



Fast Room Temperature Solution-phase Approach for Selective Synthesis of Nanostructured $\text{Cu}(\text{OH})_2$, Cu_2O and CuO

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

A simple room-temperature solution-phase and efficient method for the selective preparation of nanostructured copper hydroxide ($\text{Cu}(\text{OH})_2$), copper oxide (II) CuO or Cuprous oxide (Cu_2O) from a Cu^{2+} solution was developed. Mono-disperse cubic Cu_2O were obtained by sodium hydroxide addition to this solution in the presence of ethylene glycol (EG) while monoclinic CuO nanoparticles were obtained in the presence poly-ethylene glycol (PEG) as dispersant agent. By adjusting the amounts of EG, octahedron and truncated octahedron aggregates of copper oxide

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(I) nanoparticles (Cu_2O) can be formed, whereas in case of PEG, $\text{Cu}(\text{OH})_2$ nanowires, CuO sheet-shaped nanoparticles () can be obtained. These observations were confirmed by X-ray diffraction, infrared spectroscopy and scanning electron microscopy. It appears that the EG and PEG act as size-controlling and growth-directing agents in addition to their role as a dispersant.

Keywords: Nanostructured Cu_2O ; CuO ; ethylene glycol; polyethylene glycol; solution-phase; room temperature.

1. INTRODUCTION

Semiconductor nanoparticles have attracted a considerable attention due to their fundamental importance and potential future applications. Among them, copper(I) oxide (Cu_2O) is a p-type semiconductor with a direct band gap of 2.14 eV, which makes it promising as a low-cost material in applications such as catalysis and photovoltaic devices [1]. Copper(II) oxide (CuO), which is also a p-type semiconductor [2], with an indirect band gap of 1.2 to 1.5 eV, is widely used as a heterogeneous catalyst because of its high activity and selectivity in oxidation and reduction reactions [3]. This material was also used in Li-ion batteries as an active electrode material [4], in field emission [FE] emitters, gas sensors [5], and solar cells [6].

In recent years, several efforts were devoted to synthesize cuprous oxide (Cu_2O) and cupric oxide (CuO) nanoparticles with different morphologies using several methodologies such as thermal oxidation [7], aqueous solution [8], hydrolysis [9], template-based sol-gel [10], reverse micelle technique [11] and electrochemical methods [12]. However, and in order to control the morphology of nanostructured copper oxides, these oxides were often prepared by high-temperature approaches [13] such as hydrothermal [14], solvothermal [15] and microwave-hydrothermal methods [16]. Therefore, the development of cost-effective synthesis methods which require less energy and material still remains a challenge in this field. It is known that the size of the nanoparticles can be controlled easily through the use of surfactants in the reaction mixture [17]. Surfactants with long hydrocarbon chains and hydrophobic ends are important in manipulating particle sizes [18]. Various surfactants can alter the shape, size and other surface properties of the nanoparticles to different extents depending upon their molecular structure i.e. the nature of the head group, the length of the hydrophobic tail and the type of counter ions. The termination of the nanoparticle growth is controlled by the diffusion and the

attachment rates of surfactants on the nanoparticle surface. Thus, surfactant supported stabilization of the nanoparticles in aqueous solution has been demonstrated to be one of the most effective nanoparticle synthesis method [19-20].

In the present work, we report a simple room-temperature solution-phase route for the preparation, of mono-disperse cubic Cu_2O and monoclinic CuO nanoparticles in the presence of ethylene glycol (EG) and poly-ethylene glycol (PEG) respectively as size controlling and growth directing agent. The influence of the dispersant agent's concentration on the structure and morphology of the obtained Cu_2O and CuO nanoparticles was investigated. The prepared nanoparticles were characterized by X-ray diffraction measurements (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), scanning electron microscopy (SEM) and Nitrogen adsorption (BET).

2. EXPERIMENTALS DETAILS

2.1 Materials

The chemicals used in the present work are copper fine powder $63\mu\text{m}$ (99.5% purity Aldrich), Hydrochloric acid (37%, Aldrich), Hydrogen peroxide (30%, Aldrich), ethylene glycol (anhydrous, 99.8%, Aldrich), polyethylene glycol (Mn 6000) (99.9% purity, Sigma Aldrich), Sodium hydroxide (anhydrous, $\geq 98\%$ purity, Sigma Aldrich), Ethanol (absolute, $\geq 98\%$ purity, Aldrich) and deionized water.

2.2 Method

2.2.1 Synthesis of Cu_2O

0.5 g of Copper fine powder was first dissolved in 10 mL of 3.6 M HCl. A chosen volume (10 mL, 20 mL and 30 mL) of ethylene glycol (EG) was then added to the as-prepared solution depending on the desired EG concentration. The mixture was vigorously stirred for 20 min at room

temperature and 2 mL of H₂O₂ (30%) was added drop-wise for 20 to 30 minutes to give a light blue colored solution. Then, 2.5 g of NaOH dissolved in deionized water (30 mL) was added drop-wise under constant stirring for 20 min, producing an intense brown colored precipitate. The mixture is filtered, washed several times with deionized water and ethanol and finally dried for 12 hours at 60°C. The formation of Cu₂O nanoparticles is confirmed by the reddish color of the product.

2.2.2 Synthesis of CuO

Copper powder was dissolved in hydrochloric acid as described above. In this case, polyethylene glycol (PEG) aqueous solution was used as dispersant agent. Upon addition of NaOH, following the procedure described above, a brown-black colored precipitate was obtained within 10 to 15 minutes. The precipitate was then centrifuged, filtered, washed several times with ethanol and deionized water and dried for 12 hours at 60°C. The CuO nanostructures were obtained as black colored powder.

2.3 Characterization

The porous nature of the obtained samples was investigated using physical adsorption of nitrogen at liquid-nitrogen temperature (-196°C) with an automatic volumetric sorption analyzer (Quantachrome instruments). Prior to the measurement, the samples were degassed at 120°C for 12 h under vacuum. The specific surface areas were determined according to the Brunauer-Emmett-Teller (BET) method. Phases and structural characterizations of the synthesized powders were characterized by X-ray powder diffraction (XRD) using a "Phillips X'pert MPD" diffractometer operating at 40 kV and 30 mA, equipped with a Cu anticathode of wavelength ($\lambda = 1.5406 \text{ \AA}$). The collected nanoparticles samples were also analyzed by a scanning electron microscope (SEM) type "JEOL JSM – 5500" operated at 10 kV. Chemical bonding information on the prepared nanostructures was studied with Fourier Transform Infrared Spectroscopy (FT-IR).

3. RESULTS AND DISCUSSION

Cu₂O and CuO nanoparticles were prepared at room temperature from copper powder dissolved in hydrochloric acid in the presence of a chosen volume of EG (noted Cu₂O-10 mL, Cu₂O-20 mL

and Cu₂O-30 mL) or a given volume of 0.16M PEG solution (noted CuO-20 mL and CuO-30 mL). The synthesis was conducted in the presence of sodium hydroxide solution and H₂O₂ as oxidant. The role of each dispersant on the synthesis of both types of nanoparticles have been reported in this work. In case of ethylene glycol as a dispersant agent, the X-ray diffraction patterns of the prepared samples show only peaks that are characteristic of Cu₂O oxide (Fig. 1a) with no additional impurity peaks or phases. The four diffraction are assigned to the (110), (111), (200) and (220), are characteristics of the cubic cuprous oxide as given by JCPDS 78-2076 data software. The formation of Cu₂O was also be confirmed by the reddish color of the product. It could be seen that the XRD patterns for all the three samples are the same except for the variation in the intensity and the width of some of the peaks.

Table 1 shows the values of crystallite size calculated by the Scherer's formula based on the major peak located at 36.40 degree. It was found that the XRD crystallite size was in the range of 17–24 nm for Cu₂O nanoparticles. The increase of the EG volume in the experiments promotes the formation of smaller crystallites and narrower size distribution of Cu₂O nanoparticles.

Fig. 1b shows the XRD patterns of the samples obtained in the presence of selected volumes of 0.16M PEG solution (10 mL, 20 mL and 30 mL). For the first sample obtained by adding 10 mL of PEG solution, all the observed diffraction peaks correspond to the lattice planes of Cu(OH)₂ with the orthorhombic symmetry (JCPDS No. 35-0505). This is also confirmed by the characteristic blue color of Cu(OH)₂. When the PEG solution volume was increased to 20 mL and 30 mL, the XRD patterns of the obtained samples (CuO-20mL PEG and CuO-30mL PEG) are attributed to the monoclinic CuO phase (JCPDS No. 48-1548). In addition, the crystallite size of CuO becomes smaller with increasing PEG solution volume (See Table 1).

The morphology of the nanostructured Cu₂O and CuO samples prepared by the chemical precipitation method was characterized by SEM. As shown in Fig. 2a, mono-disperse and regular octahedral Cu₂O particles are obtained after adding 10 mL of EG. By increasing the EG volume to 20 mL, the Cu₂O crystal morphology is changed from nano-octahedron

attributed to the symmetrical stretching vibration $\nu(\text{OH})$ of hydrogen bonded OH [24] and shows clearly the presence of water molecules. A band in the region of 1640 cm^{-1} is related to the bending vibration for H_2O [25].

The FT-IR spectra of $\text{Cu}(\text{OH})_2$ and CuO are shown in Fig. 4b. In the case of CuO , there are three absorption bands at 470 cm^{-1} , 600 cm^{-1} and a strong one at 496 cm^{-1} which is attributed to

the stretching mode of the Cu-O bond [26]. The broad peaks located at 1423 cm^{-1} can be attributed to the $\nu\text{C-O}$ vibration mode. The two bands at 3437 cm^{-1} and 1640 cm^{-1} are the characteristic peaks of the O-H stretching and H_2O bending modes respectively. By increasing the volume of PEG aqueous solution from 20 mL to 30 mL, all absorption bands between 1000 cm^{-1} and 2000 cm^{-1} disappear.

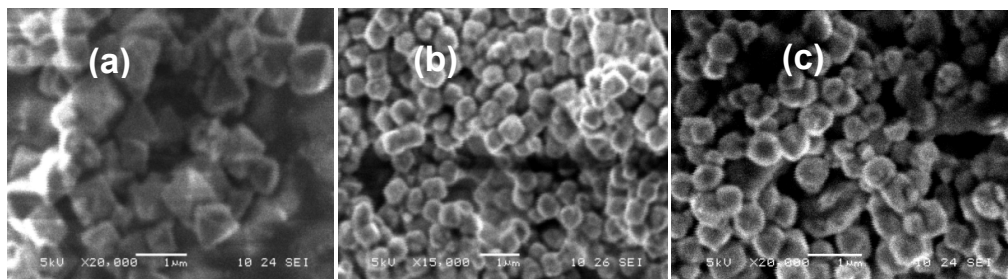


Fig. 2. SEM images of Cu_2O -10EG (a) and Cu_2O -20EG (b) nanoparticles

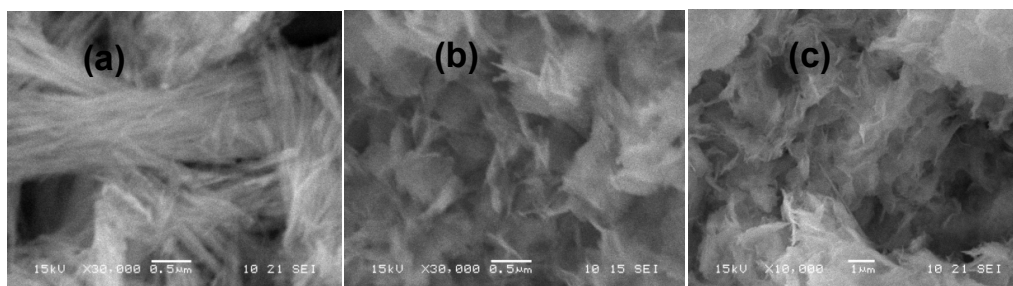


Fig. 3. SEM images of CuO -10PEG (a), CuO -20PEG (b) and CuO -30PEG (c) nanoparticles

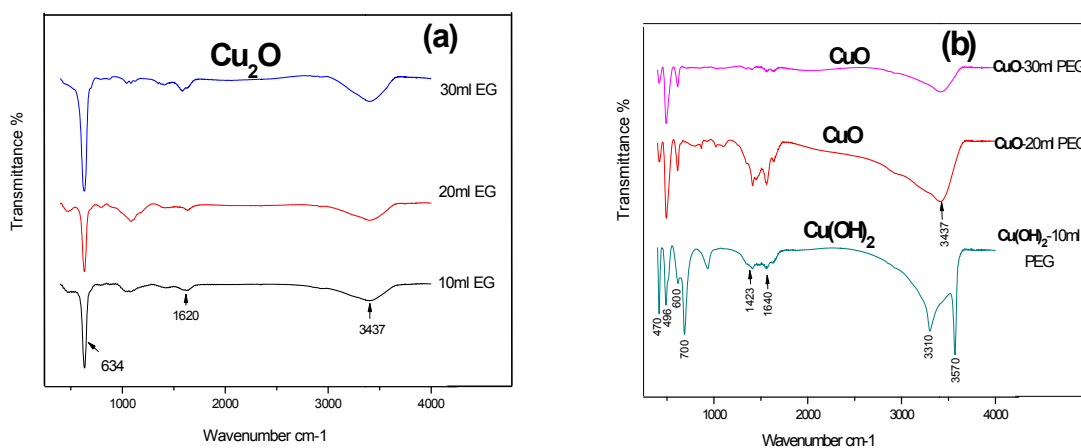


Fig. 4. FTIR spectra of Cu_2O and CuO nanoparticles prepared with (a) EG dispersant and (b) PEG dispersant

The comparison of the FT-IR spectra of $\text{Cu}(\text{OH})_2$ and CuO indicates clearly that the band centered at 3437 cm^{-1} for CuO , shifts and splits into two bands at 3570 and 3310 cm^{-1} in the case of $\text{Cu}(\text{OH})_2$. These broad peaks are attributed to the stretching modes (νOH) of hydrogen-bonded hydroxyl groups. The band at 3310 cm^{-1} is usually attributed to bound OH, while the band at 3570 cm^{-1} is assigned to free hydroxyl groups [27]. The broad and overlapping band in the region of 1650 cm^{-1} is related to the bending vibration of H_2O [25]. The peak at 700 cm^{-1} corresponds to the bending vibration of hydrogen-bonded OH groups ($\delta\text{O-H}$) and the strong absorption at 470 cm^{-1} is due to Cu-O-H bending ($\delta\text{Cu-O-H}$) and Cu-O stretching vibrations ($\nu\text{Cu-O}$).

The textural characteristics of all samples were obtained by N_2 adsorption-desorption isotherms measurements. The pore volume and the specific surface area were calculated by BET method from the adsorption branch. The BET surface area and pore volume of CuO nano-sheets are in the range of $30\text{-}37\text{ m}^2/\text{g}$ and $0.04\text{-}0.06\text{ cm}^3/\text{g}$ respectively, which are slightly larger than those of $\text{Cu}(\text{OH})_2$ nanowires ($22\text{ m}^2/\text{g}$ and $0.04\text{ cm}^3/\text{g}$). Comparatively, the Cu_2O shows low BET surface area ($10\text{-}12\text{ m}^2/\text{g}$) and small pore volume ($0.02\text{ cm}^3/\text{g}$).

4. CONCLUSION

This work has clearly shown that the structure as well as the morphology and the shape of copper oxide nanostructures can be controlled through an appropriate choice of a dispersant. X-ray diffraction and SEM analysis showed that Cu_2O octahedron-shaped nanoparticles, Cu_2O truncated octahedron nanoparticles when EG was used as a dispersant agent, while $\text{Cu}(\text{OH})_2$ nanowires and CuO Nano sheets are obtained when PEG was used for this purpose. These suggest that these two dispersing agents act also as growth directing agents.

This study may provide a new simple and fast solution-phase method to synthesize nano-materials with high purity, great stability and variety of shapes without the need for specialized instruments and extreme conditions. The rate of particle aggregation is a major factor that controls the morphology and crystallinity of the final product.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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