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Optical Characterizations of Zn-doped CuO Nanoparticles

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Abstract : In this work we evaluate structural and optical properties of Zn-Doped CuO nanoparticles grown by microwave assisted solvothermal method. The formation of Zn-Doped CuO nanoparticles were confirmed by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and UV-Visible spectroscopy. The average particle size have been found to be about 40 to 80 nm , The SEM image showed that the prepared product consists of spherical nanoparticles with narrow size distribution. The UV-Visible spectrum of Zn doped-CuO nanoparticles shows a strong blue shift compared to that of bulk and also shows the band edge-absorption peak and is found to be at 350 nm. The obtained band gap value is 2.65 eV for Zn-Doped CuO nanoparticles.

Keywords : Nanostructure, Chemical synthesis, X-ray diffraction.

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Introduction

Manipulation of size, shape, morphology and composition of technologically important materials, within the dimension of nanometers to micrometers, has been a great challenge for material scientists for the last few decades. One-dimensional (1D) nanomaterials, such as nanotubes, nanowires, and nanobelts or nanoribbons have received much attention because they are considered to be the key structural components of future electronic, optical, and mechanical devices. Their unique properties can be harnessed for the design and fabrication of nanosensors, solar cells, field emitters, and transistors. Cu-based nanomaterials have been extensively studied due to their many potential applications.

There are several methods reported to synthesize copper oxide NPs like sol-gel, hydrothermal route, electrochemical [1-2] etc. Recently, direct oxidation of metallic copper substrates had been demonstrated as a simple and convenient route to form the CuO nanowires[3]. Since the morphology of nanomaterials has profound influence on their physical properties, developing a method for morphologically controllable synthesis of CuO nanoparticles is very important. Hydrothermal or solution method has been considered as the most promising route in terms of safety and environmental friendliness for the large-scale production of CuO nanostructures. Although great progresses have been made in the synthesis of CuO nanostructures, it still remains a major challenge to develop a facile, one-step route for the synthesis of CuO architectures composed of nanoscale building blocks [4].

As a well-known p-type semiconductor with a narrow bandgap of 1.2 eV, CuO has been extensively studied because it is an important component of copper oxide superconductors [5]. With regard to its commercial value and interesting properties, Metal oxide CuO has also been widely exploited in a versatile range of applications such as optical, electronic, magnetic and catalytic properties. In addition, size dependent vibrational properties of the nanomaterials are also observed in several semiconductors and oxides materials catalysts [6], magnetic storage media, field emission devices , gas sensors , lithium batteries , and solar cells [7-8]. Copper (II) oxide is widely used as a catalyst because of its high activity and selectivity in oxidation and reduction reactions [9-11]. Transition metal oxide such as copper oxide (CuO and Cu_2O), iron oxide (FeO, Fe_2O_3 or Fe_3O_4) and zinc oxide (ZnO) nanomaterials have special physicochemical properties arising from the quantum size effect and high specific surface area, which may be different from their atomic or bulk counterparts [12].

Methods and Materials

In this paper, Zn-doped CuO nanomaterial was synthesized by a simple microwave assisted solvothermal method. Analytical reagent (AR) grade Copper acetate, Zinc acetate, Urea, Ethylene glycol (as solvent) are used as precursors. Copper acetate and urea are taken as solute in the molecular ratio 1:3 and dissolved in 100 ml ethylene glycol as individually. The prepared solution is kept in a domestic microwave oven (operated with frequency 2.45 GHz and power 800W). Microwave irradiation is carried out till the solvent is evaporated completely. In the end, we remove the organic impurities of the obtained colloidal precipitate. The prepared sample is dried in atmospheric air and annealed it for 30 minutes at 100^0C to improve the ordering. The reaction time, yield percentage and color of the samples are noted. The synthesized NPs have been characterized by using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and UV-visible absorption analysis.

2.3 Characterization

The powder X-ray diffraction (XRD) was performed using automated X-ray diffractometer (X-PERT PRO Philips System) operating CuK_α at wavelength 1.54056 Å. The average crystallite size (D) has been calculated using Scherer's relation $D = K\lambda / \beta \cos\theta$, where the constant K is taken to be 0.94, λ is the wavelength of X-ray used, where β the is full width of half maximum (FWHM). The morphology of the powder samples was characterized by scanning electron microscope (SEM) JEOL/EO JSM-6390. The UV spectrum was obtained using LAMBDA-35 UV visible spectro photo meter. The optical bandgap energy (E_g) is also estimated for the prepared sample. UV-Visible absorption spectrum of synthesized nanoparticles shows the band edge-absorption peak is found to be at 350 nm. The optical band gap of the produced nanoparticles is calculated using the Tauc's relation [13]

$$\alpha h\upsilon = (h\upsilon - Eg)^n$$

where $h\upsilon$ is the incident photon energy, n is the exponent that determines the type of electronic transition causing the absorption and can take the values 1/2 and 2 depending whether transition is direct or indirect respectively. Plots between $(\alpha h\upsilon)^2$ and $h\upsilon$ for Zn-doped CuO samples are drawn and the best linear relationship indicating that the optical band gap of the doped CuO nanoparticles is due to a direct allowed transition. The value of the band gap is determined from the intercepts of the straight line.

Results And Discussion

3.1 XRD Analysis

XRD pattern of as prepared Zn-doped CuO nanoparticles is shown in Figure 1. It gives a single-phase with a monoclinic structure. The lattice parameters are calculated using the least square refinement from the UNITCELL-97 program .The obtained parameters are a= 4.682 Å, b= 3.424 Å, C=5.127 Å with volume cell of 81.52 Å ^{3}. These values are consistent with the reported literatures and with the respective "JCPDS" (Joint Committee on Powder Diffraction Standards) card No.89-5895.No peaks of impurities are found in XRD pattern. The peaks are broad due to the nano-size Effect. The average crystallite size of Zn-doped CuO nanoparticles is found to be 40-80 nm using Scherrer formula.This indicates that the prepared CuO material is highly crystalline having characteristic of pure monoclinic crystallites without having any peak due to the possible Cu2O and Cu(OH)2 impurity and well arrange in specific orientation

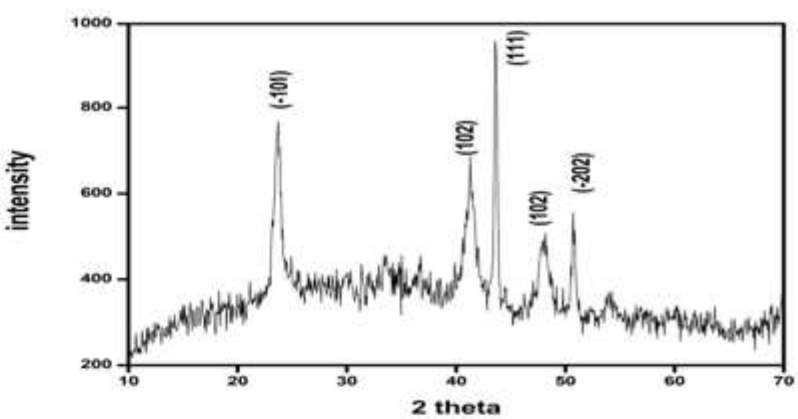

Figure1 : XRD spectrum of zinc- doped CuO nanoparticles

3.2 Structurel Studies

Figure 2 shows the SEM image of as prepared Zn-doped CuO nanoparticles. The SEM images confirm the spherical morphology of Zn-doped CuO nanoparticles. High magnification images show that the small spherical structures are grown on the surface of the big spherical structures. The resultant morphology is looking like a cluster of grapes. The size and morphology of Zn-doped CuO nanoparticles have been examined by SEM. It clearly show the surface features, by which it highlight that CuO nanoparticle was successfully prepared and it can be seen that the particles congregate together and the size of which is about 100 nm. The morphology of the prepared Zn-doped CuO is very interesting and looks like pollen grain. The formation of small structures on bigger one may increase its surface area and indirectly the catalytic activity which discussed in this paper.

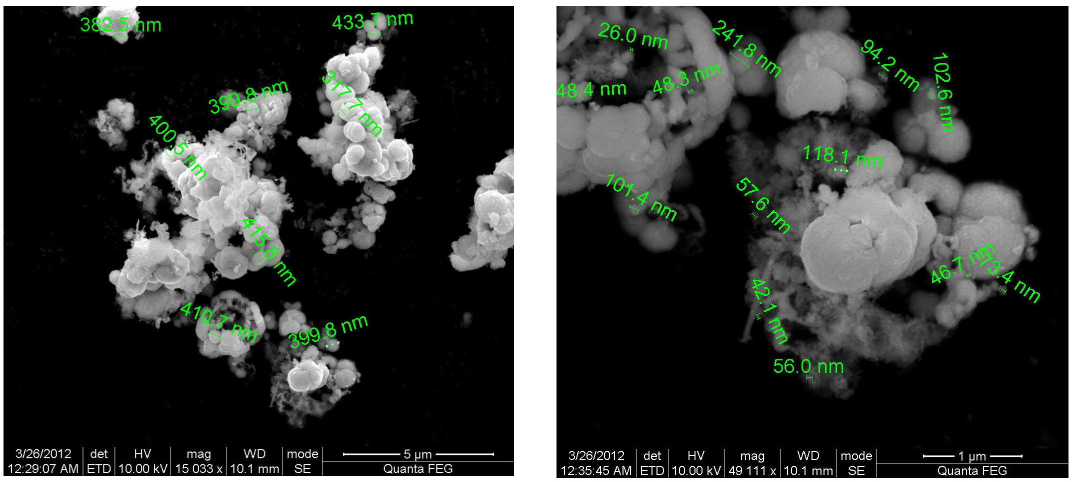

Figure 2 : SEM micrographies of Zn-doped CuO nanoparticles

3.3 Optical Studies

UV-Visible absorption, reflection spectrum and bandgap spectra for Zn-doped CuO nanoparticles are shown in Figure 3 and Figure 4. The spectrum shows the band edge-absorption peak which is found to be at 350 nm. In UV-Vis, high energy electromagnetic radiation in the wavelength range of 100-700nm is utilized to promote electrons to higher energy orbital’s. From the UV spectra, it is clear that the absorbance decreases with increase in wavelength. This decrease in the absorption indicates the presence of optical band gap in the material. The best linear relationship is obtained by plotting $(\alpha h\upsilon)^2$ against $h\upsilon$ indicating that the optical band gap of the Zn-doped CuO nanoparticles is due to a direct allowed transition. The direct band gap is determined from the intercept of the straight line at a = 0, which is found to be 2.65 eV for Zn- doped CuO. Thus, it thus can be inferred that copper oxide can be activated by visible light.

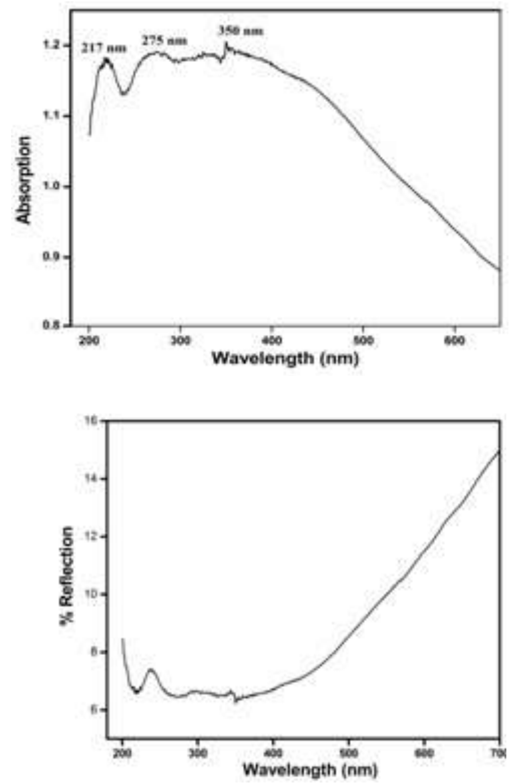

Figure 3 : UV-Vis spectrums of zinc- doped CuO nanoparticles

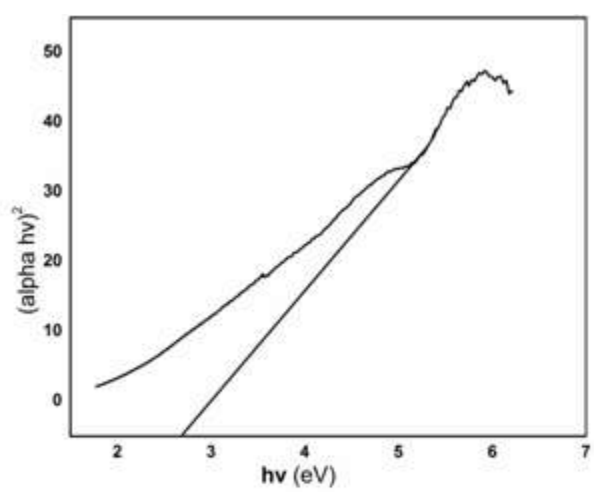

Figure 3 : Bandgap spectrums of zinc- doped CuO nanoparticles

Conclusion

Zn-doped CuO nanoparticles with monoclinic structure sizes ranging from 40 to 80 nm have been synthesized successfully by microwave assisted solvothermal method. The effects of addition of impurity on the physical properties of the NPs have been investigated. XRD patterns show the formation of the CuO monoclinic crystal phase. From the SEM micrographies, it can be understood that the crystallites prepared are of nearly spherical in shape, UV-Visible absorption spectrum of synthesized nanoparticles show the band edge-absorption peak and is found to be at 350 nm. The UV-Visible absorption spectrum of Zn- doped CuO nanoparticles shows a strong blue shift compared to that of bulk. The direct band gap is determined from the intercept of the straight line at a = 0, which is found to be 2.65 eV for Zinc-doped CuO.

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