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Preparation and study of Sn-doped CuO nanoparticles as semiconductor

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Abstract

This paper reports the effect of Sn doping on structural and optical properties of CuO nanoparticles prepared by the simple hydrothermal method in mild condition without pH adjustment and surfactant. The structural and optical properties of these CuO and Sn doped CuO particles were investigated using X-ray powder diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and photoluminescence spectroscopy (PL). powder X-ray analysis reveals that Sn^{+4} ion have substituted the Cu^{+2} ions without changing the monoclinic structure of CuO but the average particle size of nano CuO increases from 16 nm to 22 nm.The PL emission spectra revealed blue shift after introducing Sn into the CuO and an intensity decreasing as well.

Keywords: CuO nanoparticle, Sn doped CuO nanoparticles, hyrothermal method and Photoluminescence

1. Introduction

The design, synthesis, and characterization of nano-materials are the subject of most of the research [1,2]. This is because of the realization that some of the physical and chemical properties of nano-materials are sometimes considerably different from those of the bulk state [3]. Also metal-oxide-semiconductors have been widely used for optoelectronic applications like smart windows, solar cells, light emitting diodes and flat panel display [4–8]. The elementary structure applied in the electronic devices and modern semiconductor technology is the metal /semiconductor structures. The p-type transition-metal oxide with a narrow band gap (ca. CuO nanoparticles, E_g=1.2 eV) show unique properties, such as superparamagnetism and high magnetic susceptibility at low temperatures [9]. Copper oxide nanomaterials may have the advantage of a lower surface potential barrier than that of the metals, which affects electron field emission properties. Copper-oxide is considered as a potential field emitter, an efficient catalytic agent, and a good gas sensing material. It also plays an important role in the solar cell [10,11]. One of the most important methods to modify the characteristics of materials is the introduction of dopants in the parent system. It has been revealed that several dopants Cr, Co, Mn, Al, Mg, Cu and Fe would escort to enhance the surface area of SnO_2 nanostructure. These dopants alleviated the surface and promote the decrease in size as well as change the shapes [12]. Most of studies have paid attention to the sensing and photocatalytic properties of Cu-doped SnO_2 until now. However synthesis and study of metal doped copper oxide are still few and need more research. For example, one of the papers is “Influence of Mnsubstitution on microstructure and magnetic properties of $Cu_{1-x}Mn_xO$ nanoparticles” [9] but there is no research about preparation and study the effect of Sn doping on structural and optical properties of CuO nanoparticles. The present work is focused on the cost-effective and simple synthesis of Sn-doped CuO by hydrothermal method. Study of structural and optical properties of this nano particles are reported as well.

2. Experimental section

2.1. Apparatus

The morphology and crystallite size of the samples were determined by using a scanning electron microscopy (SEM, Hitachi S4160 microscope). The crystalline structures and approximate crystallite sizes of CuO and Sn doped CuO powders were identified by XRD analysis using a Holland Philips X pert X-ray powder Infrared spectra (IR) measurements were carried out on a Vector-22 Fourier Transform infrared spectrophotometer. The excitation and photoluminescence (PL) spectra of sample were measured with a Perkin-elmer LS-55 fluorescence spectrometer.

2.2. Materials

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$Cu(CH_3COO).H_2O$, $SnCl_4.5H_2O$ and NaOH was used as starting material. All of the chemical reagents used in the experiments were analytic grade without further purification and treatment.

2.3. Synthesis

Sn doped CuO nanoparticles were prepared by a simple hydrothermal method. Typically, 11 mmol of NaOH powder was added into 20 ml of aqueous solution containing $Cu(CH_3COO).H_2O$ (5 mmol) under vigorous stirring. the 20 ml of a solution containing $SnCl_4.5H_2O$ (0.25 mmol) was introduced to the above solution dropwise under stirring. After 15 min of continuous stirring, the mixture was then transferred into a Teflon-lined stainless autoclave and maintained at 180˚Cfor 15 h and cooling it down to room temperature. The brown precipitate was collected and washed with distilled water and absolute ethanol several times to remove impurity and finally dried at 60˚C.

3. Result and Discussion

Figure 1a shows XRD patterns of synthesized un-doped CuO nanopowder. All the diffraction lines are assigned well to monoclinic phases of copper oxide with a reference pattern (JCPDS 80-1916). Fig.1b shows the XRD patterns of Sn doped CuO. The XRD patterns of Sn doped CuO are similar to pure CuO, which confirms that Sn acts as a substitutional dopant [12]. According to scherrer formula, (equation 1) [11]

$$D= 0.9\,\lambda\,/\beta\ \mathrm{COS}\Theta \qquad \text{Equation 1}$$

Where λ, B, and Θ are the X-ray wavelength (1.5418 A for Cu-Kα), Bragg diffraction angle, and the full width at half-maximum of the diffraction peak (FWHM), respectively. According to calculation, crystal grain sizes 22 and 16 nm were obtained for Sn doped CuO and CuO, respectively. As expested, crystalline size of Sn doping in CuO increased [13].

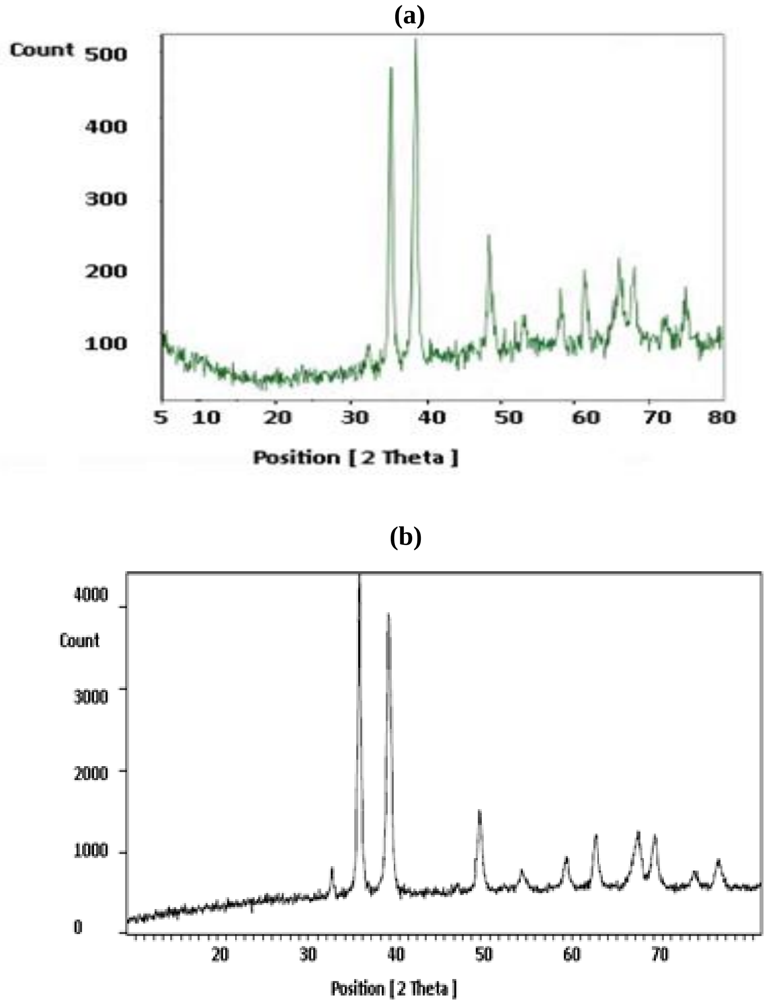

Figure 1. XRD pattern of (a) CuO and (b) Sn doped CuO nanoparticles.

Figure 2 shows the FT-IR spectra of CuO (a) and Sn doped CuO (b) the peak at 3447 and 3444 cm^{-1} are due to the stretching vibration of OH groups, which generally semiconductor nanostructure materials absorbed from the environment owing to their meso-porous structure [14]. In spectrum (a) two frequency peaks at 596 and 521 cm^{-1} relates to M-O band vibration frequencies support the presence of monoclinic phases [15]. Figure 3 is a typical SEM image of Sn doped CuO nanoparticles with the average diameter of 20 nm, which agrees with the result of XRD analyses.

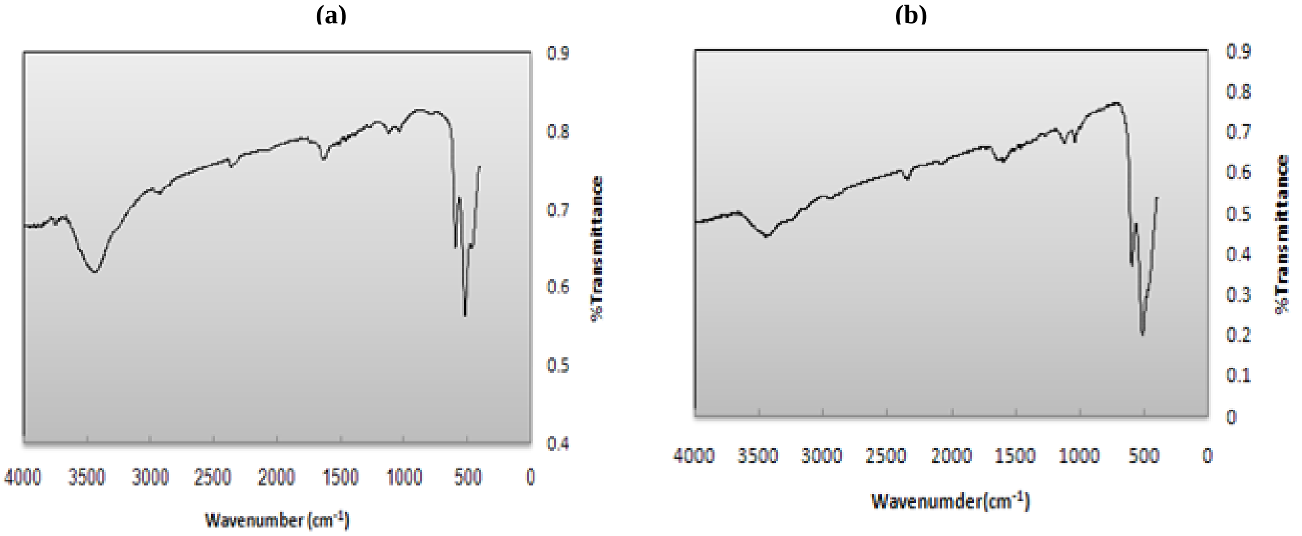

Figure. 2. FT-IR spectra of (a) CuO and (b) Sn doped CuO nanoparicles

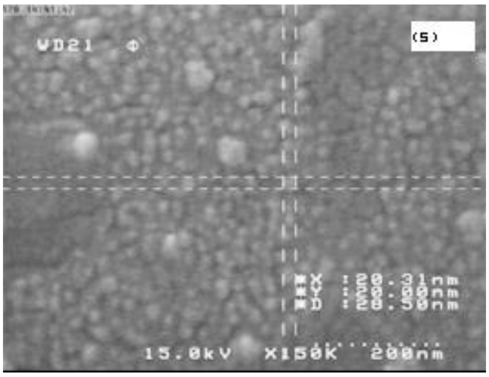

Figure.3.SEM image of Sn doped CuO nanoparicles

PL emission spectra were recorded for the Sn doped CuO and pure CuO samples (shown in figure 4). The excitation wavelength was 200 nm. In metal oxide nanostructures, the PL emission is broadly divided into two sections including near band edge (NBE) UV emission and deep level (DL) defect related to the visible emission [16]. The high intensity visible emission is related to the relatively high concentration of impurities and crystal defect [17]. In general, oxygen vacancies, which usually act as radiative center, play an important role in the luminescence properties of the metal oxide semiconductors [18]. The oxygen vacancies present in three different charge states: V_o^0, V_o^+ and V_o^{2+} in the oxide [19,20]. As V_o^0 is a very shallow donor, the most oxygen vacancies will be in their paramagnetic V_o^+ state under flat-bandconditions. And the origin of luminescence is assigned to the recombination of electrons in singly occupied oxygen vacancies with photoexcited holes in the valence band [21]. V_o^{2+} center (an oxygen vacancy containing no electrons) located slightly above the valence band [22,23]. Emission intensity of CuO nanoparticles are seen to reduce with the introducing Sn doping (fig.4). Infact, by incorporating Sn into the CuO host lattic, V_o^+ and V_o^{2+}centers are reduced to maintain the balance of the valence compared with the initial condition, hence reduce the intensity of oxygen vacancy related emission.

4. Conclusion

We have successfully synthesized CuO and Sn doped CuO nanoparticles using simple hydrothermal method. SEM images show that the average particles size of synthesized Sn doped CuO is 20 nm. XRD analysis confirms that Sn^{+4} ions have been replaced with Cu^{+2} ions without affecting the crystal structure, while the average particle size of nano-CuO increased to 22 nm. Emission intensity reduction of CuO in photoluminescence spectra is according to Sn doping.

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