

CuO Elaboration and Studies of the Influence of Heat Treatment on the Structural Properties

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In the present work we synthesize nano powders of CuO by precipitation method, using CuCl₂ as precursor. The obtained powder has undergone a heat treatment annealing 100°C, and 450°C. Structural analysis by X-Ray diffraction, Fourier transform infrared (FTIR) microscopy and scanning electron microscopy (SEM) reveal that CuO nano particles are in nano graphs forms and with improved crystallization at 450°C, annealing temperature as monoclinic crystal lattice structure. The radius of NCs calculated by the Scherrer formula is 12.31 nm.

Keywords: Precipitation method, Precursor, X-ray diffraction, FTIR, FWHM.

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1. INTRODUCTION

Over the past two years research was increased to find new materials for applications in various fields. The size has become a fundamental parameter which, in addition to the composition and structure, it is possible to modulate and increase performance. Under the advances of nanotechnology and the many opportunities in fields of application. Some nano metal oxide powders make their entrance as electrode materials like CuO. For this type of application, the stability of these materials is a fundamental parameter. For the perspective that we want synthesize nano powders CuO and then study their behavior and structural stability under heat treatment.

2. PREPARATION OF CUO NANO POWDERS

One advantage of the sol-gel (soft chemistry) method is the simplicity of the process, which requires a basic material. For that effect we used a source of Cu the CuCl₂ 2H₂O bi hydrated copper chloride with a concentration of 0.2 M (0.2 mol / L). The synthesis of the powder of CuO first requires the preparation of two separate solutions. A first solution made from (3.4 g) copper chloride CuCl₂ 2H₂O in powder that was dissolved in 100 ml of distilled water, this solution was stirred for 5 min at room temperature to obtain a homogeneous solution of concentration $c = 0.2$ mol / L. In another time a second solution was prepared. We used 3.2 g of NaOH Sodium hydroxide that is dissolved in 100 ml of distilled water at room temperature to obtain a solution of concentration $C = 0.8$ mol / L. We took 100 ml of the first copper chloride solution (CuCl₂ 2H₂O) 0.2M we put in a beaker to which we added 1 ml of acetic acid (CH₃COOH), the resulting mixture is brought to 100 ° C, with magnetic stirring for half an hour. During heating the second solution of sodium hydroxide (0.8M) is added drop by drop, we observed the gradually transformation of the color of the mixture, leading to the black dark color. The appearance of the black precipitate highlighted the formation of copper oxide.

3. STRUCTURAL CHARACTERIZATION

3.1 Structural Characterization by X-ray Diffraction

This technique allows to determine the crystal structure (the lattice parameter), the composition and the grain size of the CuO powder. The diffractometer used is a (Brucker D8 Advance). The X-ray source is a copper anticathode ($\lambda_{CuK\alpha} = 1.5406 \text{ \AA}$) supplied by a voltage generator -Current of 22kV-15A, with a pitch of 0.05 °, X-ray diffraction spectra are made in the fringe 2θ between 20 ° and 80 °. The X-ray diffractograms of the CuO powder are performed for three kinds of samples: the powder of CuO (without annealing), the powder annealed at $T = 100$ ° C and the annealed powder at $T = 450$ ° C, the spectra are respectively shown in Figures 1, 2, and 3.

3.2 Results and Discussion

From the diffraction patterns of X-rays we can notice good resolution of the peaks, reflecting the good quality of crystallization of CuO compound. This analysis allowed us to deduce a monoclinic phase with the lattice parameters ($a = 4.685$, $b = 3$, $c = 5.132$, $\beta = 99.52$ °) and a symmetry space group (C2/c).

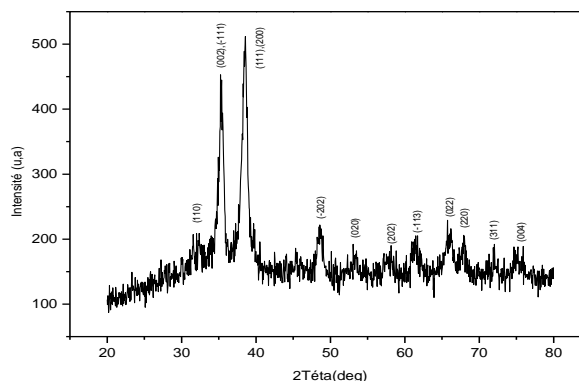


Fig. 1 – XRD of CuO powder without annealing

compared with ASTM No. 41-0254 data. The first three most intense peaks at positions $2\theta = 38, 68^\circ, 35.52^\circ$ and 48.68° , respectively correspond to the diffractions plans: (-111, 002), (111, 200), (-202), of the prepared powder with annealing at 450°C and 100°C . For the powder without annealing we notice a slight difference of the diffraction peaks to the small angles and an increase of the intensity of the first three most intense peaks at $2\theta = 38, 55^\circ, 2\theta = 35.27^\circ, 2\theta = 48.63^\circ$, corresponding respectively to the same previous plans (-111, 002), (111, 200), (-202) this reflects the stability of the material structure depending on the heat treatment. In addition all the peaks are broad indicating the small crystallite size. we note that the intensity of XRD peaks increases with the increase of the annealing temperature, this increase is accompanied with a decrease of FWHM, which reflects a phenomenon of recrystallization and growth of the crystallites in preferred directions with increasing the annealing temperature [1].

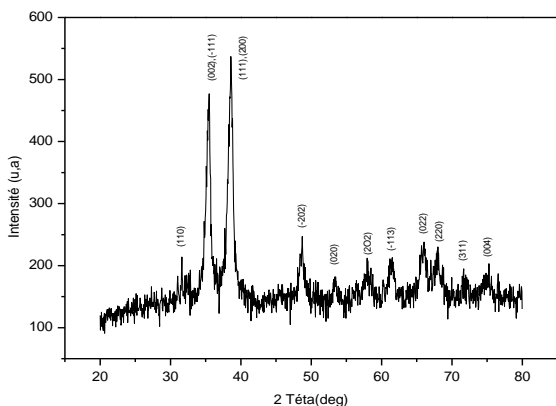


Fig. 2 – XRD CuO powder annealing at 100°C .

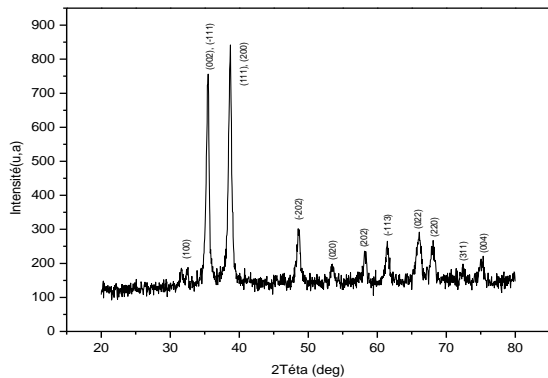


Fig. 3 – XRD CuO powder annealing at 450°C

3.2.1. Grain size

The crystallite size is calculated from the Scherrer formula (1).

$$D = K\lambda/\beta\cos\theta \tag{1}$$

For the first three most intense peaks of the planes (-111, 002), (111, 200) (-202). The radii of the three values of grain powders with different annealing temperatures are shown in Table 1. Note that the crystallite size for the three powders vary between 10.92 nm and 14.18 nm putting in evidence the nanometric size of our com-

pound. In summary we graphically representing the annealing effect of temperature on the crystallite size (Fig. 7). There is a linear variation.

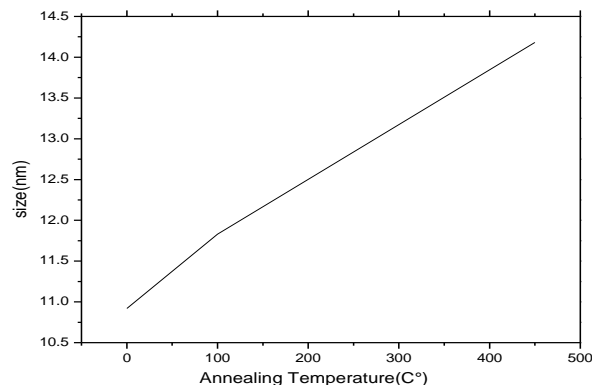


Fig. 4 – grain size as a function of annealing temperature.

Table 1 – Radius of CuO crystallites.

CuO	Orientation	grain radius
CuO without annealing	(111, 200)	10,92nm
CuO 100°C	(111, 200)	11,83nm
CuO 450°C	(111, 200)	14,18 nm

3.3 Analysis by FTIR Absorption Spectroscopy.

FTIRI spectra has been used for a complement of information and for the discernment between the various phases of the prepared compounds. The infrared spectra of our samples were recorded on a spectrometer FTIR-8400 -S of Shimadzo brand, in the spectral range $400\text{-}4000\text{ cm}^{-1}$. Figures 5 and 6 show the infrared absorption spectra of the prepared powders : CuO without annealing, CuO annealing at 450°C .

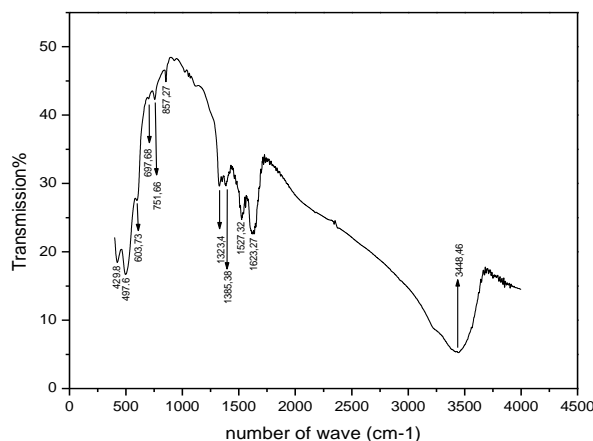


Fig. 5 – CuO infrared spectra (without annealing).

3.4 Analysis by FTIR Absorption spectroscopy

The infrared spectra show the same shape and have a slight shift characteristic bands with heat treatment. The three bands characteristic of the CuO powder without annealing are located: at $429.8\text{ cm}^{-1}, 497.6\text{ cm}^{-1}$ and 603.7 cm^{-1} (instead of $437.8\text{ cm}^{-1}, 509, 7\text{ cm}^{-1}$ and 607.7 cm^{-1} , for the spectrum of the CuO powder annealed at 450°C),

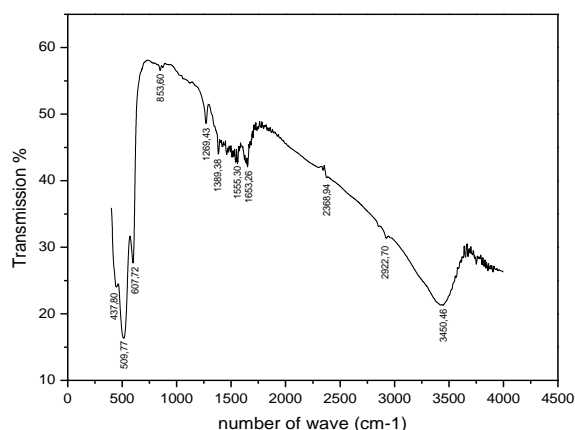


Fig. 6 – CuO infrared spectra with annealing at 450°C

all of these bands may be assigned to mode Au, Bu mode, and the other mode Bu of CuO, the high-frequency mode located at 603.7 cm^{-1} (to 607.7), is attributed to the elongation of the Cu-O bond along the directions [101] [2], while the peak at 497.6 cm^{-1} (at 509.7 cm^{-1}) may be assigned to the bending vibration of the Cu-O bond along the direction [101]. [3]. For the CuO powder spectrum without annealing there were no other active infrared mode in the spectral range from 603.7 to 697.8 cm^{-1} [4-6], which totally eliminates the existence of another phase like Cu_2O . The peaks in the range 697.8 - 859.6 cm^{-1} are attributed to the organic molecule (Acetic Acid) used in the synthesis, so the band at 697.8 cm^{-1} corresponding to the vibration of deformation of the connecting C-H [7]. The two peaks located at 1323.4 cm^{-1} and 1385.4 cm^{-1} correspond to the elongation of the vibration of C-H bond. The two bands located at 1623.2 cm^{-1} and 3448.4 cm^{-1} are assigned respectively to the vibration deformation and elongation of the O-H bond, which indicates the presence of water

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(H_2O). For the spectrum of the powder annealed at 450 °C the two peaks at 697, 8 cm^{-1} and 751,6 cm^{-1} are absent in the spectrum of CuO, and the peak at 859.6 cm^{-1} is clearly attenuated in the spectrum of CuO calcined at 450 °C, which always corresponds to the C-H bond of bending vibration [8]. The peak at 1323.4 cm^{-1} disappeared and the peak located at 1389,3 cm^{-1} (instead of 1385.4 cm^{-1} in the spectrum of the powder without annealing) always corresponds to the vibration of elongation of the C-H bond, which shows that the organic molecules which enter in synthesis were partially decomposed by the heat treatment. The two bands located 1653.26 cm^{-1} and 3450 cm^{-1} (in lieu of 1623.2 cm^{-1} and 3448.4 cm^{-1} for spectrum of powder without annealing) are shifted to higher number of wave are respectively assigned to the stretching vibration of the O-H bond. The latter bands are attenuated as compared to spectral bands of the powder without annealing, prove that the water which is present in the sample before annealing, is structural and enter in synthesis and it been evaporated after calcinations, so the water present in the sample annealed at 450 °C can be attributed to moisture absorbed after calcinations.

4. CONCLUSION

With a simple and inexpensive process, it is possible to prepare CuO powder with nanoscale about 12.32 nm. The results obtained by X-ray diffraction and FTIR confirm the purity of CuO. Calcination shows an increase in the size of CuO crystallites in association with the increase of calcinations temperature. CuO structure thus prepared is stable with temperature variation. This characteristic is a fundamental property for CuO as electrode material.