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RESEARCH PAPER

Simple Preparation as well as Structural, Microstructural and Optical Properties of Cu Doped ZnO Nanostructures

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ABSTRACT

In this study, the nanostructures of $Zn_{1-x}Cu_xO$ with x=0.000, 0.025, 0.050 and 0.075 were successfully synthesized by sol-gel auto combustion method using glycine as a fuel. The prepared powders were calcined at 300 °C. The effect of Cu doping on structural and optical properties of powders was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-visible absorption spectroscopy (UV-vis) and photoluminescence (PL). The XRD patterns showed all samples have wurtzite structure. There is an extra peak belong to CuO at 2θ=38° in the XRD pattern of the sample with x=0.075. The average crystal size of the prepared powders is about 29-47 nm. The SEM micrographs revealed that all doped nanostructures have Leaf-like structure with the thickness about 15-20 nm. Absorption spectra showed a red shift and decrease in the band gap in the $Zn_{1-x}Cu_xO$ system. The PL spectra showed that the maximum Emission wavelength increases with dopant concentration.

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INTRODUCTION

Recently, the semiconducting nanomaterials have attracted attention due to their unique physical, chemical and optical properties. Among many kinds of semiconductors that have been studied, Zinc oxide (ZnO) is a promising material which is of great interest for a variety of applications. ZnO with hexagonal wurtzite structure has a direct band gap around 3.3 eV as well as large exciton binding energy of 60 meV at 300K. Due to its outstanding such as optical properties, high mechanical and chemical stability and low cost, zinc oxide is extensively applied in the solar cells, gas and luminescent sensors. Doping can make some changes in the electrical and optical properties of ZnO and also, it can affect the crystal growth when it is performed during the nanoparticles formation process. One effective way to modify the optical and electronic properties of nanostructured semiconductors is doping with suitable elements by introducing traps and discrete energy states in the band gap for the excited electrons [1-6]. In the recent years, many researchers have studied the doping of ZnO with divalent metal ions such as Co^{2+} [4], Ag^{2+} [7], Mg^{2+} [8] and Cu^{2+} [6], Among these mentioned elements, Cu^{2+} is an important element due to its possibility to change the microstructure and the optical properties of the ZnO system and its chemical and physical properties that are similar to those of Zn [9]. As zinc oxide has some native defects such as oxygen vacancies and zinc

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interstitials that can affect the optical properties of the ZnO by creating a donor levels in its band gap, it is interesting to study the structural and optical properties of Cu-doped ZnO. Many wet chemical methods are used for the synthesis of ZnO nano materials such as solvothermal [10], hydrothermal [11] co-precipitation [12] and microwave method [13-14] Sonochemical [15]. In particular, the sol–gel auto-combustion route is one of the most attractive and useful methods for the preparation of nanostructures materials due to its advantages like; the production of ultra-fine particles, narrow size distribution, good stoichiometric control and short processing time [16]. In this study the $Zn_{1-x}Cu_xO$ system nanostructure were synthesized via a sol-gel auto combustion method using glycine as a fuel and its structural and optical properties were studied.

MATERIALS AND METHODS

$Cu(NO_3)_2.3H_2O$, $Zn(NO_3)_3.4H_2O$ and glycine (NH_2CH_2COOH) were purchased from Merck and used without further purification. The phase formation of the prepared samples was identified using X-ray diffraction (XRD; Cu-K_α radiation, λ=1.5418Å). The microstructure was investigated by use a field emission scanning electron microscope (FE-SEM). The optical properties of the samples were carried out using UV-visible absorption spectroscopy (UV-vis) and photoluminescence (PL).

Synthesis of nanopowders

Briefly, metal nitrates in stoichiometric ratio were dissolved in deionized water. Then, glycine solution was added to the mixture and after constant stirring for 30 min the resultant solution was heated at 80 ºC to transform into a xerogel. During heating the dried gel burnt out in a self-propagating combustion manner to form a fluffy powder. The reaction is described in the following formula:

$$(1-x)Zn(NO_3)_2 + xCu(NO_3)_2 + NH_2CH_2COOH \rightarrow Zn_{1-x}Cu_xO$$

The as-burnt precursor powder was calcined at 300 ºC in air for 2 hours. Finally, $Zn_{1-x}Cu_xO$ nanostructures were obtained from drying at 300 °C of washed powders.

RESULTS AND DISCUSSIONS

structural study

To determine the phase purity and crystal structure of the prepared samples, the x-ray diffraction analysis was performed. Fig. 1 shows the XRD diffraction peaks of pure ZnO and Cu

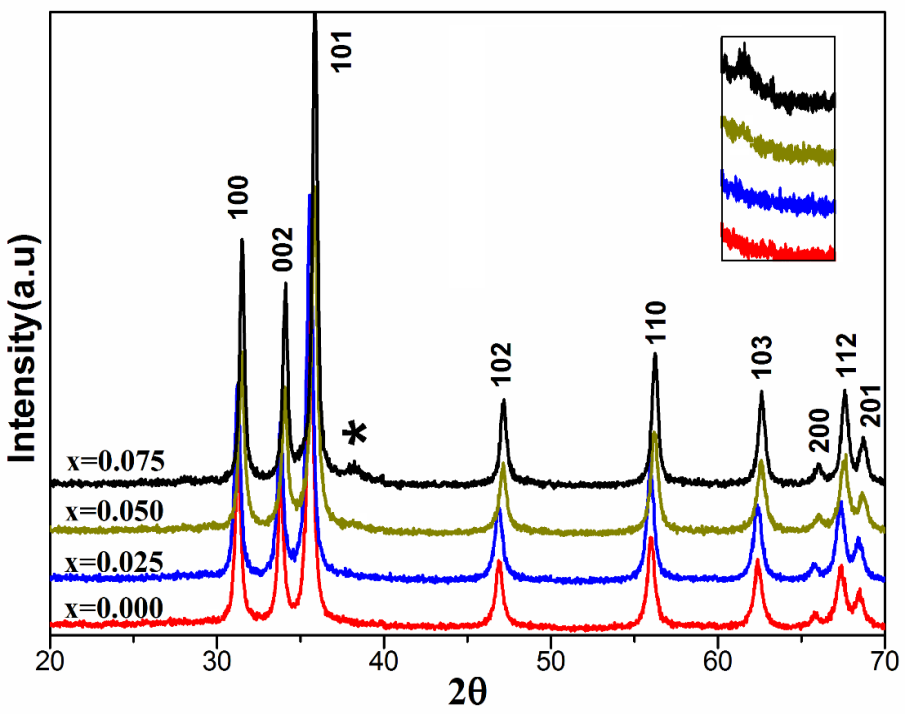

Fig. 1. XRD pattern for different Cu content (x) of $Zn_{1-x}Cu_xO$ nanostructures.

Table. 1. The cell parameters 'a' and 'c', c/a ratio, average crystal size (D) of different $Zn_{1-x}Cu_xO$ nanostructures.

x	*a* (Å)	*c* (Å)	*c/a* (Å)	D(nm)
0.000	3.3029	5.3522	1.6204	29.46
0.025	3.3012	5.3979	1.6351	47.14
0.050	3.2750	5.3639	1.6378	42.89
0.075	3.2719	5.3753	1.6429	39.32

doped ZnO ($Zn_{1x}Cu_xO$) nanostructures with x=0.000, 0.025, 0.050 and 0.075. These peaks confirms that ZnO has wurtzite structure with crystalline peaks at 2θ= 31.8° 34.4°, 36.1°, 47.4°, 56.6°, 62.8 and 69.1° that can be respectively indexed to the planes of (100), (002), (101), (102), (110), (103) and (112) (JCPDS standard data, Card No. 36-1451).

The preferred orientation for all samples is along (101) plane that is the most stable phase of ZnO. The XRD patterns of cooper doped ZnO are similar to the undoped one for the lower Cu concentration

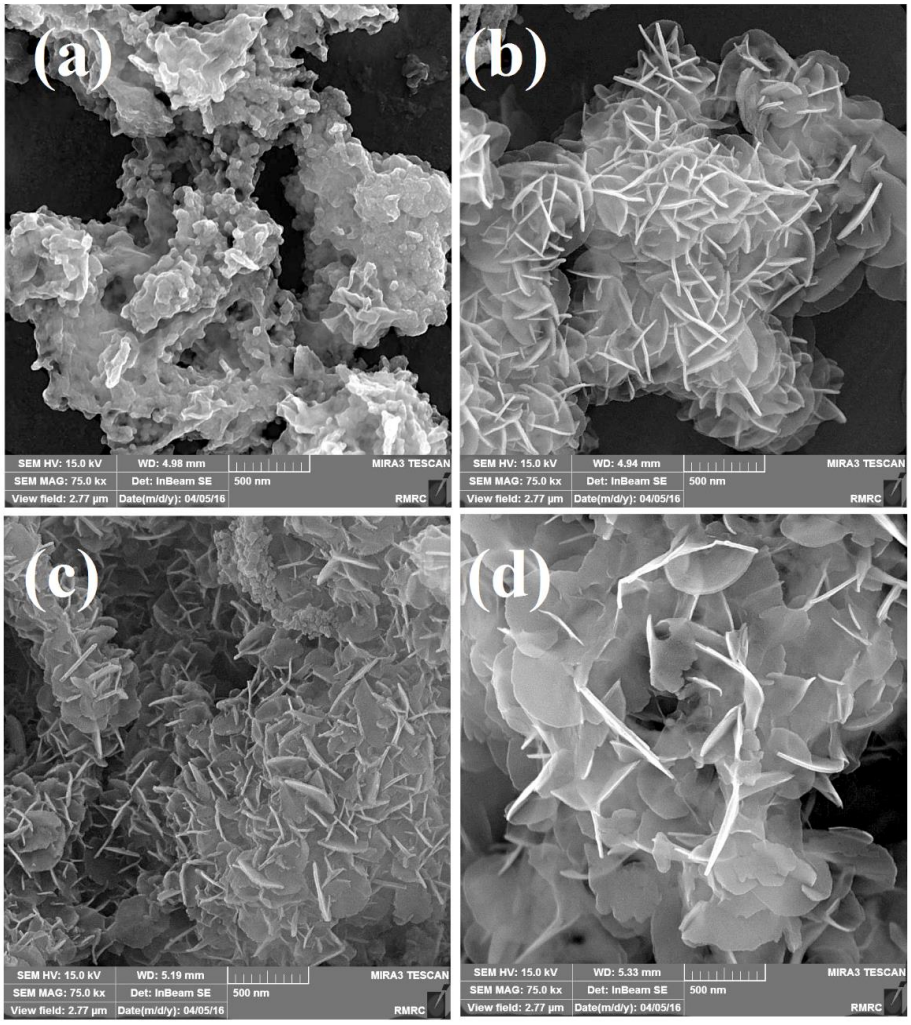

Fig. 2. SEM images of undoped ZnO (a) and Cu doped with x=0.025 (b), 0.05 (c) and 0.75 (d) ZnO nanostructures.

(x=0.05) and no diffraction peaks of CuO or other impurity phases were detected which is due to the incorporation of Cu^{2+} ions into the Zn^{2+} sites without changing the crystal structure of the ZnO lattice. Similar behavior was reported in the other studies like [17] and [18] which confirms that the wurtzite structure of ZnO doesn't alter as long as the dopants concentration are kept under the solubility limits. However, there is an extra peak at 2θ=38° (denoted as *) for the sample with x=0.75 that according to the JCPDS card No. 05-0661 is corresponding to the CuO along (111) plane. This confirms the results reported by other researches which noted that the solubility limit of Cu in ZnO is below 5% [19].

The average crystal size of the prepared powders (listed in Table 1), calculated from the broadening of diffraction peaks of (101) plane using Debye Scherrer's equation is about 29-47 nm. The lattice parameters a and c, listed in Table 1, are calculated from the following equation [20]:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \left(\frac{l}{c}\right)^2 \quad (2)$$

The values of the lattice parameters a anc c have been found to be in a good match with those JCPDs card No: 36-1451. The variation of c/a ratio shows the deformation of structure of the ZnO. Table 1. shows that the value of the c/a ratio increases with incorporation of Cu in the ZnO nanostructures.

Morphological study

The surface morphology of the pure and Cu doped ZnO nanostructures are represented in Fig 2.

A general comparison indicates that the

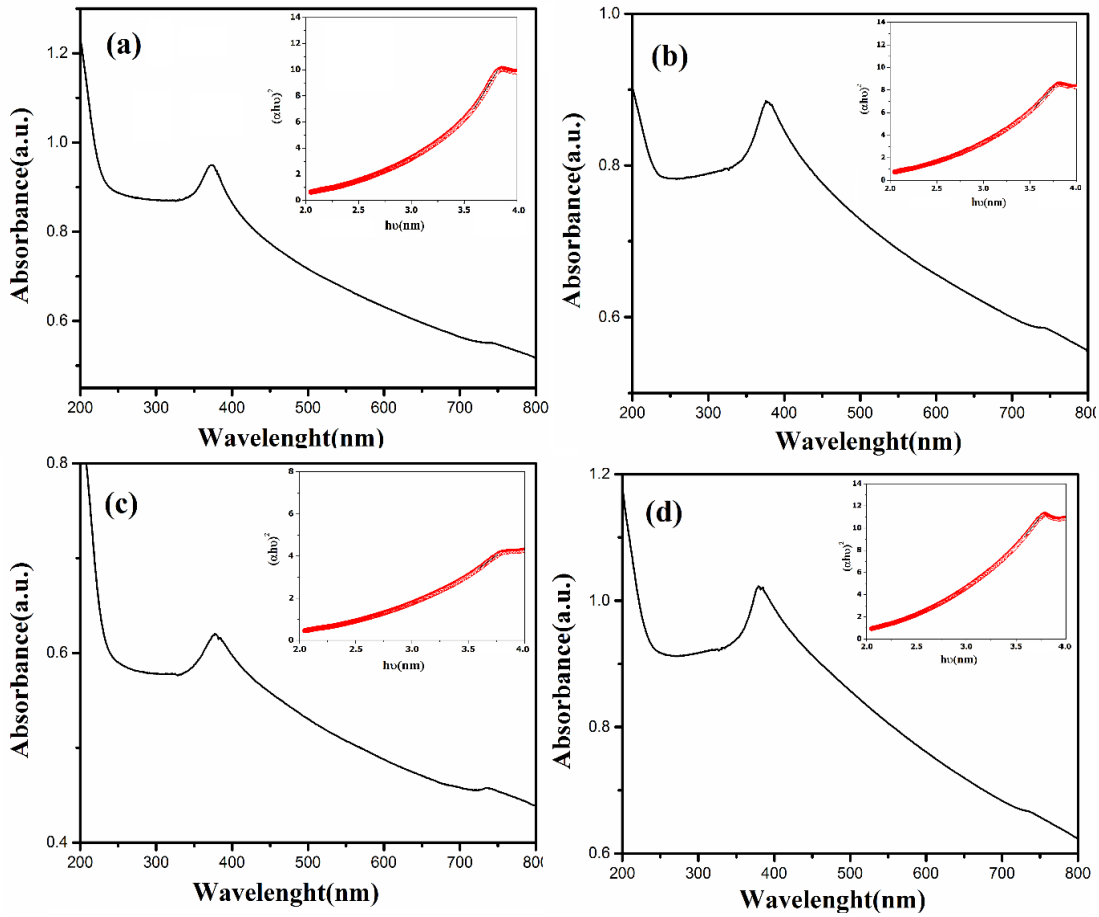

Fig. 3. UV–Visible spectra of $Zn_{1-x}Cu_xO$ powders with x= 0.00 (a), 0.025 (b), 0.050 (c) and 0.075 (d). The inset figures show the $(\alpha h\upsilon)^2$ versus hυ curves for the band gap determination.

morphology of samples is dependent on the Cu content. The surface of ZnO is rather smooth in Fig. 2a. However, after doping with Cu, the sheets with random orientations are rough and the particles shows leaf-like morphology. The leaves are observed consisting of very thin irregular sheets with lateral dimension of 100–400 nm and thickness of 15-20 nm, as shown in Fig. 2b–d. Moreover, the diameter and thickness of the sheets increased by increasing x. Because of the high effective surface samples, this type of nanostructures can be a functional areas such as sensors used.

Optical study

The optical absorption spectra of the undoped and Cu doped ZnO, carried out from 200 to 800 nm, are shown in Fig 3. It is seen that the pure ZnO powder shows a strong exciton peak (λ_A) at 374 nm with corresponding exciton energy of about 3.31 eV, calculated from $Eex=ch/\lambda_A$, where c is the speed of light and h is Planck's constant. In addition, incorporation of Cu^{2+} ions into the ZnO structure leads to a red shift in λ_A to 376, 377 and 379 nm, with Eex values equal to 3.30, 3.29 and 3.27 eV for x= 0.025, 0.050 and 0.075, respectively.

The optical band gap (Eg) of prepared powders was measured by Tauc's equation using the following formula [21]:

$$\upsilon\alpha h=A(h\upsilon-E_g)^n \quad (3)$$

where α is absorption coefficient, A and h are the constants, E_g is the optical band gap of the sample and the exponent n=1/2 for direct band gap. The inset in Fig 3 shows the plot of $(\alpha h\upsilon)^2$ versus hυ for pure the prepared nanostructures. The values of E_g has been distinguished by extrapolating the linear portion of the plots of $(\alpha h\upsilon)^2$ against hυ to the energy axis. Results show that the Eg values are equal to 3.06, 2.82, 2.73 and 2.75 for x=0.00, 0.025, 0.050 and 0.075, respectively. The reduction in band gap with the increase in Cu content, may be ascribed to the creation of some energy donor levels by Cu^{2+} ions in the band gap and also, a strong mismatch in the electronegativity between the Zn and Cu atoms [22].

Fig. 4 shows PL spectra of as-prepared undoped and Cu doped ZnO nanopowders. In case of undoped ZnO, a UV emission peak, related to the recombination of electron–hole in near band edge levels is observed at 415 nm, while low intensity peaks at 482 is observed in the blue–green region. the PL spectra of copper-doped ZnO samples reveals that, UV emission peak shifts to the longer wavelength with Cu content that might be a sign of

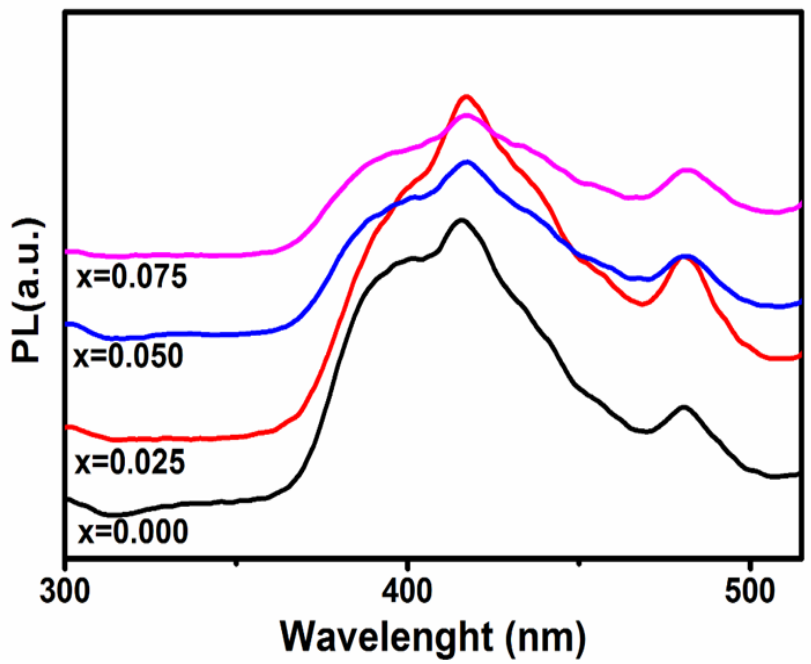

Fig. 4. PL emission spectrum of undoped and Cu doped ZnO nanopowders

the optical band gap decreasing.

CONCLUSION

The nanostructure of $Zn_{1x}Cu_xO$ with x=0.000, 0.025, 0.050, 0.075 have been successfully synthesized by a sol-gel auto combustion method. The structural, microstructural and optical properties of powders were determined by using of XRD, FE-SEM, Uv-Vis and PL.The x-ray diffraction patterns showed the prepared powders have wurtzite structure. The sample with x=0.074 had an extra peak of CuO at $2\theta=38^{o}$. FE-SEM micrographs revealed that all doped nanostructures have Leaf-like structure with the thickness about 15-20 nm. The optical studies showed a red shift and a reduction in optical band gap of $Cu_XZn_{1-X}O$ nanosheets in comparison with the pure ZnO. Absorption spectra showed and the band gap of samples decreased by increase of Cu content. The PL spectra showed that the maximum Emission wavelength increases with dopant concentration.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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