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Influence of the synthesis media in the properties of CuO obtained by microwave-assisted hydrothermal method

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Abstract Copper monoxide (CuO) was successfully obtained by microwave-assisted hydrothermal method, using different conditions—in a solution without base, in a solution alkalinized with NaOH or with NH_4OH. The powders were analyzed by thermal analysis (TG/DTA), X-ray diffraction (XRD), infrared spectroscopy, UV–Visible spectroscopy, and scanning electronic microscopy. XRD results showed that CuO was obtained with monoclinic structure and without secondary phases. Thermal analysis and infrared spectra indicated the presence of acetate groups on the powder surface. TG curves also showed a mass gain assigned to the Cu(I) oxidation indicating that a reduction possibly occurred during synthesis. The high and broad absorption band in the UV–Vis spectroscopy from 250 to 750 nm indicated the coexistence of Cu(II) and Cu(I), confirming the Cu(II) reduction, inside the CuO lattice. It was also possible to confirm the Cu(II) reduction by a displacement of the Me–O vibration bands observed in the IR spectra at around 500 cm^{-1}.

Keywords CuO · Microwave-assisted hydrothermal method · Reduction

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Introduction

Since 1990s, copper nanoparticles have attracted much attention of researchers due to their applications in catalysis [1]. Copper monoxide (CuO) is a p-type semiconductor with a narrow band gap being widely used in applications such as gas sensors, magnetic storage media, solar cells, and dyes [2].

Several methods of chemical synthesis have gained popularity for oxide preparation, including CuO. Among them, the microwave hydrothermal method has been widely used due to the advantages of using of the microwave heating.

The hydrothermal growth can be considered as an especial case of chemical vapor transport synthesis. Some compounds have low solubility in water even when temperature reaches its boiling point, but change when temperature and pressure are above 100 °C and 1 atm. Use of an alkalinizing agent can also change the solubility so that growth can be performed [3]. For instance, the variation in the synthesis conditions can vary the particle morphologies and also change adsorption and chemisorptions properties. The microwave use leads to an energy transfer direct into the material, which is converted into heat, with a higher interaction among atoms/molecules and the magnetic field.

Different authors synthesized CuO using the microwave-assisted hydrothermal method. Keyson et al. [4] used copper carbonate and ammonium hydroxide as alkalinizing agent and showed that this oxide could be obtained within short period of time, 60 min. Volanti et al. [5] used a polymeric template growth (polyethylene glycol) and showed that this template controlled the size and shape of the CuO particles. Otherwise Xu et al. [6] and Wang et al. [7] used an ionic liquid (1-*n*-butyl-3-methyl imidazolium tetrafluoroborate—[BMIM][BF_4]) and showed that this solution had a meaningful influence in the CuO morphology. Wang et al. [7] also reported the influence of the time conditions in the CuO synthesis and showed by DSC curves that CuO decomposes to form Cu_2O at around 1039–1043 °C. Wang et al. [8] reported the same synthesis using copper acetate in ethanolic solution with NaOH and showed by using UV–Vis spectroscopy that absorption peak of CuO is located at about 340 nm and no presenting the absorption band assigned Cu_2O that we reported in this study.

In this study, CuO was synthesized by the microwave-assisted hydrothermal method to determine the influence of the alkalinizing agent in the material properties.

Experimental

For the copper oxide preparation, the microwave-assisted hydrothermal method was used. Three solutions were prepared with 1 g of copper acetate (ALFA AESAR P.A. without further purification) and 100 mL of distilled water, using different alkalinizing agents or without it. The first one (a) was not alkalinized, the second one (b) was alkalinized with NH_4OH (Vetec P.A.), and third one was alkalinized with NaOH 2 mol/L (Vetec P.A). All solutions were hydrothermalized at 150 °C for 60 min, obtaining a black powder as precipitate. After that the powder was washed/dried and characterized by thermal analysis (TA), infrared spectroscopy (FTIR), X-ray diffraction (XRD), and UV–Vis spectroscopy.

Thermogravimetry (TG) and differential thermal analysis (DTA) (SDT 2980—TA instruments) were carried out in air atmosphere with a flow rate of 110 mL min^{-1} and at a heating rate of 10 °C min^{-1} up to 900 °C. Sample masses of about 10 mg were evaluated in alumina crucibles. IR analyses were performed using an MB-102 Bomem spectrophotometer, in the range of 400–2000 cm^{-1}, using KBr pellets. XRD patterns were obtained using a D-5000 Siemens diffractometer employing Cu Kα radiation. The UV–Vis spectra were obtained in a spectrophotometer (UV-2550 Shimadzu) at the 200–800 nm wavelength range.

Results and discussion

The results of thermal analysis are presented in the Fig. 1 and in Table 1.

The materials presented small mass losses, due to its high thermal stability. The first mass loss step was assigned to the elimination of water and gases adsorbed on the powder surface. The low temperature of mass loss indicated that water was present on the surface of the material, not being assigned to structural water. In the CuO synthesis W/A, the TG curve showed higher mass loss than other synthesis. This can be also observed in the DTA analysis which showed an exothermic peak characteristic of combustion indicating that organic compounds are still present on the material surface. A mass gain between the temperatures of 550 and 620 °C was also observed for all samples. This gain was attributed to the oxidation of the Cu(I) which indicated that a reduction occurred during synthesis. As showed in Table 1, the highest reduction was obtained in the sample alkalinized with NaOH, while the absence of the alkalinizing agent led to lowest reduction degree. A small mass loss above 600 °C was also observed for all samples.

Chang et al. [9] reported the oxidation of the Cu_2O between 140 and 430 °C and Nagase et al. [10] observed the oxidation up to 350 °C. In relation to CuO reduction Wang observed this reaction at about 1030 °C. In this study, the oxidation reaction was observed at higher temperature. This different behavior was probably because Cu_2O was not obtained in this study. The oxidation reaction was related to Cu(I) present in the monoclinic CuO lattice.

The short range ordering and the presence of functional groups on the powder surface were studied by IR spectroscopy (Fig. 2). The samples presented bands at 1643 cm^{-1} assigned to adsorbed H_2O and at 1087 cm^{-1} assigned to OH groups. Both molecules were present on the powder surface as indicated by TG results. The bands at 1573 and 1427 cm^{-1} were assigned to $RCOO^-$ adsorbed on the powder surface [11]. These results indicated that the mass loss associated to the exothermic peak in DTA curve was due to acetate combustion, while the small mass loss above 600 °C was due to the elimination of hydroxyl groups.

The three peaks characteristic of CuO were observed at about 600, 500 (Cu–O stretching along $[\bar{2}02]$ direction) and 432 cm^{-1} (Cu–O stretching along [202] direction) [2]. According to the literature [11, 12], those peaks were characteristic of the monoclinic phase and their low width indicated a high short range order. Moreover, comparing to literature data a small dislocation of those peaks was observed. This was probably due the reduction of the Cu(II) into Cu(I) [12], as already indicated in the TG/DTA analysis.

The UV–Vis spectroscopy (Fig. 3) was used to confirm the Cu(II) reduction, as Cu(I) and Cu(II) bands are usually observed in different positions. The region from 250 to 350 nm was assigned to Cu(II) absorption band in agreement to Zhu et al. [13] who showed that Cu(II) led to a broad absorption band at about 295 nm. Otherwise, the presence of the Cu(I) was observed at higher wavelengths,

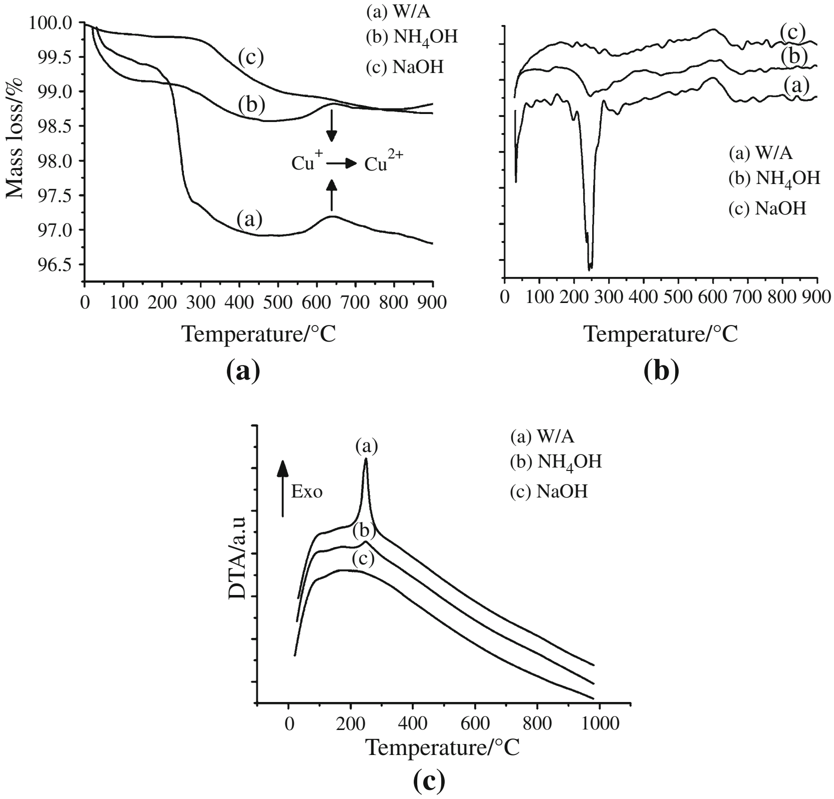

Fig. 1 **a** TG, **b** DTG, and **c** DTA curves of the CuO synthesized at 150 °C/60 min, without alkalinizing agent (W/A), with NH$_4$OH and with NaOH

Table 1 Data from thermal analysis curves of the CuO powders

Samples	Steps	Temperature range/°C	Mass loss/%	DTA peak temperature/°C	DTG peak temperature/°C
CuO synthesis without alkalizer	1st	31–175	0.66	–	47
	2nd	175–267	1.80	250	242
	3rd	267–451	0.64	–	325
	4th	525–638	(+) 0.27	–	593
	5th	638–900	0.42	–	669
CuO synthesis with NH$_4$OH	1st	28–159	0.21	–	126
	2nd	168–411	0.87	249	247
	3rd	412–528	0.18	–	448
	4th	551–642	(+) 0.12	–	600
	5th	642–900	0.17	–	682
CuO synthesis with NaOH	1st	20–141	0.83	–	–
	2nd	160–460	0.57	249	192
	3rd	511–637	(+) 0.25	–	603
	4th	637–900	0.27	–	680

around 400–750 nm, in agreement to Qu et al. [14] who synthesized Cu$_2$O by wet-chemical route and showed the presence of absorption bands between 400 and 600 nm with a peak centered at 500 nm for Cu(I) in the Cu$_2$O sample.

In this study, a high absorption was observed from 250 to 750 nm indicating the presence of the two copper oxidation states. Sample alkalinized with NaOH seems to present the highest amount of Cu(I), as Cu(II) band has the smallest relative intensity. This result was in agreement with the TG curves and IR spectra.

To study the long range order the XRD was used (Fig. 4). All diffraction peaks were indexed according to JCPDS 45-0937, indicating that in all samples the monoclinic copper oxide was obtained, without secondary phases. Peaks assigned to hydrated phases were not observed. All samples also presented a high long range order. In spite of the Cu(II) reduction, the cubic structure of the Cu$_2$O was

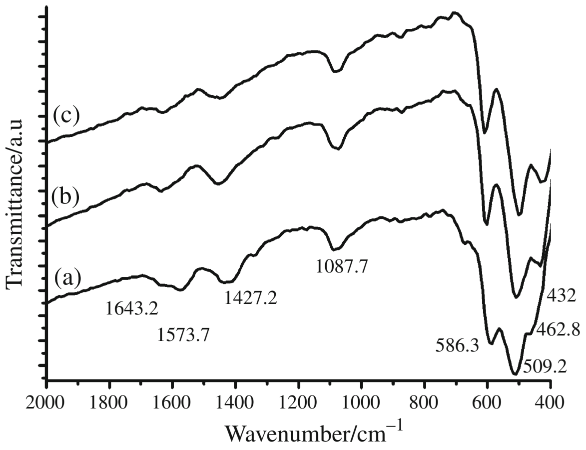

Fig. 2 IR spectra of the CuO synthesized at 150 °C/60 min. (*a*) W/A; (*b*) with NH_4OH; and (*c*) with NaOH

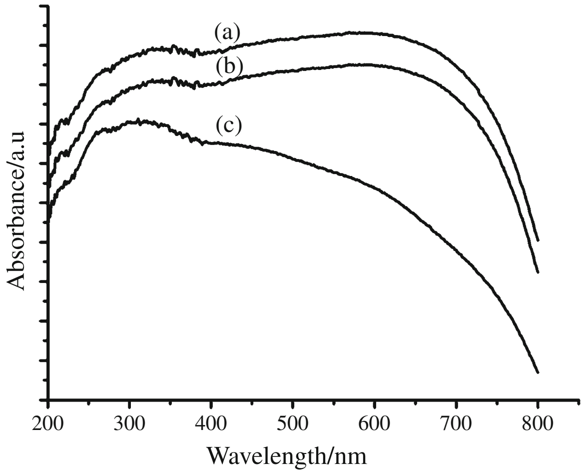

Fig. 3 UV–Vis spectra of CuO synthesized at 150 °C/60 min. (*a*) W/A; (*b*) with NH_4OH; and (*c*) with NaOH

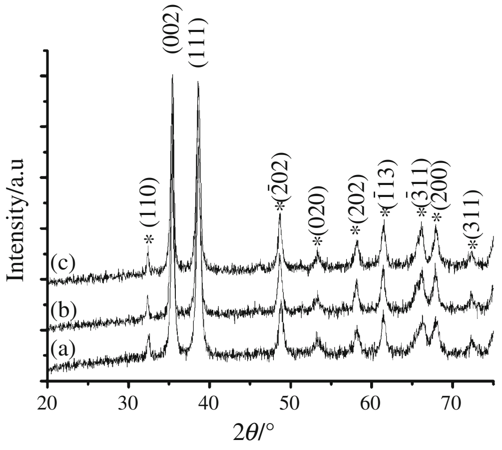

Fig. 4 XRD patterns of CuO synthesized at 150 °C/60 min. (*a*) W/A; (*b*) with NH_4OH; and (*c*) with NaOH

not observed in the XRD patterns, indicating that reduced copper is inside the CuO monoclinic lattice, as showed in Eq. 1 leading to the formation of oxygen vacancies.

$$Cu_2O \xrightarrow{CuO} 2Cu'_{Cu} + V_o^{\bullet\bullet} + O_o^x. \quad (1)$$

The scanning electron microscopy (SEM) was used to observe the influence of the synthesis media in the particle morphology (Fig. 5). The micrograph of the sample W/A (Fig. 5a) showed small particles agglomerated to form spherical morphologies of about 1 μm of diameter. In the sample alkalinized with NH_4OH (Fig. 5b), a flower-like

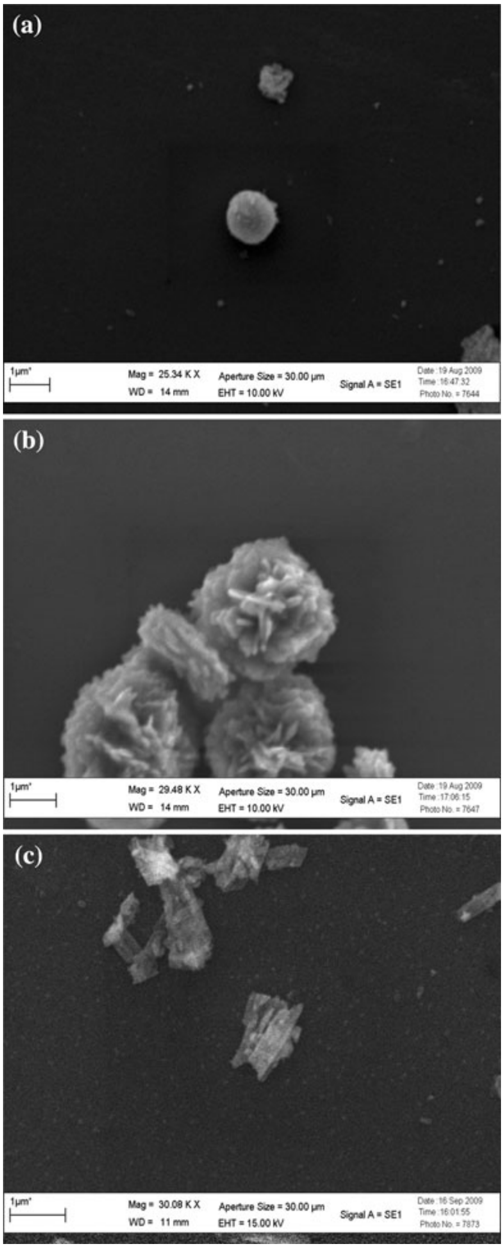

Fig. 5 Micrograph of CuO synthesized at 150 °C for 60 min. (*a*) W/A; (*b*) with NH_4OH; and (*c*) with NaOH

morphology formed by plates was observed. When NaOH was used (Fig. 5c) many small particles and plates were observed. Although the growth mechanism was not determinate yet, we believe that the difference in the morphology can be due to the re-dissolution reaction that occurs during the hydrothermal treatment, as described by Luo et al. [15] for $BaMoO_4$. This process can be influenced by the alkalinizing agents.

Min et al. [16] synthesized CuO by the hydrothermal method using metallic copper as substrate, different media and without template. Different morphologies were obtained as a function of the media polarity that controls the growth of the CuO crystal. It was also observed that the support led to different morphologies without the aid of templates. In this study, different morphologies were also obtained without templates, but this behavior was assigned to the different pH obtained in each solution (pH = 5, 12, and 14, for samples obtained W/A, with NH_4OH and with NaOH, respectively) indicating that different concentrations of OH^- were present, besides the counterions NH_4^+ and Na^+ that influenced the crystal growth.

Conclusions

The microwave-assisted hydrothermal method was effective in the copper oxide synthesis, especially when NaOH was used as alkalinizing agent. A single monoclinic phase was observed, with hydroxyl and acetate groups on the material surface, whose amount depended on the alkalinizing agent. The reduction of Cu(II) was confirmed by thermogravimetry, infrared spectroscopy, and UV–Vis spectroscopy. Another important point was the influence of the alkalinizing agent in the material morphology.

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