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Optical and Luminescent Properties of NiO-CuO Nanocomposite by The Precipitation Method

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ABSTRACT

NiO-CuO nanocomposites were synthesized via precipitation method by using a cationic precursor [(nickel acetate dihydrate, Ni(CH₃CHOO)₂·2H₂O), copper acetate dihydrate, (Cu(CH₃CHOO)₂·2H₂O)], an anionic precursor (alkali hydroxide, NaOH), complexing agent (2-hydroxy propane-1,2,3-tricarboxylic acid, C₆H₈O₇), and mono hydric alcohol (monohydroxymethane, CH₃OH) as a solvent. The prepared (NiO-CuO) nanocomposites were characterized by physico-chemical studies such as X-ray diffraction (XRD), energy dispersive X-ray (EDX), scanning electron microscopy (SEM), optical absorption (UV) and photoluminescence (PL). The optical absorption spectra exhibit that the band gap energies of the NiO-CuO nanocomposite decrease with the increase in the calcination temperature, which can be attributed to the improvement in the crystallinity of the NiO-CuO. The PL intensity of the NiO-CuO nanocomposite peaks which decreased with the increase in the calcinations temperature was observed from the PL spectra; it was due to the lesser oxygen vacancy defects that occurred. The schematic formation of the NiO-CuO nanocomposite is also discussed.

1. Introduction

Nickel oxide (NiO) is a p-type semiconductor with a broad band gap ($E_g = 3.6-4$ eV) and cubic structure; it has device applications in sensors, solar cells, photo catalysis and optical devices etc., [1, 2]. Copper oxide (CuO) is a p-type semiconductor with a narrow band gap ($E_g = 1.2$ eV) and monoclinic structure; it has potential applications in optoelectronic devices, sensors, catalysts, lithium ion batteries and solar cells [3, 4]. When the narrow band gap of a semiconductor metal oxide nanomaterial is intermixed with the broad band gap of another semiconductor metal oxide nanomaterial, it exhibits enhanced physico-chemical properties, compared than the single compound of the semiconductor material, and could use for new device applications [4-7]. The technological application of mixed coupled semiconductor materials on a nanometer scale has been paid much attention in material science [4-7].

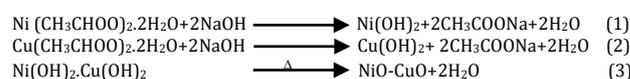
Various chemical methods such as chemical vapour deposition, sonochemical, impregnation sol-gel and precipitation methods to prepare mixed coupled semiconductor metal oxide nanocomposites were investigated [4-7]. We have employed the precipitation method [6] to produce the NiO-CuO nanocomposite. This method is very simple, and has easy manipulation and scale up, less agglomeration and environmental pollution.

In the present work, the NiO-CuO nanocomposite was synthesized by the precipitation method at different calcination temperatures. Moreover, the optical and luminescent properties of NiO-CuO nanocomposite at different calcination temperatures were investigated. In addition, the possible formation mechanism of NiO-CuO nanocomposite has also been proposed.

2. Experimental Methods

A weight of 2.48 g of Ni(CH₃CHOO)₂·2H₂O and 1.99 g of Cu(CH₃CHOO)₂·2H₂O were separately dissolved in 100 mL of CH₃OH under stirring. The weight 0.80 g of NaOH was added separately to the nickel acetate and copper acetate solution for 30 min. The copper hydroxide precursor solution intermixes with the nickel hydroxide precursor solution under stirring for a few min. The weight 2 g of C₆H₈O₇ was added

into the above solution for 30 min and it kept was dried at 120 °C for 12 h in a muffle furnace. After that, it was cooled to room temperature, and washed with ethanol several times. Finally, brown-black NiO-CuO powders were obtained, when calcined at 500 and 700 °C. The reactions involved in the process can be expressed as follows [4]:



2.1 Instrumental Characterizations

The prepared samples were characterized by X-ray powder diffraction (XRD) using the Schimadzu model; the XRD pattern 6000 with Cu K_α radiation ($\lambda = 1.5417$ Å) was recorded in the range of 30–70°. The morphological and elemental analyses were studied by the high resolution scanning electron microscope (HR-SEM) (FEI Quanta MKII FE SEM) with energy dispersive X-ray (EDX). The optical properties were studied by the UV-visible absorption spectra (Varian Cary5E spectrophotometer). The luminescence properties were studied by the PL emission spectra (Fluoromax-4 Spectrofluorometer).

3. Result and Discussion

Fig. 1a shows the XRD patterns of the NiO-CuO powder calcined at 500 and 700 °C. The observable diffraction peaks are in good agreement with those of the standard patterns of cubic structure NiO (JCPDS No. 47-1049) [2] and monoclinic structure (JCPDS No. 80-1268) CuO [3], respectively. No characteristic peaks due to any impurities and sharp peaks are present in the pattern, indicating that the prepared samples are of high purity and crystallinity. With an increase in the calcination temperature (700 °C), the diffraction peaks become more intense and narrow compared to those at 500 °C, indicating the growth of NiO-CuO. This result indicated that the crystallinity of NiO-CuO was significantly improved at higher calcination temperatures [8, 9]. The growth of NiO-CuO particles was further confirmed by the SEM studies, which is discussed later. From the XRD pattern, the calculated average crystallite sizes of the NiO-CuO powder are ~45-70 and 50-95 nm for 500 °C and 700 °C respectively, using Debye Scherer's equation [4]. This demonstrates that increasing the calcination temperature led to an appreciable increase in the crystallite size as well as crystallinity [8].

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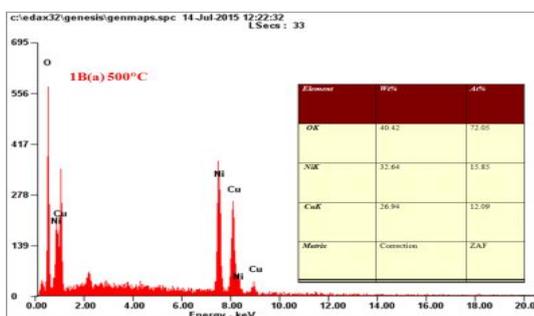
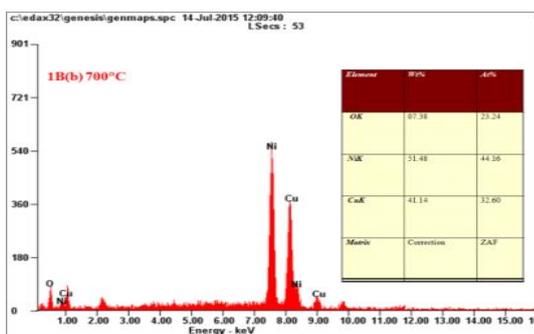
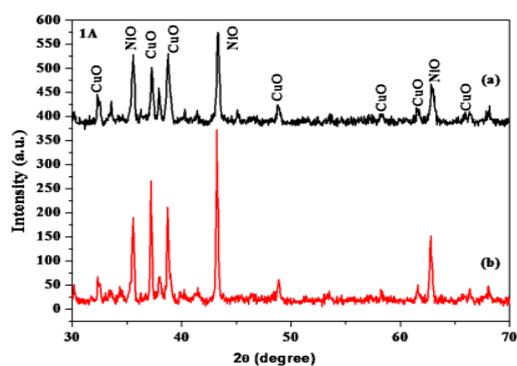


Fig. 1 a) XRD pattern and b) EDX spectra of the NiO-CuO nanopowder calcined at 500 °C and 700 °C

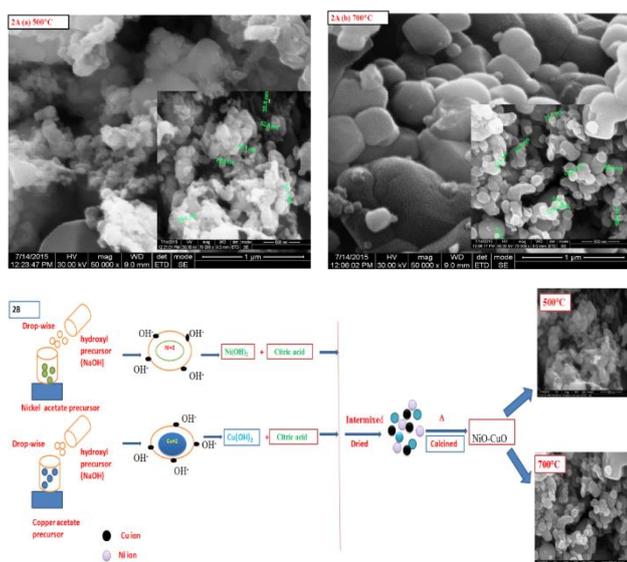


Fig. 2 a) SEM images of the NiO-CuO nanocomposite calcined at 500 °C and 700 °C and b) Schematic formation of the NiO-CuO nanocomposite

Further evidence of the composition of the NiO-CuO samples is obtained by the EDX measurement, which is an excellent technique for understanding the relative composition of a material. Fig. 1b shows the EDX spectra of the NiO-CuO powder calcined at 500 °C and 700 °C. It reveals the presence of Ni, Cu and O elements without any other impurity species. Based on the above it is seen that, Ni-O and Cu-O bonds are present, which is supported by the XRD result. Moreover, in the case of the lower calcination NiO-CuO sample, increased oxygen peaks were

observed, whereas in the higher calcination temperature sample, decreased oxygen peaks were observed in the EDX spectra. This was due to the higher calcination temperature which led to reduced surface defects such as oxygen vacancy, which is later discussed in the PL emission analysis. In addition, the atomic and weight percentages of the NiO-CuO nanocomposite powder are shown in the inset of Fig. 1.

The low-magnified SEM images of the NiO-CuO nanocomposite are shown in Fig. 2a. It shows that both the samples are composed of aggregated spherical particles. The average particle sizes of the NiO-CuO samples were found to be ~35-76 nm and 40-107 nm for 500 °C and 700 °C respectively, from the highly-magnified SEM images as shown in the inset of Fig. 2a. This is comparable with the average crystallite size calculated from the XRD studies, showing only a slight variation. It is clearly seen that higher calcination temperatures have a pronounced effect on the increase of the agglomerated spherical particles and average particle sizes of NiO-CuO [8]. The observation indicated that the particle size of the NiO-CuO nanocomposite increased at the higher calcination temperature; probably the crystallite size improvement is responsible for the XRD sharpness in Fig. 1a. Moreover, the calcination temperature behavior of the SEM studies of NiO-CuO, is similar to that of semiconductor (SnO₂) nanomaterials [9].

The UV-visible absorption spectra of the NiO-CuO nanocomposite are shown in Fig. 3a. The absorption edges of the NiO-CuO nanocomposite are observed in the UV and visible region. Generally, the absorption edges of NiO-CuO were observed in the UV and visible region, reported previously by Bayal et al [6]. With an increase in the calcination temperature, the absorption edge shifts slightly towards a longer wavelength, which may be attributed to the decreasing band gap of the NiO-CuO nanocomposite, which was confirmed from the optical absorption curve $((\alpha h\nu)^2$ versus photon energy) as shown in the inset of Fig. 3a. Further, the optical band-gap energies (E_g) of the NiO-CuO nanocomposite are found to be ~2.40-3.62 eV and 2.25-3.40 eV for 500 °C and 700 °C for respectively, by using the $(\alpha h\nu)^2$ versus photon energy (shown in the inset of Fig. 3a). There are two prominent band values, which can be assigned to the characteristic E_g values of the NiO and CuO components, respectively [6]. The appearance of two kinds of characteristic E_g values also confirms that the NiO-CuO sample is a composite material composed of NiO and CuO. Moreover, the E_g values decrease with the increase in the calcination temperature, which can be attributed to the improvement in the morphology and crystallinity of the NiO-CuO, samples [6], which was clearly seen in the SEM studies (Fig. 2a). Moreover, the obtained E_g values of the NiO-CuO samples are close to the reported value of the CuO-NiO nanocomposite [6, 10]. The presence of the narrow and broad E_g values of the NiO-CuO nanocomposite could be used for photoconductive applications [6].

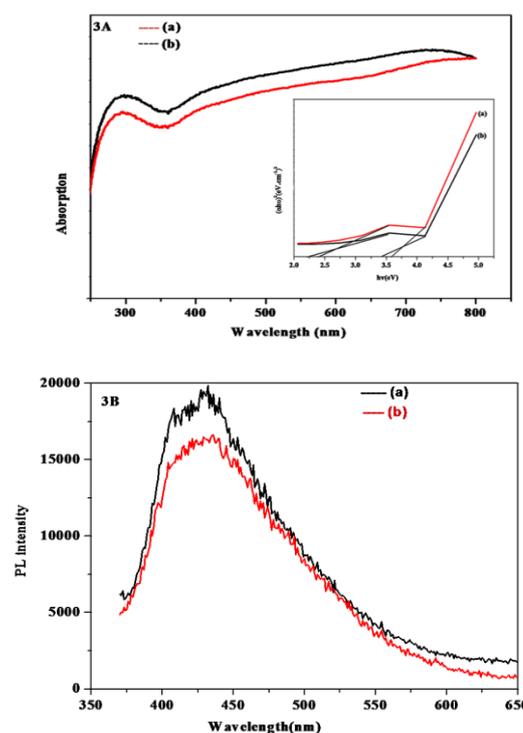


Fig. 3 a) UV- visible absorption and b) PL emission spectra of the NiO-CuO nanocomposite calcined at 500 °C and 700 °C.

Fig. 3b shows the PL emission spectra of the NiO-CuO nanocomposite. The broad visible emission peak at ~400-500 nm appeared under an excitation wavelength of 350 nm. The observed visible emission peaks have been attributed to the oxygen vacancy defects [9]. In general, the oxygen vacancies are the most common defects in the poly- or nanocrystalline oxide, and are to be the radiative center in the luminescence process [9]. From the PL emission spectra (Fig. 3b), it is clearly seen that the PL intensity of the peaks decreased with the increase in temperature, which is closely related to previous report by Gu et al., namely, that the PL intensity of the peaks decreased with the increase in temperature in semiconductor nanomaterial [9]. The above and literature results thus indicated that the higher calcination temperatures of the semiconductor produce a reduction in the oxygen vacancy defects.

4. Conclusion

In summary, NiO-CuO nanocomposites were prepared at different calcination temperature by the precipitation method. The XRD pattern indicates the formation of the mixed coupled phase (cubic-monoclinic) of NiO-CuO. The EDX spectra confirm the presence of Ni, Cu and O peaks, respectively, which further supports the formation of NiO-CuO. Agglomerated spherical morphologies with the average particle sizes of NiO-CuO nanocomposites of ~35-76 nm and 40-107 nm for 500 °C and 700 °C, were observed in the SEM studies. The SEM results have shown that the average particle size and agglomeration increase with an increase in the calcination temperature, which can be attributed to the improvement in the crystallinity of the samples. With the increase of the calcinations temperature, the optical band gap edge of NiO-CuO shifts towards the longer wavelength, and the optical band gap curve shows that the band gap decreases at higher calcination temperature. The calcination process can also affect the PL emission spectra of the NiO-CuO nanocomposite.

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