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 (Eg=1.2 eV), have attracted great attention...
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, alkoxide-based 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 sulfoates. 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
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].

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\begin{align*}
\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot \text{xH}_2\text{O} & \xrightarrow{90-110^\circ\text{C}} \text{CuSO}_4 \cdot 3\text{Cu(OH)}_2 + \text{xH}_2\text{O} \quad (1) \\
\text{CuSO}_4 \cdot 3\text{Cu(OH)}_2 & \xrightarrow{200-400^\circ\text{C}} \text{CuSO}_4 \cdot 2\text{Cu(OH)}_2 + \text{CuO} + \text{H}_2\text{O} \quad (2) \\
\text{CuSO}_4 \cdot 2\text{Cu(OH)}_2 & \xrightarrow{400-700^\circ\text{C}} 3\text{CuO} + 2\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \quad (3)
\end{align*}
\]

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 CuO.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
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:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \quad ...(4) \]

where, D is the mean crystalline size (nm), \( \lambda \) is the wavelength of Cu Kα (0.154 nm), \( \beta \) is the full width at half maximum intensity (FWHM) in radian and \( \theta \) is the Bragg angle (°) [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.

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 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.

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

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

**Fig. 6.** TEM images of the CuO nanoparticles at (a) 75,000× and (b) 200,000 × 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 CuSO₄ solution.

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