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Synthesis and Characterization of New Copper based Nano-composite

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Copper based nano-material containing different phases of copper, $CuO/Cu_2O/Cu$, was prepared by glycine assisted combustion method. The structural properties of the final product including the crystallite size, lattice constant and unit cell volume were determined by X-ray diffraction (XRD) technique. The morphological characteristics of as prepared $Cu/Cu_2O/CuO$ system were studied by scanning electron micrographs (SEM) technique. The results revealed that the investigated method led to formation of mixture of $CuO/Cu_2O/Cu$ by using a certain amount of glycine as a fuel. The preparation method studied led to formation of uniform, spongy, fragile and nano-crystalline $CuO/Cu_2O/Cu$ material.

Keywords: XRD; SEM; $CuO/Cu_2O/Cu$ nano- particles.

1. INTRODUCTION

Nano-materials involved transition metals and metal oxides become one of the hottest topics in materials science due to their special properties and potential applications. The properties of these materials are highly dependent on their morphology and size. So, the scientific researchers concentrated their researches during the preparation of nano-materials on controlling in the morphology and size of the as prepared materials [1-3]. Amongst these materials, the supported and unsupported Cu and Cu oxide nano-particles are of great interest due to their advantages such as non-toxicity, abundance, high optical absorption coefficient and low band gap energies [4-6]. These characteristics make them prospective candidates for different applications such as catalysis, semiconductor equipment, solar/photovoltaic energy conversion, gas sensing, antimicrobial materials, luminescence sources field, emission devices, lithium-ion electrode materials and dye-sensitized solar cells [7- 10].

In fact, the copper solid possesses multiple oxidation states forming CuO, Cu_2O and Cu phases. Temperature-programmed reduction (TPR) studies of the reduction of bulk CuO have typically shown a direct transformation to Cu, without the formation of intermediate phases such as Cu_2O or Cu_4O_3 [11]. In several cases, Cu_2O has been observed to form as an intermediate phase in the reduction of bulk CuO under conditions of decreased temperature and/or decreased oxygen partial pressure, and only as a transient species [12- 14].

Metallic copper, Cu, has cubic crystal structure. The conductive paths and layers in the electronic devices depend upon Cu due to its low cost and high electrical conductivity. Cuprous oxide, Cu_2O, has cubic crystal structure and presents p- type semiconductor behavior with a direct band gap of $\approx$ 2eV. In addition, Cu_2O has unique optical and magnetic properties with potential applications such as solar energy conversion, a negative electrode material for lithium ion batteries, photocatalytic degradation of organic pollutants under visible light, a stable photo catalyst for the photochemical decomposition of water into O_2 and H_2 under visible light irradiation and a low-cost photovoltaic power generator [15-19]. Finally, both metallic copper and cuprous oxide possess substantial catalytic activity. Cupric oxide, CuO, has a monoclinic crystal structure and presents p- type semiconductor behavior with an indirect band gap of 1.21 – 1.51 eV. Nano-materials based on CuO have the advantage of a lower surface potential barrier than that of the metals, which affects electron field emission properties. CuO based nano-materials play an important in the optoelectronics, solar cell, sensors and catalysis [20- 23].

The synthesis of copper nano-particles with controllable sizes, shapes and surface properties is vital for exploring copper based nano-materials for different industrial applications. Copper oxides, CuO and Cu_2O, with different sizes and morphologies have been prepared by several methods such as thermal oxidation, simple solution, simple hydrolysis, template-based sol–gel, and electrochemical, hydrothermal, solvothermal and microwave-hydrothermal [24-32]. However, various reports on the preparation and characterization of nano-crystalline copper oxides are relatively few to some other transition metal oxides such as ZnO, TiO_2, SnO_2 and Fe_2O_3.

Pike et al. reported that the reduction of the bulk CuO resulted in Cu without formation of Cu_2O as an intermediate phase [33]. But, the reduction of CuO nano-particles ranging from 5 to 12 nm brought about formation of a stable Cu_2O intermediate phase under a certain reducing conditions. In other words, the reduction of monoclinic CuO nano-particles led to cubic Cu_2O which converted into face centered cubic Cu by the further reduction. This indicates that there is a critical particle size, above this limit the direct reduction occurs ($CuO \rightarrow Cu$), whereas below the mentioned limit the sequential reduction takes place ($CuO \rightarrow Cu_2O \rightarrow Cu$).

As previously various techniques are available for the preparation of nano-materials. But, these techniques are involved require special chemicals and equipments. In my previous researches, a variety of oxide materials such as NiO and γ- Fe_2O_3 were prepared by the low temperature initiated self-propagating and gas producing combustion method [1-3]. Combustion synthesis processes are characterized by high-temperatures, fast heating rates and short reaction times. These features make combustion synthesis an attractive method for the manufacture of technologically useful materials at lower costs compared to conventional ceramic processes. Other advantages of combustion synthesis include the use of simple equipment, formation of high-purity products, stabilization of meta stable phases and formation of almost any size and shape. Indeed, alumina supported copper system including Cu, Cu_2O and CuO was prepared by glycine assisted combustion route [34].

In this investigation, the first goal is preparing of nano-crystalline $Cu/Cu_2O/CuO$ system via glycine-assisted combustion method. The second goal for this investigation is the study of the structural and morphological properties of the as prepared $Cu/Cu_2O/CuO$ system. The techniques employed were XRD and SEM.

2. EXPERIMENTAL

2.1. Materials

Two samples of copper based materials were prepared by mixing calculated proportions of copper with different amounts of glycine. The mixed precursors were concentrated in a porcelain crucible on a hot plate at 350 °C for 5 minutes. The crystal water was gradually vaporized during heating and when a crucible temperature was reached, a great deal of foams produced and spark appeared at one corner which spread through the mass, yielding a brown voluminous and fluffy product in the container. In our experiment, the ratios of the glycine: copper nitrates were (0 and 1): 1 for S1and S2 samples, respectively. In other words, the ratios of glycine to metal nitrates (G/N) were 0.00 and 1.00 for S1 and S2 samples. The chemicals employed in the present work were of analytical grade supplied by Fluke Company. A general flowchart of the synthesis process is shown in Fig. 1.

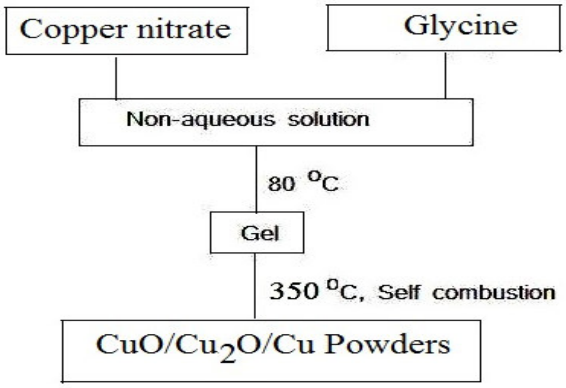


Figure 1. Process flowchart for fabricating the as prepared samples.

2.2. Techniques

An X-ray measurement of various mixed solids was carried out using a BRUKER D8 advance diffractometer (Germany). The patterns were run with Cu K_α radiation at 40 kV and 40 mA with scanning speed in 2θ of 2 ° min^{-1}.

The crystallite size of copper phases present in the investigated solids was based on X-ray diffraction line broadening and calculated by using Scherrer equation [35].

$$d = \frac{B\lambda}{\beta \cos\theta} \qquad (1)$$

where d is the average crystallite size of the phase under investigation, B is the Scherrer constant (0.89), λ is the wave length of X-ray beam used, β is the full-with half maximum (FWHM) of diffraction and θ is the Bragg's angle.

Scanning electron micrographs (SEM) were recorded on SEM-JEOL JAX-840A electron micro-analyzer (Japan). The samples were dispersed in ethanol and then treated ultrasonically in order disperse individual particles over a gold grids.

3. RESULTS

3.1. Structural analysis

The XRD pattern for S1 and S2 samples are given in Fig. 2. Study of this figure revealed that: (i) The S1 sample consisted of well crystalline CuO particles (Cupric oxide or Tenorite with Monoclinic structure) as a single phase. (ii) The S2 sample contains different phases of copper crystallites that are Cu, Cu_2O and CuO.

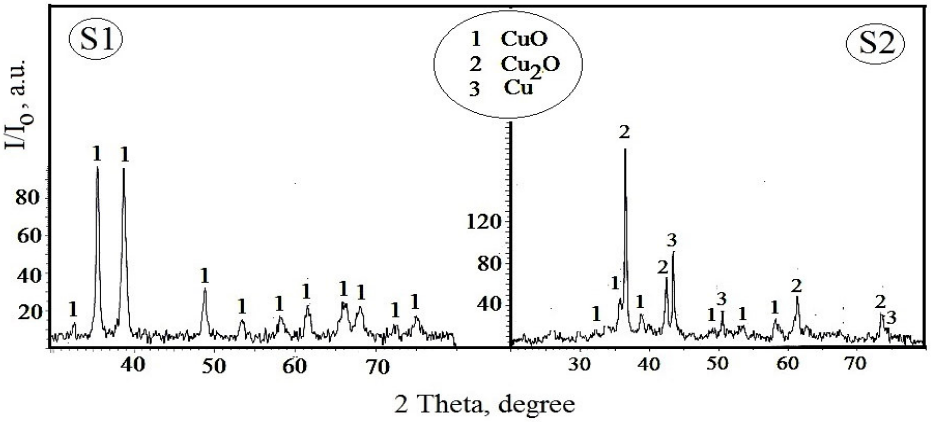


Figure 2. XRD patterns for the S1 and S2 samples.

This means that the presence of a certain amount of glycine during the preparation process of copper based materials resulted in reduction of some CuO to produce Cu (Cubic structure) and Cu_2O (Cuprous oxide or Cuprite with Cubic structure) phases. Inspection the diffraction lines found that the major phase in the S2 sample is cuprous oxide. (iii) The glycine assisted combustion method brought about a decrease in the intensities of diffraction lines related to the cupric oxide phase with subsequent appearance for Cu and Cu_2O as shown in Table 1. This indicates that the presence of fuel affects both size and formation of products. In other words, judicious adjustment of the metal precursor- to-fuel ratio can control in both size, morphology and phase transformation of the final product with subsequent changes in the different properties of this product.

Table 1. The effect of glycine content on the height of some diffraction lines for the crystalline phase involved in the as prepared.

Samples	Crystalline phases	Peak height (a. u.)		
		CuO (0.252nm)	Cu_2O (0.246nm)	Cu (0.209nm)
S1	CuO	98	-	-
S2	CuO, Cu_2O, Cu	47	190	89

3.2. The size control of copper nano- crystals

The glycine assisted combustion route brought about different changes in the crystallite size (d) of different copper phases as shown in Table 2. However, Table 2 shows the lattice constant (a, b and c) and unit cell volume (V) of Cu, CuO and Cu_2O nano- particles which calculated by using the X-ray data. Using glycine as fuel during preparation process brought about slightly changes in the values of lattice constant (a, b and c) and unit cell volume of CuO nano-crystals. This treatment led to a decrease in the crystallite size of CuO phase. On the other hand, the crystallite sizes for different copper phases are arranged in the following order: CuO > Cu_2O > Cu. In the S2 sample, although the peak height of Cu_2O greater than that of CuO, it found that the crystallite size of Cu_2O and Cu is less than that of CuO. This indicates formation of agglomerated Cu_2O and Cu nano particles.

Table 2. Some structural parameters of copper phases.

Solids	**CuO**					**Cu_2O**			**Cu**		
	d (nm)	a (nm)	b (nm)	c (nm)	V (nm^3)	d (nm)	a (nm)	V (nm^3)	d (nm)	a (nm)	V (nm^3)
S1	55	0.469	0.342	0.513	8.228	-	-	-	-	-	-
S2	39	0.468	0.343	0.512	8.219	26	0.425	7.695	23	0.362	4.724

3.3. The morphology study

The figures 3 and 4 show the SEM images for S1 and S2 samples with different magnifications. The S1 sample contains agglomerated CuO nano-particles. Addition of a certain amount of glycine during the preparation process led to formation of spongy and fragile CuO/Cu_2O/Cu material (the S2 ample) containing voids and pores as shown in Fig. 2. These voids and pores could be attributed to the release of large amounts of gases during combustion process depending upon the decomposition of glycine and copper nitrate. In addition, we can be seen from the different SEM images that the agglomeration of the nano-particles of the investigated materials decreases by using the glycine as fuel.

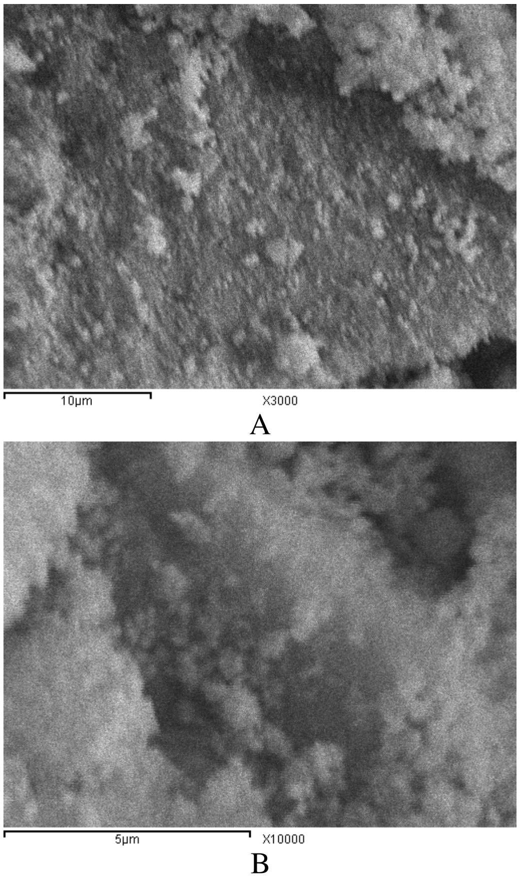
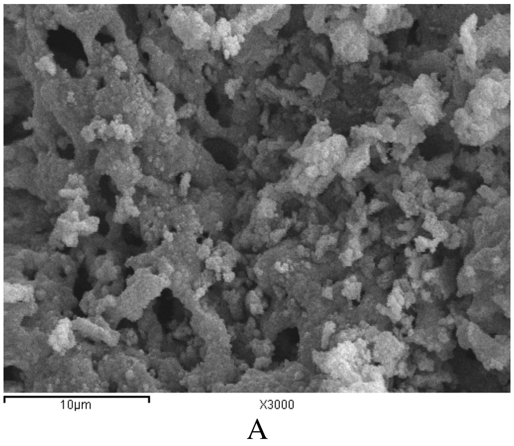
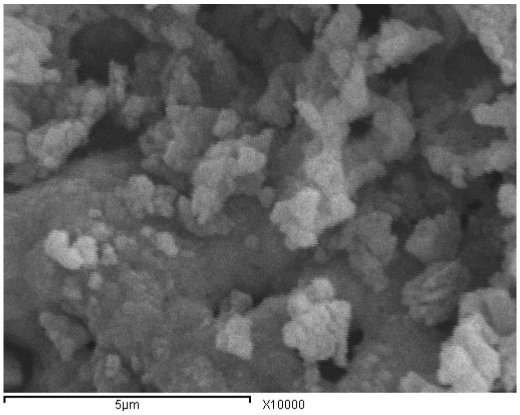


Figure 3. SEM image of the S1 sample with different magnifications.





B

Figure 4. SEM image of the S2 sample with different magnifications.

However, the presence of glycine as fuel brought about an increase in the homogeneity and distribution of particles for the copper based materials studied.

4. DISCUSSION

The chemical and structural relations of the CuO/Cu_2O/Cu system are more complex. Indeed, two copper oxides can form in air: CuO (melaconite or tenorite) is the stable oxide form at room-temperature, where the Cu ion is in the +2 valence state. Cu_2O (cuprite) is intermediate copper phase, where the Cu ion is in the +1 valence state. But, cuprous oxide is thermodynamically stable above 1020 °C.

Phase equilibrium relations in the system containing a mixture of CuO, Cu_2O and Cu were determined experimentally by Pike *et al.* [33]. These authors claimed that bulk CuO normally follows a single step reduction to metallic copper. Whereas nano-crystalline CuO followed a two-step reduction process, completely reducing first to Cu_2O, then to Cu. Unlike the reduction of bulk CuO to Cu_2O, which depends strongly on reaction conditions the formation of Cu_2O from CuO nano-particles shows a greater dependence on initial particle size [11, 12, 14]. In other words, the decrease in the initial size of CuO particle enhances the formation of Cu_2O intermediate phase. Consequently, Pike and coworkers expect that there is a critical particle size for CuO, above which direct reduction occurs to form Cu, and below which sequential reduction takes place to form Cu_2O and then Cu formed [33].

In the present study, we found phase equilibrium relations in the investigated system. In other words, glycine assisted combustion method resulted in formation of mixture of Cu, Cu_2O and CuO crystallites. The presence of these crystallites with together is very important in the most catalytic reactions. Cu_2O has higher catalytic activity in the splitting of water to O_2 and H_2. Also, cuprous oxide displays greater catalytic activity than CuO in the oxidation of CO [36, 37]. The XRD measurements for the S2 sample revealed that this sample consisted entirely of mixture of CuO, Cu_2O and Cu phases.

In other words, glycine assisted combustion method led to reduction of CuO to both Cu_2O and Cu. The reaction equation was proposed as following [38]:

$$4Cu^{+2} \rightarrow Cu^{+2} + Cu^{+1} + Cu^{0} \qquad (2)$$

In addition, there are phase transformations in the copper phases with subsequent change in the crystallinity of these phases. Where, CuO phase was the major phase in the S1 sample while Cu_2O was the major phase in the S2 sample with presence of Cu phase due to presence of glycine as fuel during preparation process. The morphology study of the investigated system showed that the S1 sample consisted of spherical, uniform, homogeneity and nano-sized particles. But the S2 sample consisted of spongy and fragile nano-particles. As the phase transformation of copper crystallites increases, the morphology has been modified with subsequent decrease in the size of grains as shown in the S2 sample.

5. CONCLUSIONS

Using of glycine as fuel in preparation of copper based materials affects the structural and morphological properties of these materials. Glycine assisted combustion route brought about formation of mixture of CuO, Cu_2O and Cu. The preparation by the investigated method resulted in a decrease in the particle size of CuO with subsequent reduction to form both Cu_2O and Cu nano-particles. The images of SEM showed that the as synthesized copper based materials using a certain amount of glycine have a significant porosity. The obtained samples have a homogenously distributed species in the whole mass prepared.

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