nanorods, which may enhance their performance for the optoelectronic applications.

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