

Synthesis and Characterization of Copper(II)-Oxide Nanoparticles from Two Cu(II) Coordination Polymers

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Abstract

CuO nano particles were obtained by calcination of nano-sized [Cu(C₄H₄O₄)(bipy)(H₂O)₂].2H₂O (1) and [Cu(2,2'-bipy)](C₄H₄O₄)_{0.5}(NO₃)(H₂O) (2) which are two Cu(II) coordination polymers. The two coordination polymers [Cu(C₄H₄O₄)(bipy)(H₂O)₂].2H₂O and [Cu(2,2'-bipy)](C₄H₄O₄)_{0.5}(NO₃)(H₂O) were synthesized and characterized by Fourier transform infrared spectra (FT-IR spectroscopy), thermal gravimetric (TGA) and differential thermal analyses (DTA). CuO nano particles were characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The two coordination polymers obtained possessed nano sizes.

Keywords: Copper(II) Oxide; Nanoparticles; Coordination polymer; Calcination.

Introduction

The oxides of transition metals are an important class of semiconductors, with applications in magnetic storage media, solar energy transformation, electronics and catalysis [1-8]. Of the oxides of transition metals, copper oxide nanoparticles are of special interest because of their efficiency as nano fluids in heat transfer application. For instance addition of 4% CuO was proven to improve the thermal conductivity of water by 20% [9]. CuO is a semiconducting compound with a narrow band gap extensively used in photoconductive and photothermal applications [10]. However, studies conducted on the preparation and characterization of nanocrystalline CuO are relatively few to some other transition metal oxides such as zinc oxide, titanium dioxide, tin dioxide and iron oxide. Some methods for the preparation of nanocrystalline CuO have recently

been reported such as the sonochemical method [11], sol-gel technique [12], one-step solid state reaction method at room temperature [13], electrochemical method [14], thermal decomposition of precursors [15] and co-implantation of metal and oxygen ions [16]. Recently, the construction of coordination supramolecules or coordination polymers has emerged as a powerful and versatile strategy for engineering metallo-polymers [17]. Different from covalent conventional polymers, the coordination supramolecules are based on metal-ligand coordination bonds [18-20]. The potential use of supramolecular coordination complexes as materials in nano technological applications seems to be very extensive as nanometer-scaled materials often exhibit the interesting size-dependent physical and chemical properties that can not be observed in their bulk analogous. For this reason, nano-sized coordination supramolecular materials are

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interesting candidates for applications in many fields, including catalysis, molecular adsorption, magnetism, nonlinear optics, luminescence, and molecular sensing [21-23] but nano-scale particles of metal-organic coordination supramolecules have rarely been investigated.

The present study was an attempt to develop a simple route for the synthesis of copper (II) Oxide nanoparticles from precursor. To the best of our knowledge, there is no report available on the synthesis of CuO by using metal organic compounds such as nano-sized $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_4)(\text{bipy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (compound 1) and $[\text{Cu}(2,2'\text{-bipy})](\text{C}_4\text{H}_4\text{O}_4)_{0.5}(\text{NO}_3)(\text{H}_2\text{O})$ (compound 2) as precursors. Thus, CuO nanoparticles were successfully prepared by the calcination of the nanostructures of nano-sized compound 1 and 2 at 400 °C, respectively. Furthermore, the structural effects of coordination polymers on the morphology of the products were investigated.

Materials and Methods

Chemicals and equipments

All the reagents were of commercial purity. A multi-wave ultrasonic generator (Sonicator 3000; Bandeline, MS 72, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz was used for the ultrasonic irradiation. All ultrasonication experiments were carried out at ultrasonic power between 100–110 mW measured by calorimetry [24]. Powder X-ray diffraction (XRD) patterns were collected from a diffractometer of Philips Company with X'PertPromonochromatized Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Microscopic morphology of products was visualized by a LEO 1455VP scanning electron microscope (SEM). The thermogravimetric analysis (TGA) of compound 1 was carried out with Pyris Diamond Perkin Elmer under air atmosphere at a heating rate of 10°C/min from room temperature to 500 °C. Fourier transform infrared spectra were performed using KBr pellets on FT-IR spectrometer (Magna-IR, 550 Nicolet) in the range of 400–4000 cm^{-1} .

Synthesis of nano-sized $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_4)(\text{bipy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(2,2'\text{-bipy})](\text{C}_4\text{H}_4\text{O}_4)_{0.5}(\text{NO}_3)(\text{H}_2\text{O})$ precursors

Nano-Sized (compound 1) was prepared by reaction of between 5 ml to 0.1 M solution of succinic acid which was added drop-wise to a mixed solution of 5 ml of a 0.1 M solution of ligand 4,4'-bipyridine and a 10 ml of 0.1 M solution of Copper (II) chloride under ultrasound irradiation. After cooling to room temperature, the precipitates were centrifuged, washed

by distilled water and ethanol in sequence and dried in vacuum at 50 °C.

Nano-Sized $[\text{Cu}(2,2'\text{-bipy})](\text{C}_4\text{H}_4\text{O}_4)_{0.5}(\text{NO}_3)(\text{H}_2\text{O})$ (compound 2) was prepared by reaction between 10 ml of succinic acid which was added drop-wise to a mixed solution of 10 ml of a 0.1 M solution of ligand 2,2' bipyridine and a 5 ml of 0.1 M solution of $\text{Cu}(\text{NO}_3)_2$ under ultrasound irradiation for 30 min. Afterwards, the precipitates were centrifuged, washed by distilled water and ethanol in sequence and dried in vacuum at 50 °C.

Synthesis of CuO nanoparticles

For the preparation of CuO nanoparticles, calcinations of bulk powder compounds 1 and 2 were performed at 400 °C in static atmosphere of air for 3h. IR spectrum and powder XRD diffraction indicated that the calcination process was completed and pure CuO were produced.

Results and Discussion

The IR spectra of compound 1 is shown in Fig.1. Figures 2a and 2b illustrate thermal gravimetric and differential thermal analyses conducted on compound 1 (TGA and DTA). TGA and DTA were carried under nitrogen flow. Decomposition of $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_4)(\text{bipy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ occurred in two weight-loss steps. The first corresponding to 5.6% weight loss, occurred in the range of 137°C, which is related to the elimination of H₂O molecules due to its previous exposure to air; the second (81.9% in weight loss) beginning at 215.8°C. The weight loss observed at 215.8 °C was corresponding to silver benzoate decomposition to CuO. The TGA curve shows the total mass loss of approximately 87.5 %. The mass loss calculations indicated that the final decomposition product was CuO. Furthermore, $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_4)(\text{bipy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ devoided of any coordinated molecules. DTA curve displays two endothermic effects occurred at 241 and 293°C with two exothermic effects at 145 and 358 °C.

The morphology and structure of the products were investigated by SEM images. Figures 3a and 3b depicts the SEM images of compounds 1 and 2. Figures 3c and 3d show SEM images of CuO synthesized by $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_4)(\text{bipy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(2,2'\text{-bipy})](\text{C}_4\text{H}_4\text{O}_4)_{0.5}(\text{NO}_3)(\text{H}_2\text{O})$ as Cu source. Due to the dimeric structure of Cu (II) coordination polymers, high steric hindrance surrounds the Cu center. The structure around Cu atoms plays the surfactant role [25]. Figure 4a and b illustrates the XRD pattern of compounds 1 and 2. Figures 4c and 4d show CuO nanoparticles prepared by calcinations of compounds 1 and 2 respectively. Pure CuO phase was formed as illustrated

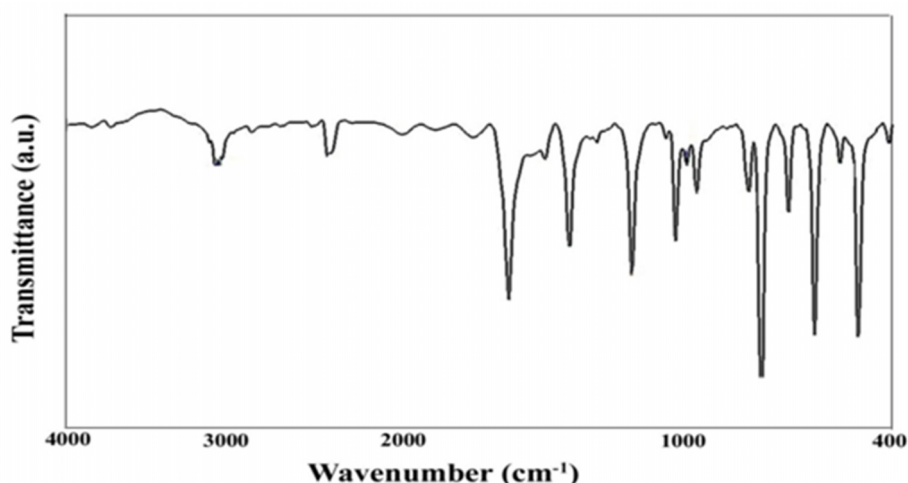


Figure 1. FT-IR spectra of $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_4)(\text{bipy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

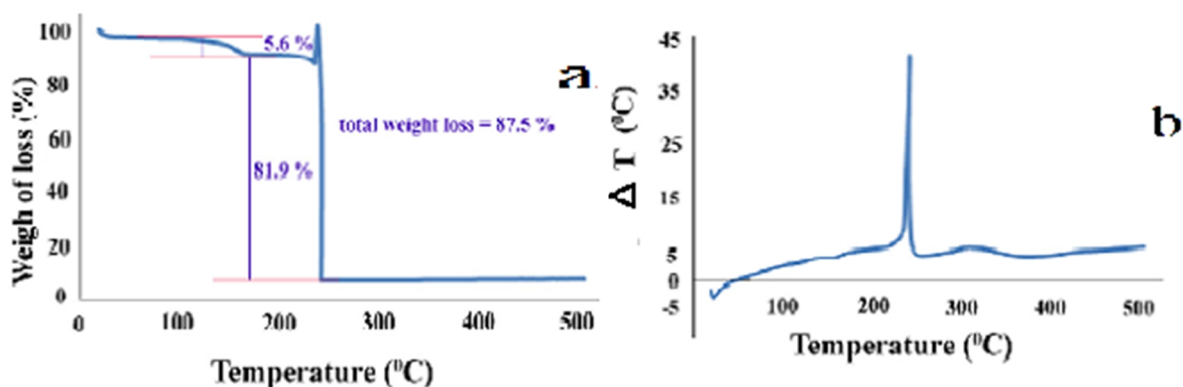


Figure 2. (a) TGA and (b) DTA curves of $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_4)(\text{bipy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

in Figs. 4c and 4d. The diffraction peaks of the products can be indexed to orthorhombic phase CuO. No remarkable diffractions of other impurities such as C or N can be found, indicating that pure CuO nanoparticles were synthesized. The sharp diffraction peaks indicate the good crystallinity of the nanoparticles and the peak broadening is due to the small particle size of CuO nanoparticles.

To study the structural effect of coordination polymers on the morphology of CuO, we compared the SEM images of CuO as illustrated in Figs. 3c and d. It is clear that the CuO nanoparticles produced from calcination of $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_4)(\text{bipy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ are much smaller than CuO nanoparticles obtained from calcination of $[\text{Cu}(2,2'\text{-bipy})](\text{C}_4\text{H}_4\text{O}_4)_{0.5}(\text{NO}_3)(\text{H}_2\text{O})$ and it is difficult to measure the

individual particle size. When $[\text{Cu}(2,2'\text{-bipy})](\text{C}_4\text{H}_4\text{O}_4)_{0.5}(\text{NO}_3)(\text{H}_2\text{O})$ used as Copper source, CuO were formed quickly, and the rate in which the core was created was more than growth, as the Copper can be released quickly [26]. Thus, the products were agglomeration. By changing Cu source to $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_4)(\text{bipy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, because of the dimeric structure of Cu (II) coordination polymers, high steric hindrance surrounds the Cu centre. Therefore, copper can be released slower than the former source, yet the rate of creating core was more than growth. therefore the particle size will be small, but the particles were not coherent.

Conclusion

In summary, CuO nanoparticles were produced by

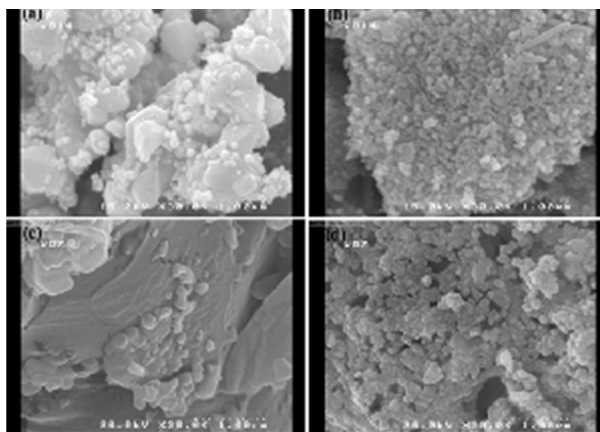


Figure 3. (a) SEM images of nano-sized $[\text{Cu}(2,2'\text{-bipy})](\text{C}_4\text{H}_4\text{O}_4)_{0.5}(\text{NO}_3)(\text{H}_2\text{O})$, (b) nano-sized $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_4)(\text{bipy})(\text{H}_2\text{O})_2].2\text{H}_2\text{O}$ (c) CuO nanoparticles obtained from calcination of $[\text{Cu}(2,2'\text{-bipy})](\text{C}_4\text{H}_4\text{O}_4)_{0.5}(\text{NO}_3)(\text{H}_2\text{O})$ (d) CuO nanoparticles obtained from calcination of $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_4)(\text{bipy})(\text{H}_2\text{O})_2].2\text{H}_2\text{O}$

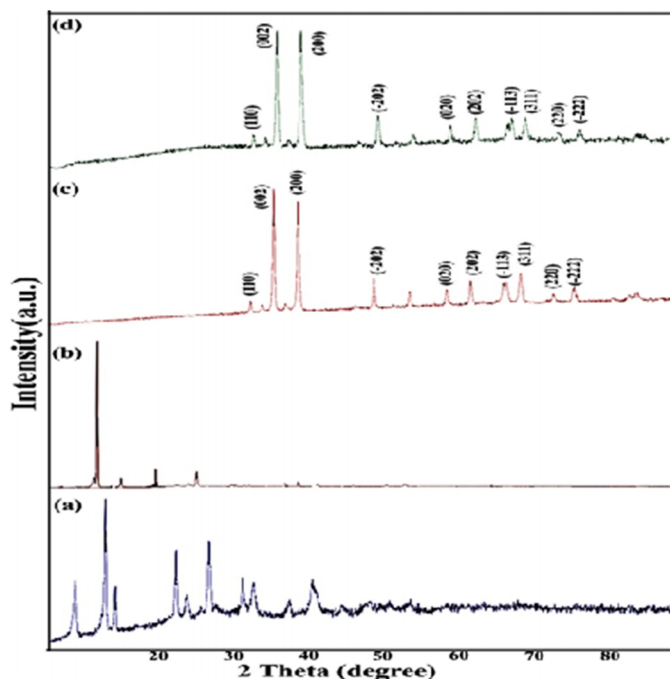


Figure 4. (a) XRD patterns of nano-sized $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_4)(\text{bipy})(\text{H}_2\text{O})_2].2\text{H}_2\text{O}$, (b) nano-sized $[\text{Cu}(2,2'\text{-bipy})](\text{C}_4\text{H}_4\text{O}_4)_{0.5}(\text{NO}_3)(\text{H}_2\text{O})$ (c) CuO nanoparticles obtained from calcination of $[\text{Cu}(2,2'\text{-bipy})](\text{C}_4\text{H}_4\text{O}_4)_{0.5}(\text{NO}_3)(\text{H}_2\text{O})$ (d) CuO nanoparticles obtained from calcination of $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_4)(\text{bipy})(\text{H}_2\text{O})_2].2\text{H}_2\text{O}$

the calcination of $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_4)(\text{bipy})(\text{H}_2\text{O})_2].2\text{H}_2\text{O}$ and $[\text{Cu}(2,2'\text{-bipy})](\text{C}_4\text{H}_4\text{O}_4)_{0.5}(\text{NO}_3)(\text{H}_2\text{O})$ as starting agents. XRD results indicated that pure CuO nanoparticles have been successfully obtained via such a simple route. We attempted to produce CuO nanoparticles without using any capping agent. Hence, we used $[\text{Cu}(\text{C}_4\text{H}_4\text{O}_4)(\text{bipy})(\text{H}_2\text{O})_2].2\text{H}_2\text{O}$ and $[\text{Cu}(2,2'\text{-bipy})](\text{C}_4\text{H}_4\text{O}_4)_{0.5}(\text{NO}_3)(\text{H}_2\text{O})$ as precursors, which can act as surfactant in the reaction medium.

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