Nanochem Res 4(2): 148-153, Summer and Autumn 2019

RESEARCH PAPER

Synthesis of CuO nanorods via thermal decomposition of copper-dipicolinic acid complex

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ARTICLE INFO

Article History:
Received 13 August 2019
Accepted 08 October 2019
Published 15 October 2019

Keywords:
CuO nanorod
template-free synthesis
copper-dipicolinic acid complex
decomposition of a Cu-complex
TEM

ABSTRACT

Template-free CuO nanorods were synthesized through a three-step chemical method with no water-insoluble materials. The first step included the preparation of a Cu-complex using dipicolinic acid, L-lysine, and copper nitrate. Then, as the second step, the obtained solution was allowed to be relaxed for a week to form some blue single-crystals, which would be assigned as a square-pyramidal copper complex according to analyzing its single-crystal structure. Finally, as the third step, the blue prepared Cu-complex should be calcined to synthesize the CuO phase. Simultaneous thermal analysis (STA) was utilized to determine the optimum calcination temperature. Its results showed that 600 ºC is the optimum temperature. X-ray diffraction (XRD) analysis approved the formation of the CuO phase without any impurity which is matched with the monoclinic CuO standard lines (PDF No.: 74-1021). Especially, the as-prepared CuO powder has shown clear nanorod morphology in transmission electron microscopy (TEM) images and exhibits a notable optical behavior and high bandgap energy (E_g = 2.8 eV) in comparison to that of bulk CuO (Eg = 1.9-2 eV).

How to cite this article
Gharagozlou M, Naghibi S.. Synthesis of CuO nanorods via thermal decomposition of copper-dipicolinic acid complex . Nanochem Res, 2019; 4(2):148-153. DOI: 10.22036/ncr.2019.02.006

INTRODUCTION

As a semiconductor, copper oxide (CuO) has been applied in the electronic devices (1), electromagnetic-wave filter (2), sensors (3), catalysts (4), and hydrogen storage systems (5). Different synthesis methods have been developed to produce CuO with specific characteristics or forms; such as chemical method (6, 7), pulsed laser ablation technique (8), chemical vapor deposition (9), etc. Aside from the particle size which is considered by different research teams to manage the characteristics of the synthesized CuO powder, morphology controlling is another parameter having considerable effects on the properties of the synthesized compounds (10). Nanorod structure is one of the popular morphologies of CuO which leads to some specific properties and applications; such as antibacterial (11), selective gas sensing (12), luminescence (13), and material storage (14) applications. To achieve such a structure, a template and/or a surfactant are needed (15-17) which either remains in the system as an impurity or release toxic by-products. Although several methods have been suggested to synthesize rod-like shape particles (18-20), our research team has developed a new method to synthesize the ZnO nanoparticles with specific morphology. This method is designed based on preparing a metal complex. In such a situation, metal ions locate in specific sites (21, 22). Thermal decomposition of these compounds not only leads to form a high purity ceramic material but also provides a condition for the preferential particle growth. This method could be considered

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in the case of other nanoparticles.

In this research, an innovative method has been evaluated to synthesize CuO nanorods without using a template. To do so, three different steps have been taken: (i) preparation of a square-pyramidal copper complex, (ii) aging the solution to appear the blue single-crystals , and (iii) heat-treatment of the as-crystallized compound to burn out the organic compounds and form CuO phase. Studying the single-crystal structure of the as-prepared Cu-complex would help to explain the formation mechanism of rod-like particles. On the other hand, STA, XRD, TEM, and DRS have been selected to evaluate the as-synthesized powder compound.

EXPERIMENTAL SECTION

Preparation method of CuO nanorods

The first step was the synthesis of square-pyramidal copper (II) complex or $(Cu(pydc)(H_2O))_n$. For doing so, dipicolinic acid (pyridine-2,6-dicarboxylic acid, $C_7H_5NO_4$, DPA) as a complex agent, L-lysine ($C_6H_{14}N_2O_2$) as an α-amino acid (AAA), and copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) as a Cu source were purchased from Merck. In a typical procedure, a water-based solution of DPA and AAA with an equal molar ratio was prepared. After 10 min of agitation, an adequate amount of copper nitrate was added and stirred for 10 min. The molar ratio of DPA/AAA/copper nitrate was 1/1/0.5. The obtained solution was allowed to relax for a week to appear some blue crystals which would be the target complex. Heat treatment of the as-synthesized powder may lead to form CuO crystalline phase.

Characterization

The single-crystal structure was determined by a Bruker SMART 1000 CCD diffractometer with Mo Kα and summarized in Table 1. Heat treatment of the as-synthesized powder may lead to form CuO crystalline phase. The calcination temperature would be gained via the simultaneous thermal analysis (STA) that was accomplished by a Perkin Elmer STA Pyris Diamond device in an air atmosphere with a heating rate of 5°C/min. The X-ray diffraction (XRD) profile was achieved by a PANalytical diffractometer. Transmission electron microscopy (TEM) micrographs were gained by a Zeiss 900 microscope. Diffuse reflectance spectroscopy (DRS) was utilized by a Jascos UV-Vis. scanning spectrophotometer (V-670). Based on the absorbance results and the Tauc technique, optical band gap energy (Eg) values were determined.

Table 1 Crystal data, structure, and selected bond lengths for the obtained blue crystals

Parameter	Results
Compound	$(Cu(pydc)(H_2O))_n$
Empirical Formula	$C_7H_7CuNO_6$
Formal Weight	264.68
Crystal System	Monoclinic
Space Group	$P2_1/c$
Unit Cell Dimensions	
a (Å)	7.222 (19)
b (Å)	19.064 (15)
c (Å)	6.436 (17)
α (°)	90.0
β (°)	107.1 (4)
γ (°)	90.0
Z	4
Crystal Size (mm)	0.10 × 0.14 × 0.22
Goodness-of-fit (F^2)	1.103
Final R Index	0.0248
R Index (all data)	0.0597
Selected Bond Lengths	
Cu(1)-O(5)	1.943 (15)
Cu(1)-O(3A)	2.434 (15)
O(3)-C(7)	1.280 (3)
Cu(1)-N(1)	1.898 (18)
Cu(1)-O(1)	2.044 (16)
Cu(1)-O(6)	2.406 (17)

RESULTS AND DISCUSSION

The first aim of this work was to synthesize a Cu-complex. AAA plays an important role in this process due to its excess amine functional group. This leads to form hydrogen bonds and adjust the pH value in the basic region facilitating the deprotonation of dipicolinic acid and formation of an anionic ligand. Table 1 represents the crystal data and structure for the blue crystals obtained and approves the formation of the $(Cu(pydc)(H_2O))_n$ complex. As can be seen, Cu ions are located in pseudo-octahedral sites and consequently they are hexacoordinated with two oxygen atoms, O(1) and O(3), and one nitrogen atom, N(1), which are originated from the dipicolinate ions, one oxygen atom, O(3A), from the adjacent ligands, and two oxygen atoms, O(5) and O(6), from the coordinated water molecules. Due to the hydrogen bonds between oxygen atoms from the coordinated water molecules and non-coordinated water molecules, the chain-like complex structure would be created.

STA was used to determine the thermal

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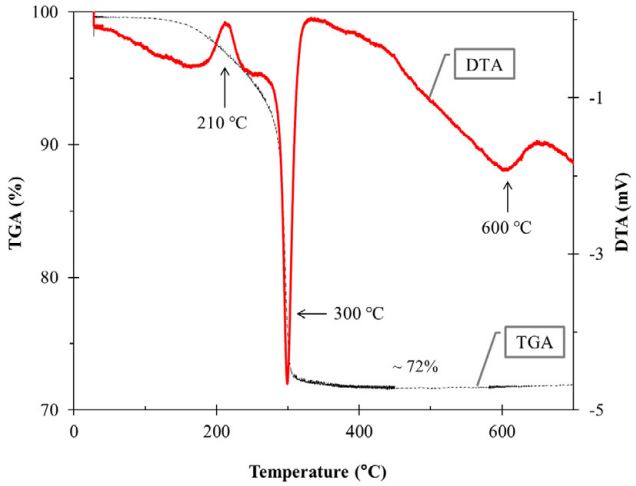

Fig. 1. STA curves of the Cu complex

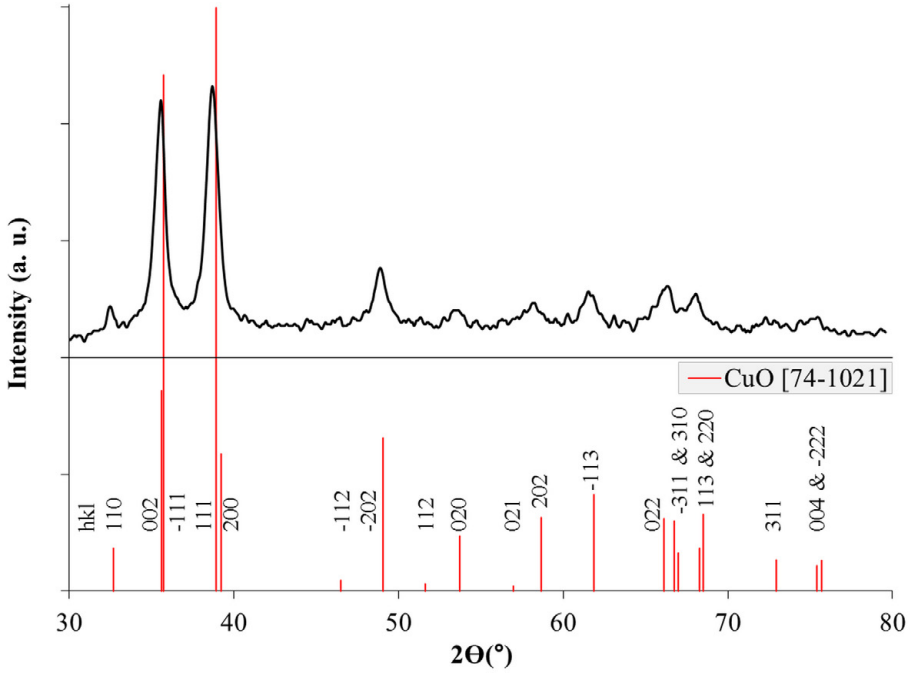

Fig. 2. XRD pattern of the calcined sample accompanied by the standard diffraction lines of CuO [PDF No.: 74-1021]

behavior of the synthesized complex and its critical temperatures. Fig. 1 shows differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) in the temperature range of 25-700 °C. Although the weight loss was about 30% at ~ 300 °C, three different DTA peaks observed at 210, 300, and 600 °C, respectively. The first peak at 210 °C, which is an endothermic process, is attributed to the removal of coordinated water. The obtained dehydrated compound remains stable up to ~ 300 °C and then a huge exothermic reaction occurred, which was accompanied by a weight loss of 30%. This might be due to the decomposition and/or combustion of organic compounds. Although the TGA profile shows a steady-state, DTA shows a reaction at the temperature range of 400-700 °C, peaked at 600 °C, that might be due to the crystallization of a ceramic oxide compound. Accordingly, this temperature was selected for the sample preparation procedure. Fig. 2 shows

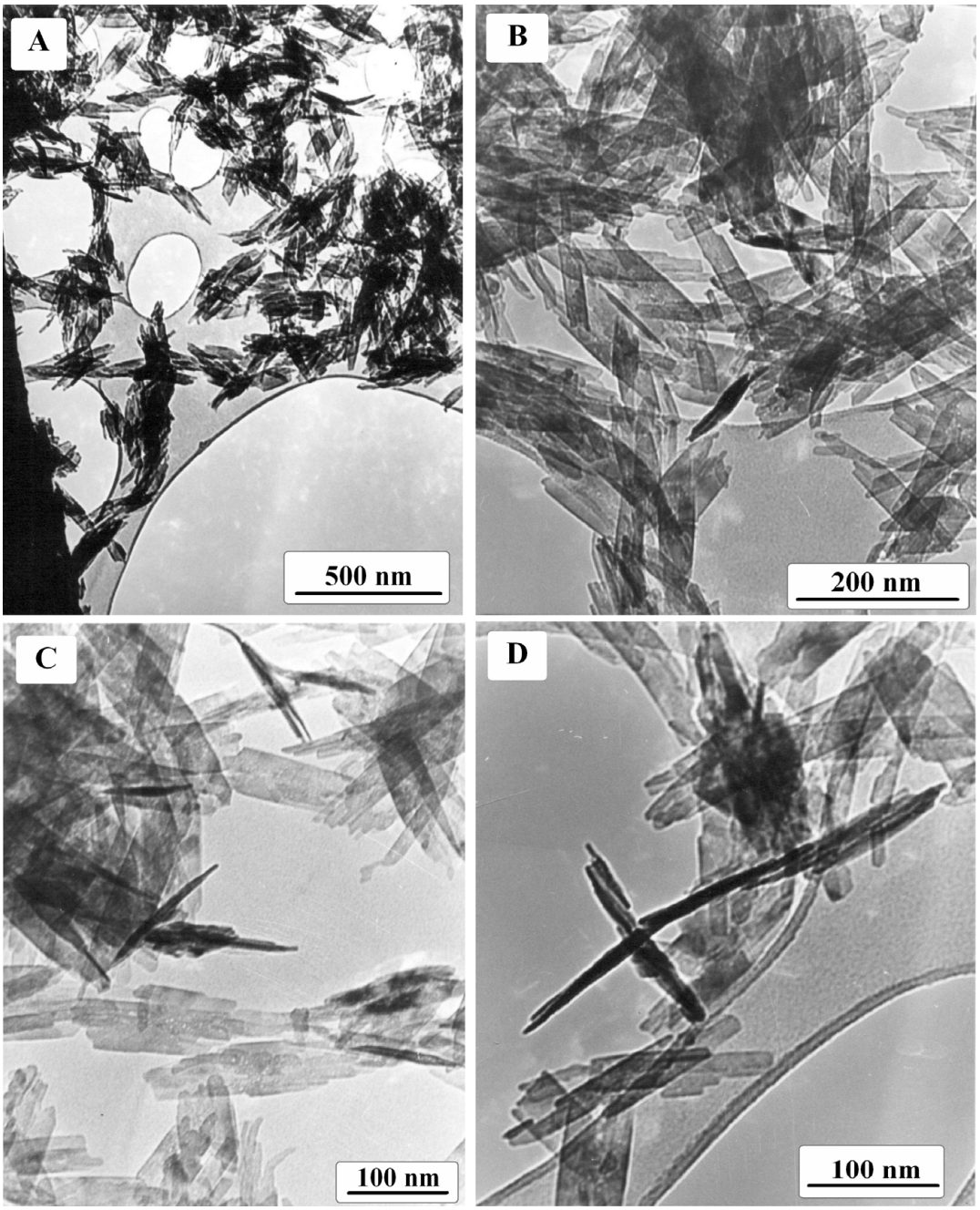

Fig. 3. TEM images of the calcined sample with the magnification of (A) 28 KX, (B) 75 KX, (C) 100 KX, and (D) 125 KX

the XRD pattern of the as-calcined sample at 600 °C, approving the formation of CuO as a unique phase with high crystalline quality which is well-matched with CuO standard lines (PDF No.: 74-1021, crystal system: Monoclinic, and space group: C2/c). More than XRD, the monoclinic structure of the synthesized powder could be considered by the TEM investment. Fig. 3 shows TEM images of the as-synthesized sample with different magnifications. These approve the formation of CuO nanorods with 150-200 nm in length and less than 10 nm in diameter. It is clear that more than 95% of the particles have a rod-like shape and could be considered as single-crystals with monoclinic structure. Therefore, preparing process of Cu-complex provided suitable chemical conditions to

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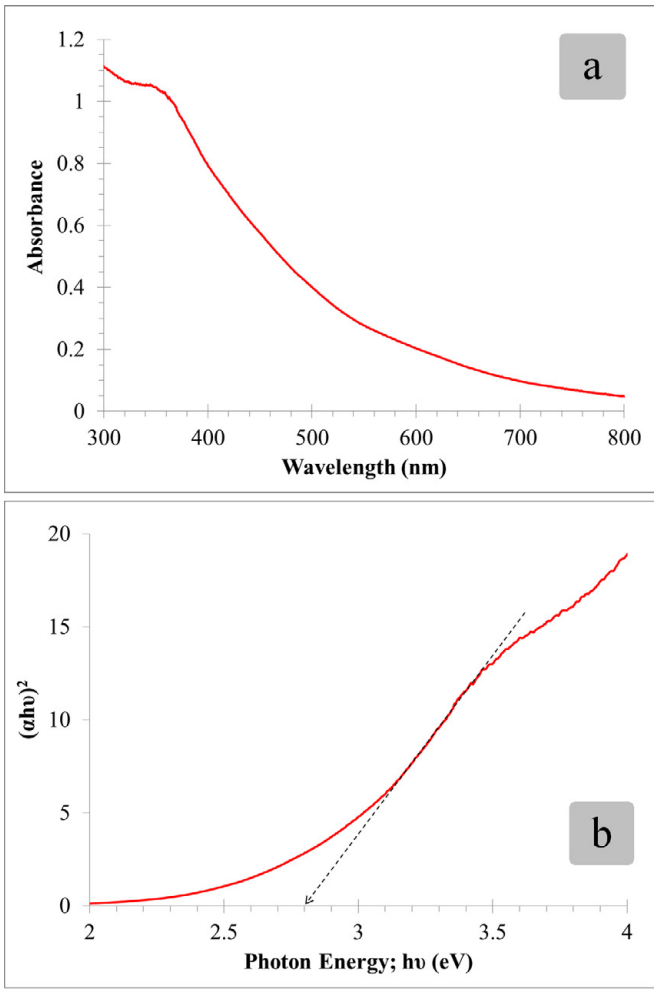

Fig. 4. (a) The absorbance curves, and (b) the Tauc curves of the synthesized sample

support the oriented single-crystalline nucleation and growth procedure. In such a complex system, Cu ions are distributed homogeneously in pseudo-octahedral sites and surrounded by one nitrogen and five oxygen atoms. This phenomenon restricts the free displacement of the atoms, resulting in efficient CuO crystallization (23). On the other hand, the situation of Cu atoms in the monoclinic Cu-complex structure is similar to that of Cu atoms in the monoclinic CuO system (24) which results in the formation of rod-like grains. The adsorption edge and bandgap energy (E_g) of the synthesized sample is one of the most important characteristics that should be determined. To this end, the solid-state UV–visible spectroscopy was recorded and the obtained results were presented as an absorbance curve and a Tauc curve in Fig. 4. The adsorption occurs at a wavelength of less than 500 nm. The Tauc plot showed that the Eg of the synthesized sample was about 2.8 eV, which is closer to that of Cu_2O phase rather than CuO. This may be referring to either the specific morphology of the as-synthesized sample or the quantum confinement phenomenon (25).

CONCLUSION

A three-step chemical technique was developed to synthesize the CuO nanorods without using any template or surfactant. For this aim, dipicolinic acid, L-lysine, and copper nitrate were used for preparing a water-based solution. After aging the obtained solution for a week, some blue single-crystals were formed. Studying the single-crystal structure of the obtained compound proved that the blue crystals

are square-pyramidal copper complex. STA results showed that 600 ° is the optimum temperature for firing the Cu-complex to achieve CuO crystalline phase. The XRD results approved the formation of pure CuO in the monoclinic crystalline structure. Particularly, TEM images validated the successful formation of nanorods with a length of 150-200 nm and a diameter of less than 10 nm. The DRS results indicated the high bandgap energy of 2.8 eV for the synthesized CuO nanorods in comparison to that of bulk CuO, 1.9-2 eV.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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