

Synthesis and characterization of various surfactants for stabilized CuO powder

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Abstract: In the present work, CuO nanoparticles were successfully prepared by the coprecipitation method using copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$) as a basic precursor, sodium hydroxide (NaOH) as a precipitator material, sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) as anionic and cationic surfactants, respectively. The synthesized powders samples were characterized by Fourier transform infrared spectrometry (FT-IR), field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). The investigation showed that the added types of surfactants have effects on the decrease of the crystallite size, on the CuO particles morphology, shape and uniform distribution as it is noticed in the XRD and SEM characterizations. Additionally, the FTIR spectra for all the powders samples showed the same Cu-O stretching vibration mode which indicates the presence of a crystalline CuO monoclinic structure. The obtained results create premises for further advanced the applications of CuO powders in various domains.

Introduction

Over the years, the interests in developing nanoparticles metal oxides have considerably increased due to the necessity of obtaining materials with outstanding physical and chemical properties. Various methods of metal oxide synthesis have been know so far, researches continue to development a new approaches with a strict control over nanoparticles morphology, size and composition for several technological applications.

Copper oxide (CuO), belonging to the nanomaterials class, which has attracted recent research because of its excellent properties, cost effectiveness and wide spectrum of practical applications (solar and electrochemical cells, gas sensors, field emitters, active catalyst and antimicrobial activity, etc.). Also, CuO as nanostructured oxide being classified as a *p*-type monoclinically structured semiconductor material with a direct band-gap value of 1.85 eV presents a particular attention. This type of material has a special concern because it extends the use in a board range of applications, such as electronics and optoelectronics, catalysts, sensors and biosensors, chemical sensing devices, nanofluids and field emitters, disinfection, cosmetic pigments, antibacterial agent, etc. [1–4]. In order for this material to exhibit viable properties in the desired field of applicability, it is intended to establish its method of obtaining and its synthesis parameters; there

have been elaborated and known various physical and chemical methods so far, such as sol-gel, coprecipitation, hydrothermal synthesis, mechanical mixing, solid state reaction, thermal decomposition of precursors, microemulsion, microwave irradiation, physical vapor deposition, ablation, etc. [3, 5, 6].

From the bottom-up type methods, precipitation is a cheap one, with applicability on a broad-scale, and which does not involve the addition of secondary reaction products [7–9]. Particularly, in order to obtain CuO, the method involves precipitation of various soluble copper salts (nitrates, chlorides, sulphates and acetates) in aqueous solutions, followed by their thermal decomposition with oxide formation [4, 5, 10].

Inorganic salts are mixed in an aqueous medium and under a rigorous pH control by using solutions of NaOH, KOH, $(\text{NH}_4)_2\text{CO}_3$ or NH_4OH , finally the precipitates obtained are subject to characteristic thermal treatment. In the synthesis process the reaction parameters (pH, rate of addition of reactants and speed of stirring, solution concentration, reaction temperature, etc.) have a determining role in the particle size, morphology and granulometry [11 – 13].

In the literature various thermal treatments at relatively high temperature (between 700 °C and 1100 °C) are presented, leading to the phenomenon of agglomeration and increase of particles average size. To prevent the tendency of agglomeration and to favour the formation of nanostructured materials, the use surfactants have been proposed to be used. The use of different surfactants allows the improvement of particles structural, physico-chemical and morphological properties due to the electrostatic and steric stabilizing mechanisms that reduce the solutions surface tension and improve the nanocrystalline material properties [6, 14 – 18].

Also, the addition of surfactants in the oxide materials precipitation process leads to increase nanoparticle stability and interaction between surfactant molecules and metal ions. The surfactants are chemical substances, focusing on the surface and solubilized materials with low affinity relative to each other. They have an asymmetrical molecular structure, consisting of a non-polar (hydrocarbon) and a polar (ionisable or non-ionisable) part. The role of surfactants is to provide an effective and efficient coating to induce electrostatic or steric repulsions that can counterbalance van der Waals attractions [19 – 22].

The specialized literature shows research studies to improve the properties and formation of CuO nanoparticles by using various surfactants of the type of oleic acid (OA), polyethylene glycol (PEG), cetyltrimethylammonium bromide (CTAB), hypochlorite dodecyl sulphate (SDS), polyvinylpyrrolidone (PVP), tetraoctylammonium bromide (TOAB), playing an important role in the synthesis process steps since the incipient phase. The reason for selecting the two types of surfactants (CTAB and SDS) in the experiments carried out in the present study is based on their remarkable effects on particle stability, size changing, morphology and the surface properties of the precipitated particles, but also because they have low price, can be found relatively easy on the market and have low toxicity [7, 14, 23 – 25].

This paper presents the study of obtaining CuO nanoparticles by the coprecipitation method, in the absence and in the presence of two types of surfactants, anionic (SDS) and cationic (CTAB). It is presented the effect of surfactants on CuO nanoparticles morphology, average size and crystalline structure. The morphological and structural properties are highlighted by using field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and Fourier transform infrared spectrometry (FT-IR).

Experimental details

For the synthesis of CuO powders: copper acetate monohydrate [Cu(CH₃COO)₂], sodium hydroxide [NaOH] and surfactants of type anionic [C₁₂H₂₅NaO₄S, SDS 99%] and [C₁₉H₄₂BrN, CTAB > 99 %], were used as starting materials. All reagents were purchased from the company Sigma-Aldrich without any previous purification.

For the synthesis of CuO in the absence and in the presence of surfactants the stock solutions of 1M [Cu(CH₃COO)₂] and 1M [NaOH] were prepared, respectively. From the stock solution of acetate one part is taken and the pH is adjusted in basic medium by adding NaOH solution in dropwise until the formation of a greenish-blue precipitate was observed.

In the case of samples with surfactant, over the source of copper the afferent surfactants (SDS and CTAB concentration 0.1 M) was added and under continuous stirring the precipitating agent (NaOH) was adding in dropwise until the precipitate formed and the pH was adjusted to about 10-11. After the precipitation formation, the stirring continues up to a temperature of 80 °C. The introduction of SDS anionic surfactant induces a homogeneous nuclear process due to considerable size effect of counter-ions on the crystal facets. By adding CTAB as a cationic surfactant there is a complete ionization and cation formation in the tetrahedric structure, but it also determines a control of the growth rates of different faces of the CuO nanoparticles [14, 26].

For all synthesized samples the same synthetic conditions (time, temperature and pH) were maintained. The precipitates thus formed are left in the rest position, then have been filtered under vacuum using a Buchner funnel, and following they were washed with a water-ethanol mixture for purification and removal of the secondary compounds. After washing, the samples were subjected to the drying step in the oven at a temperature of 80 °C, preceded by calcination sintering at a temperature of 550 °C for 3 hours in normal atmosphere. Due to the sintering temperature of the dry samples changed colour from green to blue to black.

The functional groups and the chemical bonds of the synthesized oxide samples were analyzed by Fourier Transform Infrared spectrometry (Bruker Optics, Vertex 80V) using the KBr pellet method in the wavenumber range of 4000-400 cm⁻¹ by averaging 64 scans. In the processing of all spectra, the bands attributable to the vibration mode of the C=O bond in CO₂ were extracted.

In order to investigate the morphology and particle size a Field Emission Scanning electron microscope (FE-SEM), obtained at an operating voltage at 10 kV and a magnitude of 30 000x has been used.

X-ray diffraction measurements of the synthesized CuO particles were recorded using a Rigaku Smartlab diffractometer with the radiation CuK α =1.540593 Å, indicating the limit of variation for the current between 150 mA and 190 mA. Data were collected at a scan rate of 12°/min. in the range 2 θ = 20-95°.

Results and Discussion

FTIR Spectra

The FTIR spectra of the different samples are presented as a comparison between CuO powders obtained in the absence of surfactants (Figure 1a) and in the presence of surfactants (Fig. 1b and c).

For all samples treated at 550 °C, bands attributed to both the vibration mode of the Cu-O linkages in the precursor and to the surfactants vibration mode can be seen, thus suggesting the binding of surfactants to particle surface. Bands centred at wavelengths less than 600 cm⁻¹, can be attributed to the vibration mode of Cu-O bond from samples, indicating a temperature and time sufficient for total synthesis to obtain CuO.

Thus, bands that can be attributed to the Cu-O bond at: a) 599, 511 and 430 cm^{-1} for the sample of CuO obtained in the absence of surfactants; b) 590, 488 and 423 cm^{-1} for the sample of CuO obtained in the presence of anionic surfactant (SDS); c) 608, 495 and 411 cm^{-1} for the sample of CuO obtained in the presence of the cationic surfactant (CTAB), confirming the formation of a CuO monoclinic crystalline structure.

In the case of CuO samples in the presence of surfactants (Fig. 1b and c) is observed the spectral bands centred in the region of 3000-800 cm^{-1} which can be attributed to the type of surfactant used. The FTIR spectra for the two samples presents the intense bands at 2920 cm^{-1} , 2855 cm^{-1} and 1405 cm^{-1} for the sample with anionic surfactant and 2917 cm^{-1} , 2852 cm^{-1} and 1415 cm^{-1} respectively for the sample with cationic surfactant which may be due to vibration of the C-H from organic materials. Also, the peaks from 1700-800 cm^{-1} may be assigned to specific bonds from surfactants. Based on the appearance of bands corresponding to the surfactants used in synthesized samples, reveals the interaction and binding of the surfactant molecules on the surface of CuO particles.

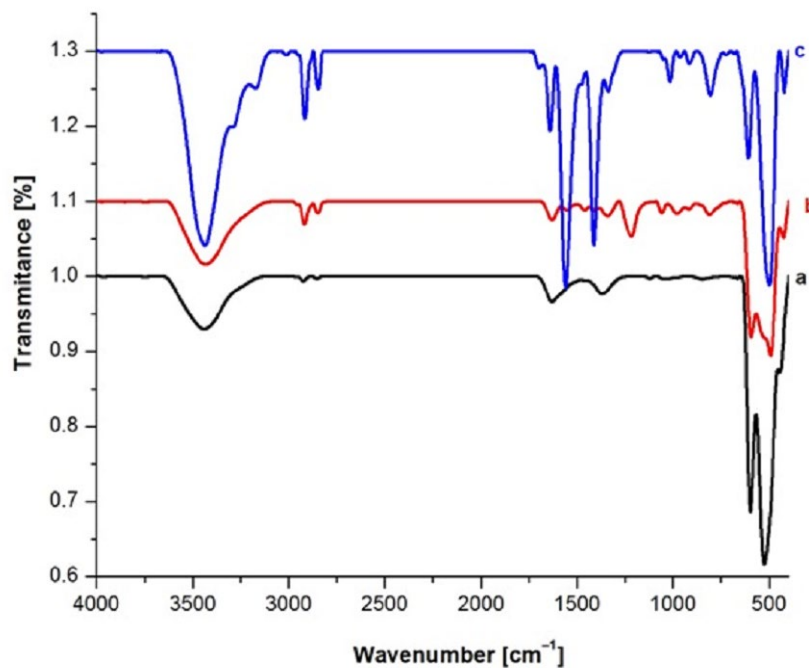


Fig. 1. FTIR spectra of CuO powders in the absence of surfactant (a) and in the presence of surfactants (b), SDS, (c) CTAB.

Morphological Analysis

Fig. 2 shows micrographs of CuO samples in the absence and the presence of surfactants. Analysis of samples by SEM was carried out for the correct estimation of their morphology, nanoparticle size, nanostructure formation and the agglomeration degree.

The CuO sample synthesized in the absence of surfactants (Fig. 2a) revealed agglomeration of particles, with dimensions in the range 40-70 nm, showing an polyhedral shape with rounded edges for defining the particles shape. The use of different types of surfactants has been derived from the necessity to control the size and morphology of the nanostructures, as well as to reduce the agglomeration tendency of particles [14,23].

Thus, in the case of the CuO samples with anionic surfactant - SDS (Fig. 2b), from SEM micrograph we observed a slight decrease of the tendency of agglomeration concomitantly with particle size reduction, but the particle size diminishes, the particle size being estimated between 20 and 60 nm. As a result of this observation, the necessity to find another surfactant in order to decrease furthermore the tendency of agglomeration arises.

The micrograph of CuO with surfactant cation - CTAB sample (Fig. 2c) shows the formation of particles with a well-defined shape, polyhedral with rounded edges, but with larger particle size due to the type of surfactant used and the high sintering temperature. This increase of particles size can be determined by the global tension forces that minimize free surface energy by controlling particle interaction, nucleation and particle size modification by keeping the particles at a nanometric level. It is well known that the speed of the cationic surfactants adsorption is rapid, indicating that the adsorption is faster compared with anionic surfactants, showing that the stabilization and the properties of the nanoparticles differ from the other surfactants.

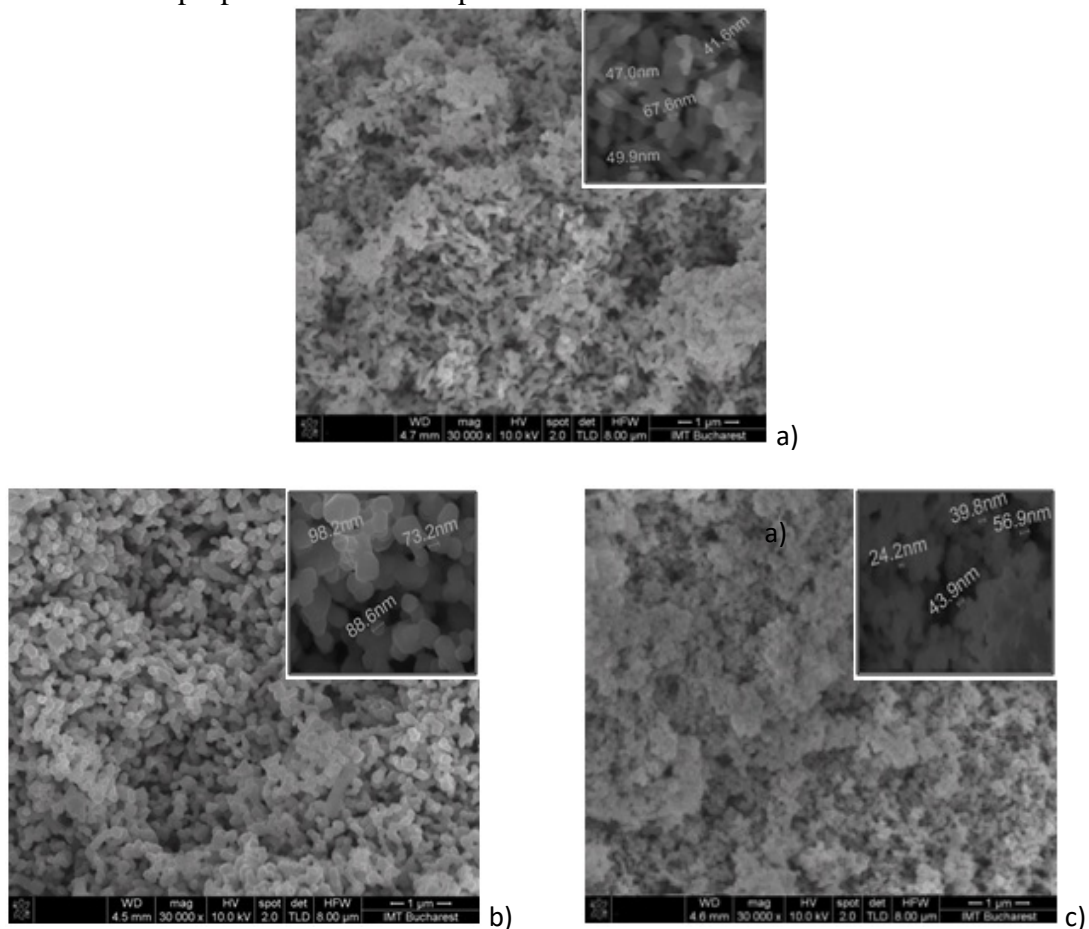


Fig. 2. SEM micrograph of CuO powder in the absence of surfactant (a) and in the presence of surfactants (b), SDS, (c) CTAB.

XRD Analysis

XRD diffraction spectra for CuO powders in the absence and in the presence of surfactants are highlighted in Fig. 3 (a-c). By using this characterization method the crystallite mean size, crystallographic structure and lattice parameters are estimate. In all three samples the diffraction

peaks were indexed in accordance with the standard data of the No 00-101-1194, being in good accordance with the existing research literature [5,25,27].

From the analyzed samples it was found that the XRD diffractograms are similar and typical with the CuO single phase monoclinic structure, the surfactants do not influence the samples crystalline structure and no other intermediate phases characteristic of them have been observed. Also, the characteristic diffraction peaks centered at about 2θ (hkl) = 32°, 35°, 38°, 48°, 53°, 58°, 61°, 68°, 72°, 75° are shown, corresponding to the crystalline planes characteristic of CuO with Miller indices at (110), (002), (111), ($\overline{202}$), (020), (202), ($\overline{113}$), (220), (311), (004).

Depending on the sample type, the two main peaks of the crystalline planes with indices (002) and (111) can be found at $2\theta = 35,474^\circ$ and $38,714^\circ$ for the CuO sample in the absence of surfactants, and at $2\theta = 35,426^\circ$ and $38,617^\circ$ for CuO samples in the presence of anionic surfactant (SDS) and at $2\theta = 35,377^\circ$ and $38,665^\circ$ respectively for CuO samples in the presence of CTAB. As a result of the use of surfactants, changes in the average size of crystallites and lattice parameters can be observed. The details of these parameters and the variation of the size of the crystals are shown in Table 1.

Calculation of the average crystallite size for all three samples was based on the Debye Scherer's formula (1):

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

Where: K is the shape coefficient (0.94), λ is the radiation wavelength (1.54 Å), β is the peak FWHM (full width half maximum width in radians), and θ is the Bragg diffraction angle obtained from 2θ value corresponding to maximum intensity peak (in radians).

Based on this formula the results indicate that the average size of crystallites varied from 16.7 nm for CuO and 12.5 nm for CuO in the presence of SDS and 20.02 nm for CuO in the presence of CTAB respectively, thus it was found that depending on the type of surfactant used, a control is performed on the degree of crystallites growth.

Table 1. Crystallite sizes, lattice parameters and range particle size of CuO powders in the absence and in the presence of surfactants.

Sample number	Crystallite sizes (nm)	Lattice parameters		Range particle sizes (nm)	
		a (Å)	c (Å)		
1	<i>CuO</i>	16.7	4.6859	5.1327	50
2	<i>CuO in the presence of SDS</i>	12.5	4.6857	5.1320	40
3	<i>CuO in the presence of CTAB</i>	20.02	4.6923	5.1394	70

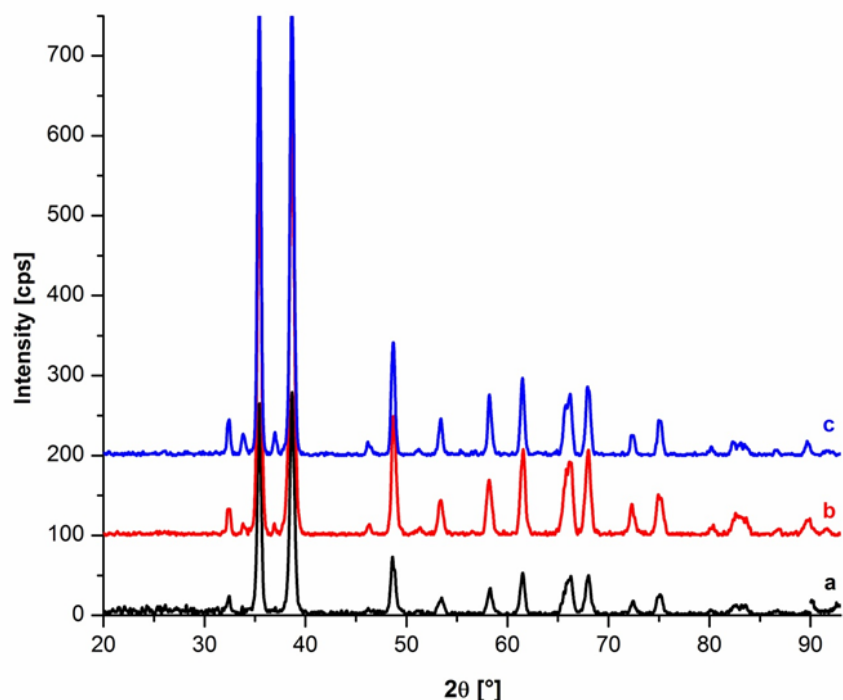


Fig. 3. XRD pattern of CuO powder in the absence of surfactant (a) and in the presence of surfactants (b), SDS, (c) CTAB.

Summary

In the present study, CuO nanoparticles were synthesized by the chemical co-precipitation method, in the absence and in the presence of two types of surfactants (SDS and CTAB), sintered at 550°C. Structural analysis clearly indicates the formation of a single crystalline phase in all synthesized samples.

FTIR spectra reveal bands centered at wavelengths less than 600 cm^{-1} characteristic of the Cu-O metal bond. Also, the presence of peaks in the region 3000-800 cm^{-1} indicates the binding of surfactants to the surface of the particles without affecting the particle crystalline structure, confirmed by XRD.

The XRD analysis indicates that regardless of the type of surfactant used, the powders synthesized had a CuO single phase monoclinic structure.

SEM images indicate that the sample obtained in the absence of surfactants shows an agglomeration tendency with dimensions ranging from 40-70 nm.

In the case of samples synthesized depending on the type of surfactant, it is found that there is a control over the morphology and particle sizes ranging between 20-80 nm and reduces the agglomeration of the CuO particles.

The results showed that function of the type of surfactant used an improvement in the dispersion of CuO nanoparticles, a control of the morphology and particle size was exerted. By optimizing the conditions of processing and the establishment of surfactants, this method may be accessible for the synthesis of the various types of oxide materials with effect in a wide range of domains.

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