

Preparation and characterization of cobalt and copper oxide nanocrystals

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Copper oxide and cobalt oxide (Co_3O_4 , CuO) nanocrystals (NCs) have been successfully prepared using microwave irradiation. The obtained powders of the nanocrystals (NCs) were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric (TGA) analysis and Fourier-transform infrared spectroscopy. The obtained results confirm the presence of both nanooxides which have been produced during chemical precipitation using microwave irradiation. TEM micrographs have shown that the obtained nanocrystals are characterized by high dispersion and narrow size distribution. The results of X-ray diffraction confirmed those obtained from the transmission electron microscope. Optical absorption analysis indicated the direct band gap for both kinds of the nanocrystals.

Keywords: *nanoparticles synthesis; metal oxides; microwave oven; TEM micrographs; X-ray diffraction*

1. Introduction

Nanocrystalline semiconductors have drawn considerable interest in recent years because of their special properties, such as a large surface to volume ratio and unique optical properties as compared to those of the bulk materials [1]. The colloidal NCs integrated in the epitaxial grown layers allow device implementation based on NCs [2]. Wet colloidal NCs prepared chemically exhibit an enormous potential regarding tuning of their optical and structural properties [3]. The oxides of transition metals represent an important class of semiconductors, which find applications in magnetic storage media, solar energy transformation, electronics and catalysis [4]. Copper oxide has attracted much attention because it is the basis of several high- T_c superconductors. However, cobalt oxide is a promising candidate as an anode material for lithium secondary batteries because of its electrochemical capacity and high recharging rate [5]. The microwave synthesis, which is generally fast, simple and efficient in energy usage, has been developed and widely used in various fields, such as

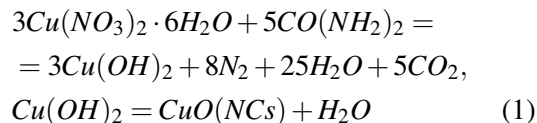
molecular sieve preparation, radiopharmaceuticals, preparation of inorganic complexes, organic reactions, plasma chemistry, analytical chemistry and catalysis [6]. In the present article, a rapid growth method has been used to prepare different monoclinic metal oxide nanocrystals using microwave irradiation. It was proved to be convenient, efficient and environmental friendly one step route to produce nanooxides. The product had good crystallinity, uniform morphology and high purity. The structural, optical and magnetic properties were studied for both kinds of nanoparticles.

2. Experimental

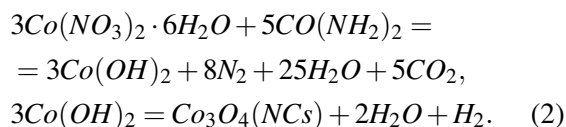
In a typical procedure, 25 mL water solution of 0.2 M $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to 25 mL water solution containing 0.2 M $\text{CO}(\text{NH}_2)_2$ in a round-bottom flask. The obtained solution was thoroughly mixed, to reach molecular level homogenization of the reaction medium. The mixture was placed in a microwave oven with 650 W power and the reaction was carried out under ambient air for 10 min. An excess of urea was used as fuel for the combustion and added under magnetic stirring for about 30 min. As the ignition occurred, the reaction went

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on vigorously for a few seconds. Urea works as a basic medium to form copper hydroxide as shown by the following reaction:



A black fine powder of CuO NCs was extracted. After cooling to room temperature, the precipitate was centrifuged, washed sequentially in distilled water, absolute ethanol and acetone and dried in air at room temperature. The final products were collected for characterization. The same steps were done for preparing the Co₃O₄ NCs as follows:



XRD measurements were performed on the powdered specimens using an X-ray (Shimadzu XD-3A) diffractometer. Copper target with $\lambda = 1.5418 \text{ \AA}$ was used as a source of X-ray. The scanning angle 2θ was in the range of 20° to 70° . TEM micrographs were recorded using a transmission electron microscope (JEOL-200CX), with accelerating voltage of 80 kV. The energy dispersive spectrometry (EDS) analysis for detecting the characteristic X-rays of the constituent elements was carried out using an X-Max 80 detector unit which was equipped with the transmission electron microscope.

The thermal behavior was studied using Shimadzu differential scanning calorimetry. IR spectra were obtained using FT-IR (Nicolet NEXUS 670) spectrometer, which is characterized by high rapid-scan capability and equipped with the photoacoustic (Model 300 of MTEC) detector. The spectra of the oxide samples were recorded in near-IR region, 400 cm^{-1} to 4000 cm^{-1} . The resolution of the measurements was 8 cm^{-1} and each spectrum was obtained by recording 200 consecutive scans. Optical properties of the nanoparticles in solution were studied using the UV-Vis (Shimadzu UV-2450) spectrophotometer in the wavelength range of 200 nm to 900 nm.

3. Results and discussion

To understand the phase symmetry of the as-prepared specimens, systematic XRD studies were performed. Fig. 1 shows the XRD patterns of the CuO and Co₃O₄ nanocrystals. The intensities and angular positions of the peaks are in good agreement with the previously mentioned values [7, 8]. No peaks related to impurities have been found in the diffractograms. In Fig. 1a, the diffraction pattern is in agreement with JCPDS Card No. 5-661. The obtained lattice parameters $a = 4.653 \text{ nm}$, $b = 3.410 \text{ nm}$ and $c = 5.108 \text{ nm}$ indicate the monoclinic structure of the CuO nanocrystals [9] which was found to be highly crystalline. The sharp X-ray peaks of the second Co₃O₄ product (Fig. 1b) indicate the monoclinic structure of the nanocrystals which was also found to be highly crystalline in agreement with the JCPDS Card No. 78-1969. Stability of the nanoparticles products can be easily checked using even one method, such as X-ray diffraction. When the sharpness degree of the diffraction peaks does not change over long time it confirms the stability of the present products. The average size of the nanocrystals can be estimated using the Debye-Scherrer formula [10]:

$$D = k\lambda / \beta \cos \theta \quad (3)$$

where k is a constant equal to 0.94, λ is the wavelength of the X-ray radiation ($\lambda = 1.5418 \text{ \AA}$), and β is the full width at half maximum of the diffraction peak corresponding to 2θ . Using equation 3, the crystallite sizes were found to be in the range of $14 \pm 1 \text{ nm}$ and 14.5 ± 1.3 for CuO and Co₃O₄ nanocrystals, respectively.

Fig. 2 shows the TEM images of the as-prepared CuO and Co₃O₄ nanocrystals. TEM micrographs have revealed that both oxides are composed of spherical particles with regular morphology and narrow size distribution. These findings are in agreement with those reported in previous studies [11, 12]. The particle size observed in TEM micrographs is $10 \pm 2 \text{ nm}$ and 13 ± 2 for CuO and Co₃O₄ nanocrystals, respectively, which is in good agreement with the results calculated by the Debye-Scherrer formula. The strain induced

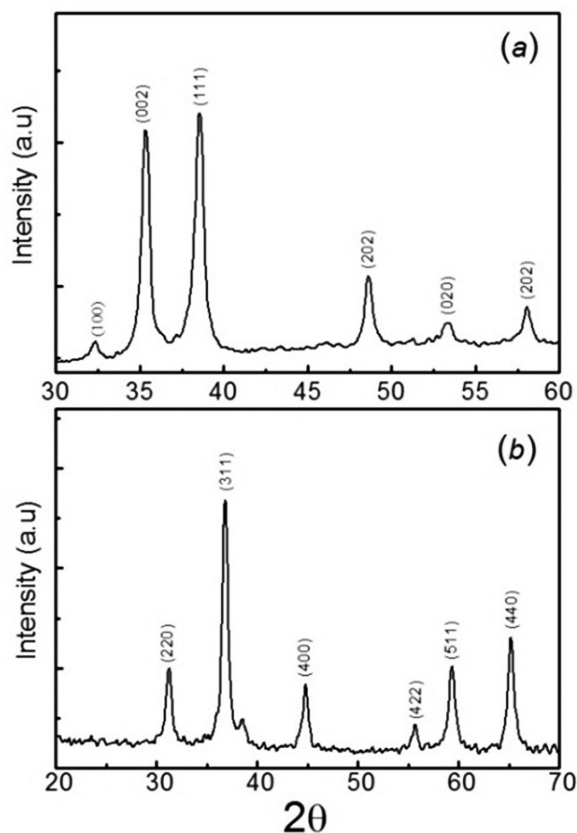


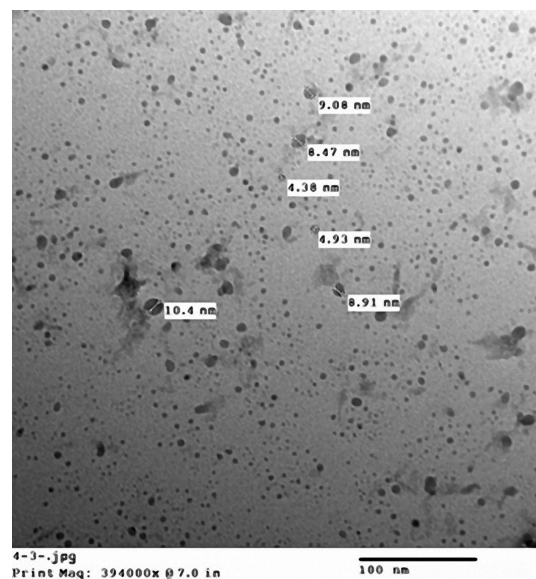
Fig. 1. XRD patterns of the as-prepared (a) CuO and (b) Co₃O₄ nanocrystals.

in powders due to the crystal imperfection and distortion [13] can be calculated using the following formula:

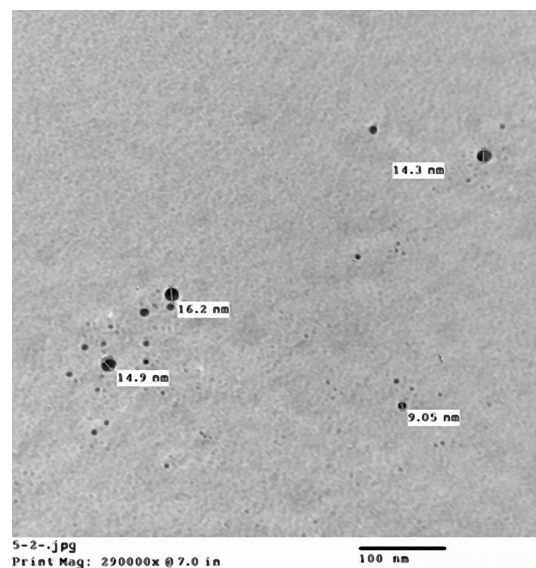
$$\varepsilon = \beta / 4 \tan \theta \quad (4)$$

The average values of induced strain are 0.0028 and 0.0027 for CuO and Co₃O₄ nanocrystals, respectively. These strain values have been assumed to be uniform in all crystallographic directions, considering the isotropic nature of the crystal, where the material properties are independent of the direction along which they are measured.

Fig. 3 shows the EDX analysis of CuO-NPs annealed at 600 °C. The results reveal the presence of copper (Cu) and oxygen (O) elements in the products and indicate that the nanoparticles are nearly stoichiometric. There are no other elemental impurities in the EDX spectra. The EDX result shows the presence of uniform distribution of copper



(a)



(b)

Fig. 2. TEM micrographs of the as-prepared (a) CuO and (b) Co₃O₄ nanocrystals.

and oxygen with atomic ratio of 1:1 in CuO. This result confirms the formation of pure CuO-NPs. The elemental analysis of the sample shows that the prepared sample is copper oxide, which is in good agreement with the results of XRD. Similar results were reported in the literature [14].

Temperature dependent weight loss of the as-prepared CuO and Co₃O₄ nanocrystals have been

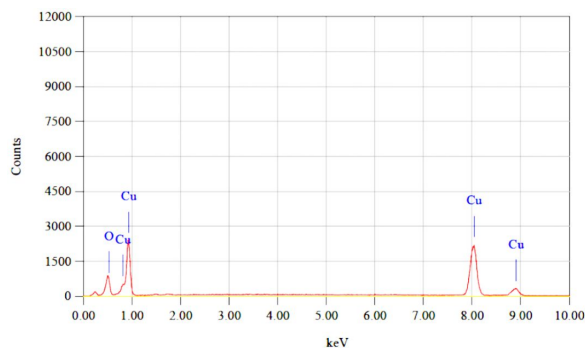


Fig. 3. Energy dispersive X-ray analysis of CuO-NPs annealed at 600 °C.

analyzed and the obtained results are shown in Fig. 4. It is easily seen from the TGA curves that the mass loss process of both oxides starts at 75 °C, which is related to evaporation of the water molecules absorbed on the surface of the products. In the same figure, another mass loss appears at about 205 °C which is due to decomposition of the $\text{Cu}(\text{OH})_2$ molecules.

Fourier transform infrared (FT-IR) spectrometry has been applied to study the surfaces of the CuO and Co_3O_4 NCs in the wavenumber range 400 cm^{-1} to 4000 cm^{-1} . In case of the CuO products, three distinctive bands have appeared as depicted in Fig. 5a.

The first strong absorption band at 533 cm^{-1} is due to vibrations of CuO functional groups, which confirms the presence of nanosized CuO particles in the nitrate matrix. The second band at 1104 cm^{-1} is related to the occurrence of O–C–O tensional tremble. Finally, the third one, corresponding to C=O stretching of carboxylate ion bond to the CuO nanoparticles as bidentate ligand, is located at 1383 cm^{-1} . Coordination of bidentate type is expected between the carboxylate ion and the Cu(II) of CuO [15]. As shown in Fig. 5b, it displays three distinctive bands originating from the stretching vibrations of metal-oxygen bond. The first band at 568 cm^{-1} is associated with the BOB3 vibrations in the spinel lattice, where B denotes the Co cations in an octahedral position, i.e. Co^{3+} ions. The second band at 662 cm^{-1} is attributed to the ABO3 vibrations, where A denotes the metal ion in a tetrahedral position. The third

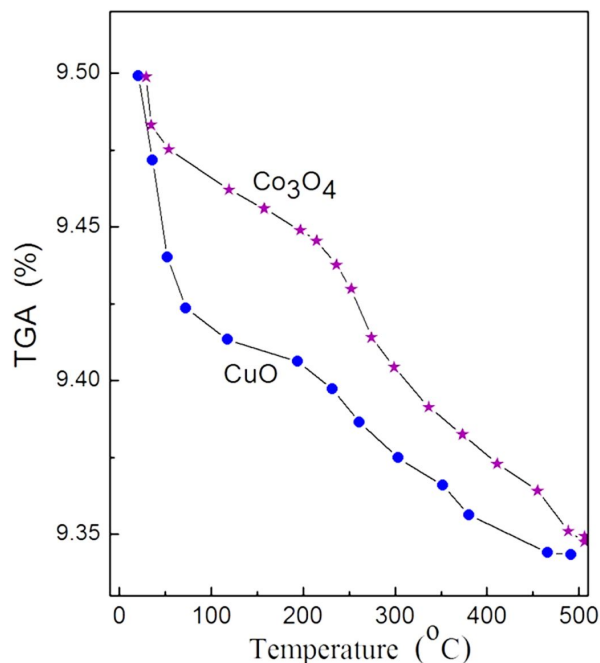


Fig. 4. TGA analysis curve for as-prepared (a) CuO and (b) Co_3O_4 .

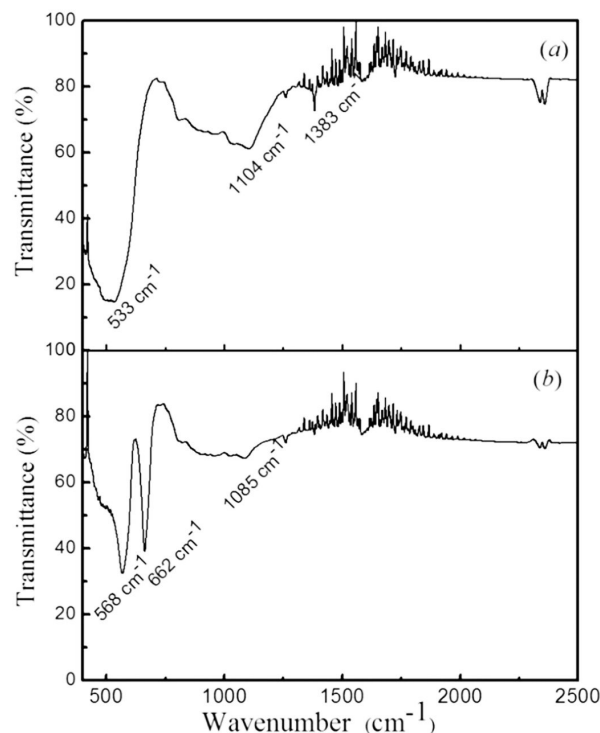


Fig. 5. FT-IR spectra of the as-prepared (a) CuO and (b) Co_3O_4 nanocrystals in the range of 400 cm^{-1} to 2500 cm^{-1} .

band at 1085 cm^{-1} is related to the occurrence of O–C–O tensional tremble.

UV-Vis electronic absorption spectroscopy study of the as-prepared oxides has been performed. The optical absorption spectra [16] have been used to calculate the absorption band gap E_0 according to the following equation:

$$(\alpha h\nu)^n = B(h\nu - E_0) \quad (5)$$

where $h\nu$ is photon energy, α is the absorption coefficient, B is a constant related to the material and the exponent n is equal to either 2 for direct transition or $1/2$ for an indirect transition. Fig. 6 shows the $(\alpha h\nu)^2$ versus $h\nu$ plots for both CuO and Co_3O_4 nanocrystals.

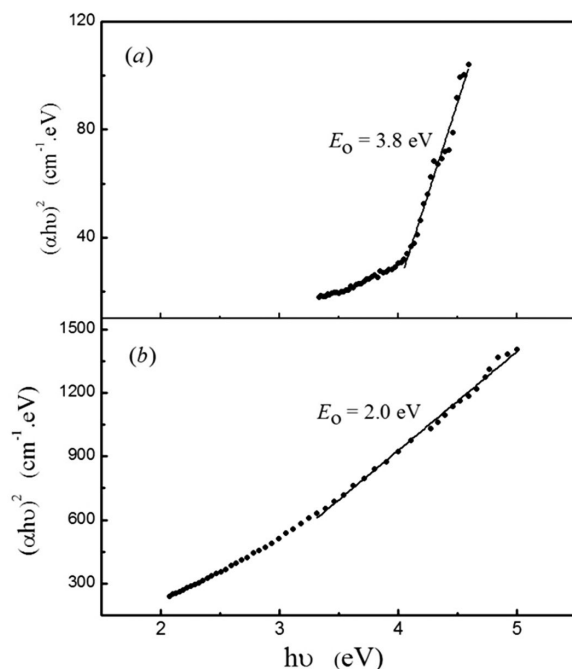


Fig. 6. $(\alpha h\nu)^2$ as a function of photon energy for the as-prepared (a) CuO and (b) Co_3O_4 nanocrystals.

The band gap of the as-prepared CuO was estimated to be 2.3 eV and 3.8 eV. The former value (2.3 eV) is higher than that measured ($E_0 = 1.85\text{ eV}$) for bulk CuO [17] but lower than that reported for the CuO nanocrystals [18]. Extrapolation of the straight segment of the obtained curve in Fig. 5b, gives $E_0 = 2.0\text{ eV}$ for direct allowed transition of Co_3O_4 nanocrystals

which is little larger than that reported for bulk Co_3O_4 ($E_0 = 1.96\text{ eV}$) specimens [19]. Similar results of the optical band gaps for both CuO and Co_3O_4 nanocrystals have been reported in the literature [20]. These band gap values are higher than the values of the bulk samples which is due to the quantum confinement effect.

4. Conclusions

Nanocrystalline CuO and Co_3O_4 particles with a monoclinic structure have been prepared successfully by a novel method using microwave irradiation. From XRD and TEM studies, it has been found that the particles are spherical in shape with an average size of 14 nm. Analyses of the FT-IR data have revealed the formation of impure CuO and Co_3O_4 phases with monoclinic crystal structure. The optical properties of both nanocrystals revealed the direct band gap of 2.3 eV for the copper oxide particles and 2.0 eV for the cobalt oxide product. These values of the band gap are higher than the values of the bulk samples which is due to the quantum confinement effect.

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