JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 13 No 1, 01006(3pp) (2021)
ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 13 № 1, 01006(3cc) (2021)

Environment-Friendly Synthesis of Undoped and Cu doped ZnO Nanoparticles and Study of their Optical Absorption Properties towards Biological Applications

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(Received 11 January 2021; revised manuscript received 22 February 2021; published online 25 February 2021)

Wet chemical method is a simple and cost-effective way to synthesize nanoparticles of high yield and mass production compared to other conventional methods. Besides, it does not require the maintenance of rigorous experimental conditions like high temperature, low pressure or flow of carrier gases. We have followed a simple wet chemical method to synthesize pure and Cu doped ZnO nanoparticles. Absorption spectroscopic study yields the absorption behavior of a material over a wide range of the electromagnetic spectrum. Absorption study of the synthesized undoped ZnO and Cu/ZnO reveals that doping with Cu decreases the absorption coefficient. It clearly indicates that the scattering of photons by phonons reduces due to Cu doping. The Urbach energy is an important parameter to understand the degree of disorder of phonon states in a material. It also enables us to study the dependence of the absorption coefficient on the wavelength of incident photons of energies lower than the band gap energy. For pure ZnO, the Urbach energy was calculated to be 0.511 eV and decreased to 0.483 eV upon doping with Cu in ZnO. The extinction coefficient was also calculated to understand the optical absorption process in the material.

Keywords: ZnO, Doping, Absorption, Phonon, Scattering, Urbach energy.

DOI: 10.21272/jnep.13(1).01006 PACS numbers: 78.67.Bf, 78.67.Rb, 87.64. – t

1. INTRODUCTION

Zinc oxide (ZnO) is a very well-known II-VI semiconductor being investigated over the last decades. It is a direct band gap semiconductor of band gap energy ~ 3.4 eV and has large excitonic binding energy ~ 60 meV at room temperature [1]. Due to this high band gap, it is being used in UV lasing [2]. Besides, it has high optical transparency in the visible region. Thus, it can be used as transparent coating in electrode of solar cells [3]. The non-centrosymmetric crystal structure of ZnO leads uncompensated charges along c-axis of the wurtzite structure. Thus, ZnO crystal is dipolar in nature and exhibit piezoelectric effect. Yang et al. has demonstrated the vibration induces piezoelectric energy from ZnO thin film [4]. There are several methods like physical and chemical vapor deposition, sputtering, vapor-liquid-solid, hydrothermal, and electrochemical method have already reported in the literature to synthesize wide variety of ZnO nanostructures [5]. Wet chemical method is a simple and cost-effective technique to produce ZnO nanostructure over a large scale of high purity [6]. Additionally, this method does not require the maintenance of high temperature, low pressure, controlled flow of carrier gases as in the case of vapor phase growth processes. The particle size can be controlled by using suitable surfactant like PVA, PVP etc. By using suitable capping agent, the directional growth of crystal is also possible [7]. Elmi et al. have reported the synthesis of high quality of ZnO nanoparticles using simple wet chemical technique [8]. There is another report by Awad et al. to produce high quality ZnO nanopencils from acetate based chemical growth process [9]. Here, in this paper, we report the growth of undoped and Cu doped ZnO nanoparticles followed by typical microstructural and optical characterization. We have also represented, in detail, several optical parameters related to the photon absorption process in semiconductor nanostructures.

2. MATERIALS AND METHOD

2.1 Synthesis of Pure ZnO Nanoparticles

In our experimental process of synthesizing ZnO, we used all the chemicals as supplied (Merck, 99.99 % pure) without further purification. We used distilled water for preparing the aquatic solution of precursors. 4.391 g of zinc acetate dehydrate was added with water to prepare 0.4 M solution. 2.097 g of LiOH was dissolved water to prepare 1 M solution. The so prepared LiOH solution was put under magnetic stirring at room temperature. The zinc acetate solution was then added drop-wise. The stirring was continued for 2 h. At the end of the reaction, a white precipitate was deposited at the bottom of the flask. The deposit was filtered, washed with distilled water and dried in a furnace at 100 °C further characterization.

2.2 Synthesis of Cu Doped ZnO Nanoparticles

In our experimental process of synthesizing Cu doped ZnO, we used all the chemicals as supplied (Merck, 99.99 % pure) without further purification. We used distilled water for preparing the aquatic solution of precursors. 4.391 g of zinc acetate dehydrate was added with water to prepare 0.4 M solution. 2.097 g of LiOH was dissolved water to prepare 1 M solution. The so prepared LiOH solution was put under magnetic stirring at room temperature. The zinc acetate solution was then added drop-wise. Now $CuCl_2$ solution of predetermined concentration was added dropwise to the above solution. The stirring was continued for 2 h.

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At the end of the reaction, a white precipitate was deposited at the bottom of the flask. The deposit was filtered, washed with distilled water and dried in a furnace at 100 °C further characterization. In all the cases we maintained the temperature of the solution at 30 °C and the stirring speed was maintained at a fixed value.

3. RESULTS AND DISCUSSION

The UV-visible absorption spectroscopic data were collected in Perkin Elmer LS-45 spectrophotometer over the wavelength range of 200-800 nm. Typical optical absorption spectra of undoped and Cu doped ZnO (Cu/ZnO) nanoparticles is shown in Fig. 1. The absorption is very high for pure ZnO in the visible region. However due to doping of Cu, the absorption reduces and thus the transparency increases. This indicates that doping of Cu reduces the defects in the structure leading to less scattering of photons from ZnO nanocrystals.

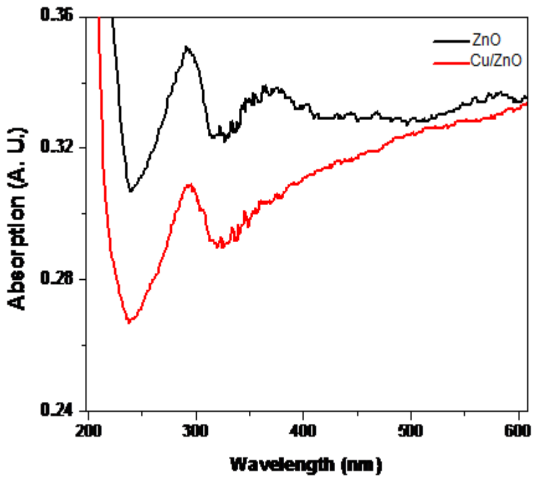

Fig. 1 – Absorption spectra of undoped and Cu doped ZnO

The optical absorption process obeys Beer-Lambert law given by [10]

$$I = I_0 e^{-\alpha x}, \tag{1}$$

where I_0 and I are the intensities of the incident and transmitted beams over a distance x, and α is the absorption.

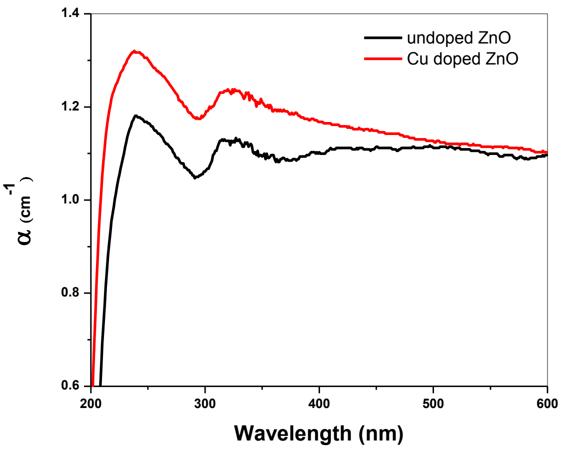

Fig. 2 – Variation of absorption coefficient with wavelength

The absorption coefficient also varies with wavelength of the incident photon and can be obtained from the absorption spectra. Variation of α for both pure and Cu doped ZnO with wavelength is shown in Fig. 2.

This wavelength dependence of optical absorption property of semiconductor obeys an exponential equation as follows:

$$\alpha = \alpha_0 \exp\left[\frac{h\nu - E_0}{E_U}\right]. \tag{2}$$

Here E_0 and α_0 are the constants, E_U is the Urbach energy [11]. Hence, the plot of lnα with photon energy $h\nu$, we can obtain the Urbach energy E_U. This variation is shown in Fig. 3. The Urbach energy of pure ZnO as calculated from Fig. 3 is 0.511 eV and is very close to the reported value of 0.61 eV [11]. However, in case of Zn/CuO this energy is reduced to 0.483 eV. This change is due to the change in crystallinity due to Cu doping.

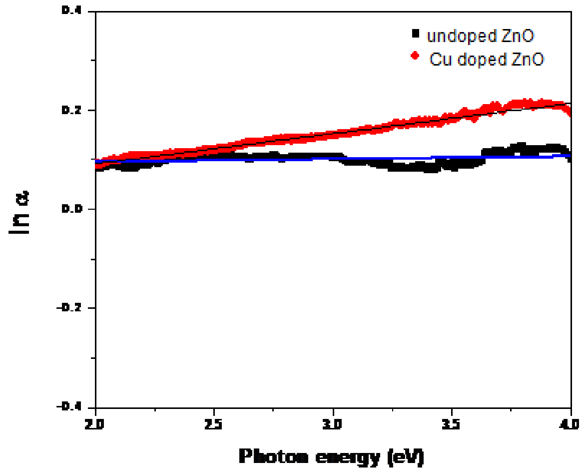

Fig. 3 – Variation of lnα with photon energy to calculate E_U

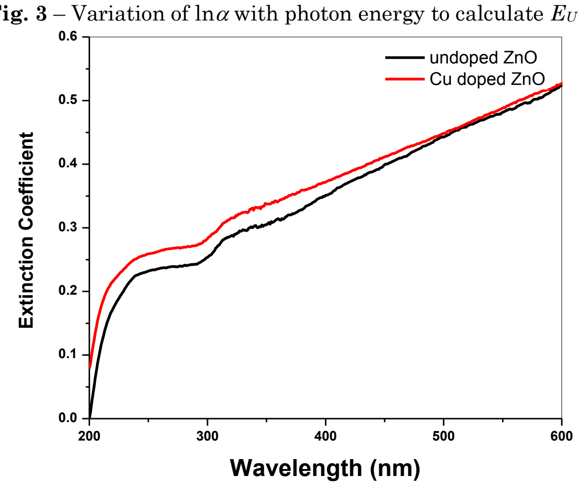

Fig. 4 – Variation of extinction coefficient with wavelength

The optical extinction coefficient (k) is defined by the relation [13]

$$k = \frac{\alpha\lambda}{4\pi}. \tag{3}$$

The variation of the optical extinction coefficient with the wavelength of the incident photon for undoped and Cu doped ZnO is shown in Fig. 4. The extinction coefficient is higher for Cu/ZnO compared to pure ZnO.

4. CONCLUSIONS

In conclusion, we have analyzed the absorption property of undoped and Cu doped ZnO nanostructures and calculated the corresponding absorption parameters. It was observed that due to Cu doping the absorption reduces. We have also calculated the Urbach energy and it was reduced due to Cu doping owing to the change in crystallinity. It was also observed that the extinction coefficient is higher for Cu/ZnO compared to pure ZnO. The synthesized materials will be very useful in antimicrobial pastes and nanoparticle-based drug delivery applications.

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