

A NOVEL TECHNIQUE TO SYNTHESIS OF TENORITE (CuO) NANOPARTICLES FROM LOW CONCENTRATION CuSO₄ SOLUTION

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Abstract

In this study CuO nanoparticles were prepared via direct thermal decomposition method using basic copper sulphates as wet chemically synthesized precursor which was calcined in air at 750 °C for 2 h. Samples were characterized by thermogravimetric (TG-DSC), X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), infrared spectrum (IR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The XRD, EDS, and IR results indicated that the synthesized CuO particles were pure. The SEM and TEM results showed that the CuO nanoparticles were of approximate spherical shape, and 170±5 nm in size. Using this method, CuO nanoparticles could be produced without using organic solvent, expensive raw materials, and complicated equipment.

Keywords: CuO; Nanoparticles; Synthesis; Thermal decomposition.

1. Introduction

Copper oxide nanoparticles are used in a wide range of applications such as gas sensors, magnetic storage media, batteries,

solar energy transformation, semiconductors, heterogeneous catalysis and field emission [1-9]. CuO, as a p-type semiconductor exhibiting narrow band gap ($E_g=1.2$ eV), have attracted great attention

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due to its potential applications in nano devices such as electronic, optoelectronic and sensing [1-5]. It has been widely used as powerful heterogeneous catalyst because of its high activity and selectivity in oxidation /reduction reactions. It is also used in the synthesis of methanol and higher alcohols from synthesis gas, the oxidation of organic and organosulfur compounds, the conversion of hydrocarbons completely into CO₂, water shift, and steam reforming of low-molecular-weight alcohols [4-8]. Up to now, CuO nanostructures have been produced with different shapes such as nanobelts [7], nanoplatelets [7], nano shuttle-like [10] and nanoparticles [7, 9, 11]. Various methods are used to prepare nanoparticles of copper oxides, including sol-gel, precipitation-stripping, solid-state reaction, alkoxidebased synthesis, sonochemical preparation, microwave irradiation, precipitation-pyrolysis and thermal decomposition [1-9, 11]. Among these techniques for the synthesis of copper oxide nanoparticles, thermal decomposition is a novel method. As compared to conventional method, it is much faster, cleaner and more economical [3].

Here, a simple procedure is described for the synthesis of CuO nanoparticles. The method is based on a convenient reaction between CuSO₄ and Na₂CO₃ in aqueous solution without using any surfactants. This method provides a convenient, low-cost, nontoxic route for the synthesis of pure nanostructures of copper oxide from copper leaching and bioleaching sites [12-14] and basic copper sulphates. It was performed at 55°C in the previous work [11].

2. Materials and Methods

The procedure pathway of the preparation process is shown in Fig. 1. CuSO₄·5H₂O (Copper (II) sulfate 5- hydrate, 99.95%), Na₂CO₃ (Sodium carbonate, 99.9%), distilled and de-ionized water were used in the experiments. All of the reagents were of analytical grade purity. Precursor was synthesized at 80°C by adding 0.5 M Na₂CO₃ solution to 100 ml of 0.5 M CuSO₄ solution with vigorous stirring.

The basic copper sulphates [Brochantite Cu₄(SO₄)(OH)₆ and Posnjakite Cu₄(SO₄)(OH)₆·H₂O] precipitate were separated by filtration and washed three times with warm deionized water to remove possible remnant ions in the final product, and dried at 70°C in air for several hours. The thermal decomposition of the precursor in air in a muffle furnace at 750°C for 2 h led to the final product of CuO nanocrystals. Thermogravimetric analysis (TG-DSC) for the precursor was performed with a STA409PG. Approximately 35 mg of samples were placed in a platinum crucible on the pan of the microbalance at a heating rate of 10 °C/min in N₂. The temperature range was 35–760 °C. The crystalline structure of the precursor and synthesized CuO were determined by X-ray phase analysis (XRD, PHILIPS, X' pert-MPD system, λ=1.54 Å) with Kα Cu radiation. IR spectra were recorded on a Bruker tensor 27 FTIR spectrometer with RT-DLATGS detector, in the range of 400 to 4000 cm⁻¹ with a spectral resolution of 4 cm⁻¹ in transmittance mode. The KBr pellet technique was used for sample preparation with about 1 wt% of sample. The

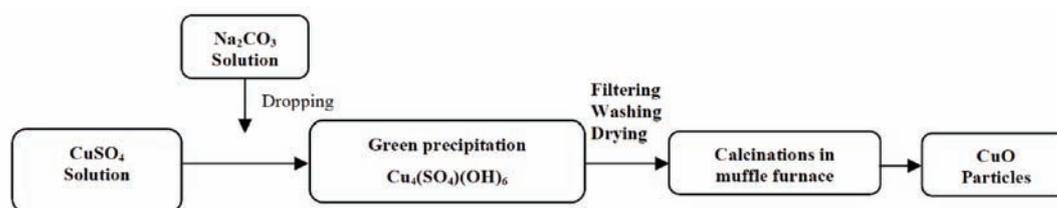
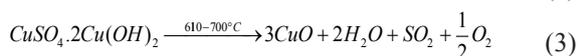
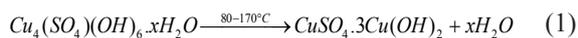


Fig. 1. Schematic of the experimental procedure.

morphology and dimension of the synthesized CuO nanoparticles were characterized by scanning electron microscopy (SEM, Tescan Vega-II) and compared to the previous research [11].

3. Results and discussion

The crystal structure and the phase purity of the precursor were characterized by XRD. As shown in Fig. 2a, almost all the diffraction peaks of the precursor could be indexed to Brochantite $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6]$ and Posnjakite $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot \text{H}_2\text{O}]$ which are in good agreement with the standard XRD data (JCPDS card No. 01-085-1316 and 00-020-0364), respectively. The basic copper sulphates were decomposed thermally to copper (II) oxide via the three distinguished thermal behaviours: (1) thermal dehydration, (2) in-situ crystallization of dehydrated amorphous compound, and (3) thermal desulferation [15]. The reaction pathway of the thermal decomposition of basic copper sulphates to copper (II) oxide includes the thermal dehydration and desulferation processes [Eqs. 1-3] [11-16].



The thermal analysis was carried out to find the crystallinity temperature. Thermogravimetric (TG) and differential scanning calorimeter (DSC) analyses are shown in Fig. 2c. Under linearly increasing temperature, the dehydration process indicates an anomaly in the DSC curve. When the sample was heated, the TG curve reveals weight losses within two broad steps (9.9 wt. % and 8.3 wt. %), the first one which is between 100 and 440°C is associated to the removal of water from the OH groups according to Eqs. 1, 2 and the second one which is between 590 and 710°C is related to the desulferation process according to Eq. 3 [11-16]. DSC of the precursor (Fig. 2c) shows three endothermic peaks around 210°C (range 200-220°C), 430°C (range 400-450°C) and 705°C (range 660-710°C) and one exothermic peak, at 535°C (range 530-560°C). The four peaks correspond well to Eqs. 1-3. Thus two endothermic peaks which are observed in the temperature range at 100-440°C in the DSC of sample may be due to the dehydration of precursor. The exothermic peak between 500 and 600°C may be due to the crystallization of the amorphous dehydrated product to CuO and $\text{CuO} \cdot \text{CuSO}_4$. This view is also confirmed by thermogravimetric (Fig. 2c), which shows no loss in weight between 500 and 600°C. Hence, it can be concluded that the

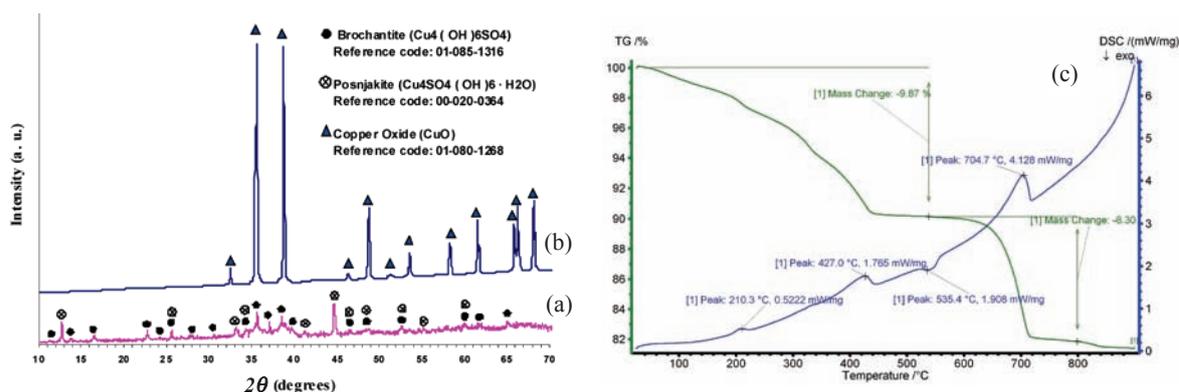


Fig. 2. (a, b) X-ray and (c) DSC curve of the precursor from 25 to 850 °C.

endothermic peak at 705 °C is due to the decomposition of CuSO₄ to copper (II) oxide [11-16].

It indicates that suitable temperature for decomposition of the precursor is over 705 °C, so the sample was calcined at 750 °C. Fig. 2b shows X-ray diffraction patterns of copper oxide (CuO) nano-crystals. The result shows that all the diffraction peaks are indexed to CuO with the standard structure (JCPDS card No. 01-080-1268), and no second phases such as Cu₂O and Cu(OH)₂ were found. The mean crystalline sizes of synthesized CuO were calculated to be about 70 nm using Debye-Scherrer Eq. 4:

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad \dots(4)$$

where, D is the mean crystalline size (nm), λ is the wavelength of Cu K α (0.154 nm), β is the full width at half maximum intensity (FWHM) in radian and θ° is the Bragg angle ($^\circ$) [17]. The EDS spectrum reveals that only Cu and O elements are detected in the prepared CuO powder, as shown in Fig. 3. Furthermore, based on the elemental analysis of the sample (Cu= 77.18%, O= 22.82%), the weight Cu/O ratio

can be calculated to be 3.38, which is close to actual value of 4 for CuO. The results of EDS analysis confirmed that the produced powder is CuO, which is in agreement with the results of XRD.

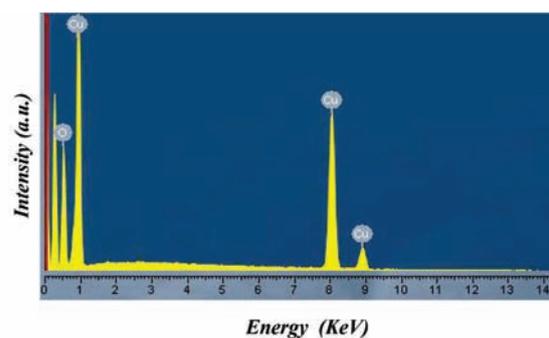


Fig. 3. EDS patterns of CuO nanoparticles.

Moreover, FTIR spectra provided information on the nature of the produced CuO. Fig. 4a and b show the FT-infrared (FTIR) spectrum of the precursor and CuO, respectively. As Fig. 4a shows absorption bands at 601 cm⁻¹ and 1118 cm⁻¹ were due to the SO₄ bending and stretching vibration, respectively [18, 19]. There is also a tiny dip in the spectra at 2359 cm⁻¹ due to the presence of atmospheric CO₂ [20]. The adsorption at 1640 cm⁻¹ and 3392 cm⁻¹ were attributed to the H-O-H bending and O-H stretching

vibration [18]. Finally, after heating for 2 h at 750°C, the absorption peak at 480-585 cm^{-1} is

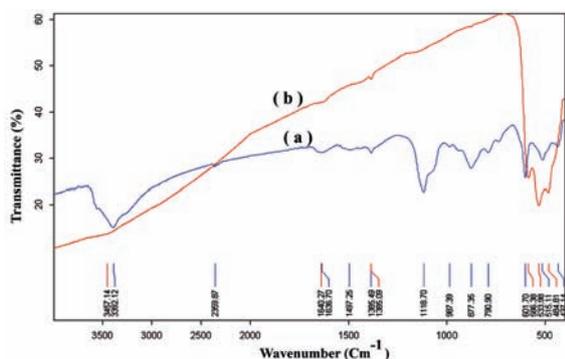


Fig. 4. FT-infrared spectra of precursor (a) and (b) CuO nanoparticles.

for Cu(II)-O [21-23], as shown in Fig. 4b.

The morphology of the CuO powder was examined by SEM (Fig. 5). From the SEM image of CuO nanoparticles it can be seen that the particles are spherical, while the morphology of the tenorite nanoparticles in the previous work were of rod shape [11].

Comparison of morphology for two temperatures showed that the shape of CuO nanostructures can be tuned by changing the temperature. Fig. 6. Shows TEM images of CuO nanoparticles. Further TEM observations indicated that the mean size of particles was about 170 ± 5 nm.

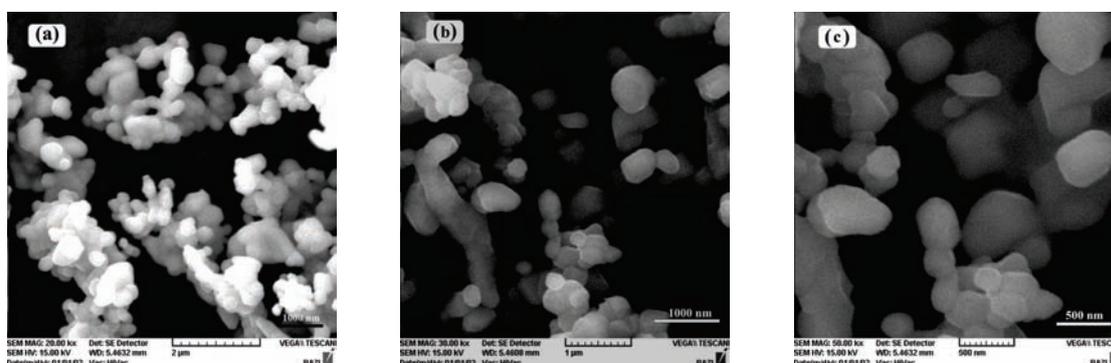


Fig. 5. SEM images of the CuO nanoparticles at (a) 20,000 \times , (b) 30,000 \times and 50,000 \times magnification.

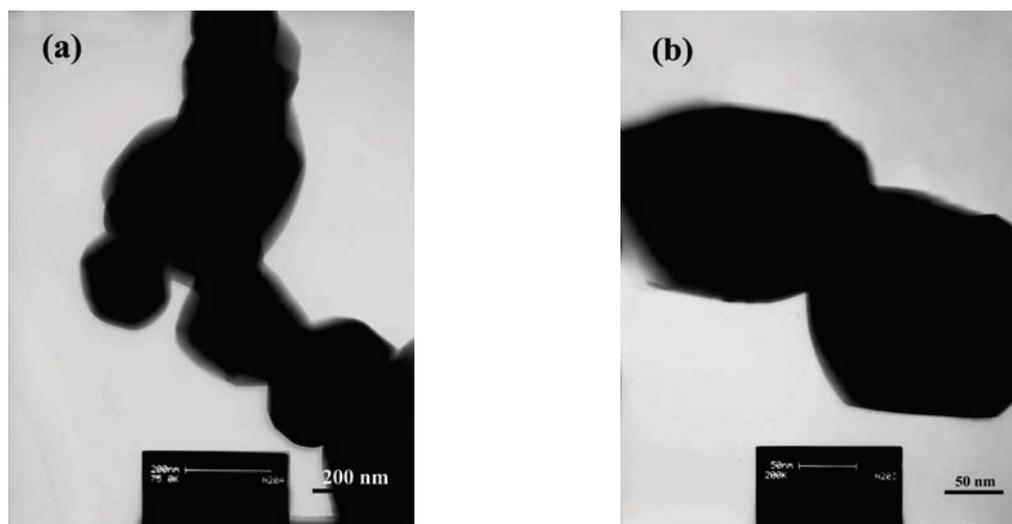


Fig. 6. TEM images of the CuO nanoparticles at (a) 75,000 \times and (b) 200,000 \times magnification.

4. Conclusions

Spherical CuO nanoparticles have been successfully prepared by a thermal decomposition method with mean diameter of 170 ± 5 nm. This method does not require organic solvents, expensive raw materials, and complicated equipment. So, it is concluded that the presented method is superior to the other methods for the synthesis of CuO nanoparticles from dilute CuSO_4 solution.

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