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Synthesis of Different Copper Oxide Nano-Structures From Direct Thermal Decomposition of Porous Copper(II) Metal-Organic Framework Precursors

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Abstract:
Copper oxide nanostructures have been successfully synthesized via one-step solid-state thermolysis of two metal-organic frameworks, [$Cu_3(btc)_2$] (1) and [Cu(tpa).(dmf)] (2), (btc = benzene-1,3,5-tricarboxylate, tpa = therephtalic acid = 1,4-benzendicarboxylic acid and dmf = dimethyl formamide) under air atmosphere at 400, 500, and 600°C. It has also been found that the reaction temperature plays a substantial role in the formation of copper oxide nanostructures. The obtained products were characterized by X-ray powder diffraction (XRPD), Energy dispersive X-ray microanalysis (EDX), and scanning electron microscopy (SEM). Different reaction conditions were discussed. This study demonstrates that the metal-organic frameworks can be used as precursors for the preparation of nanoscale materials with difference and remarkable morphologies.

Keywords: *Metal-organic framework, Solid-state thermolysis, Nano-structures, Copper oxide.*

1. INTRODUCTION

The unique properties of nano-sized metal oxides accelerate wide activities of research and open a series of technical applications, for instance in electronics, optics and catalysis [1]. To amplify reactivity, selectivity and catalytic ability of copper oxides, it should have nano-size dimensions and high specific surface area. There are various techniques to improve catalytic effect, not only by reducing the size of powder, but also with controlling morphology on the basis of increasing surface area [2-3].

Moreover, the beneficial physical–chemical properties strongly depend on the particle size and the controlled fabrication of nano-ranged materials which produces a specific challenge [4] being reflected by manifold approaches, including chemical vapor deposition [5], sol–gel processes [6], flame synthesis [7], hydrothermal and polyol synthesis [8-9]. Meanwhile, in recent years, extensive attention has been paid to design and construction of the metal-organic framework (MOF) from building blocks due to their fascinating structural properties and potential applications in catalysis, host-guest chemistry, enantioselective separation, electrical conductivity, and magnetism [10-14].

It has been thought that many novel properties and potential applications would emerge from unusual MOF [15-16]. In this work, possibility of copper oxide nano-structure fabrication was investigated through one-step solid-state thermolysis of metal-organic framework precursors.

2. EXPERIMENTAL

2.1. Materials and physical techniques

All the ligands and transition metal salts were obtained commercially and used as received. X-ray powder diffraction patterns were measured using a Philips PW1800 powder diffractometer for Cu-K_α (λ = 0.17887 Å) with a scanning speed of 1 s/step and a step size of 0.04°. The samples, coated with gold, were characterized using scanning electron microscope (SEM) (Hitachi S4160 and Philips XL30) operating at 17.0 kV and equipped with a Philips XL30 energy dispersive X-ray analysis (EDX) to fulfill element microanalysis.

2.2. Preparation of Cu(tpa).(dmf) (1)

Cu(tpa).(dmf) MOF was synthesized according to the literature [17]. In a typical synthesis of Cu(tpa)•(dmf) MOF, equimolar quantities of copper nitrate trihydrate (0.145 g) and terephthalic acid (0.1 g) were dissolved in dmf (12 mL). This solution was placed in a closed scintillation flask in an oven at 110°C for 36 h. Small blue precipitated crystals were visible inside the flask upon removal from the oven.

2.3. Preparation of $Cu_3(BTC)_2$ (2)

This procedure was taken from the work of Chowdhury et al. [18]; they have optimized the original synthesis method reported by Chui et al. [19]. Cupric nitrate trihydrate $Cu(NO_3)_2$. $3H_2O$ (0.149 g) was dissolved into deionized water (1.4 ml) in a flask, and benzene-1,3,5-tricarboxylic acid (0.065 g,) was added to ethanol (2.8 ml) and mixed thoroughly. The two solutions were then mixed and stirred at room temperature for 4 h. The resulting viscous mixture was transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated in an oven at 413 K for 48 h. The reaction vessel was then cooled naturally to room temperature. Blue powder product of Cu-BTC was collected by filtration and washed thoroughly with deionized water. This product was dried at 358 K overnight.

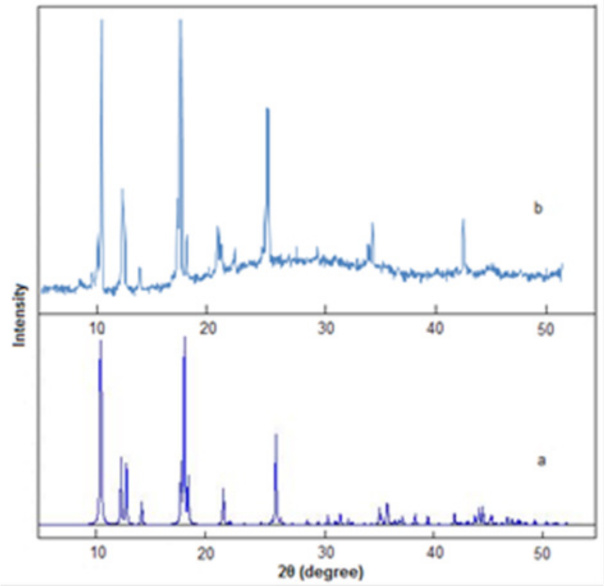


Figure 1: *(a): XRD patterns for the simulated, and (b): as synthesized Cu(tpa).(dmf) MOF.*

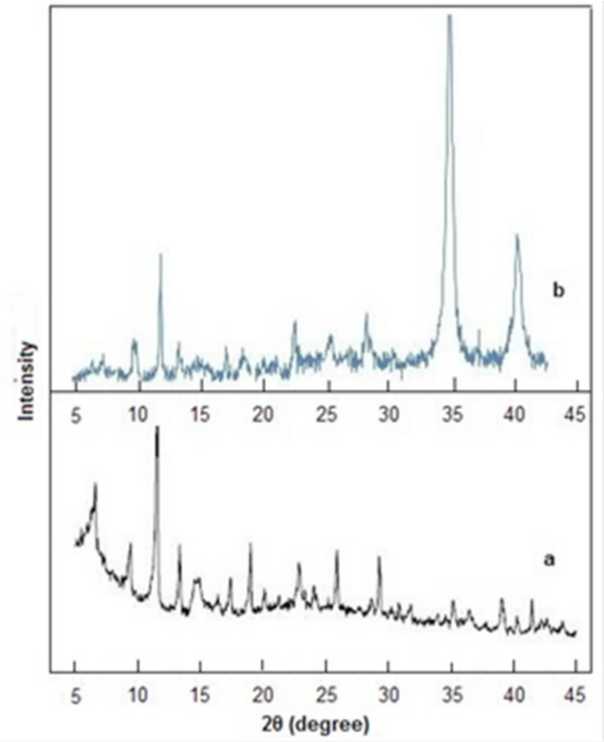


Figure 2: *X-Ray powder diffractograms recorded for Cu-BTC; (a): repoeted sample; (b): as-synthesized sample.*

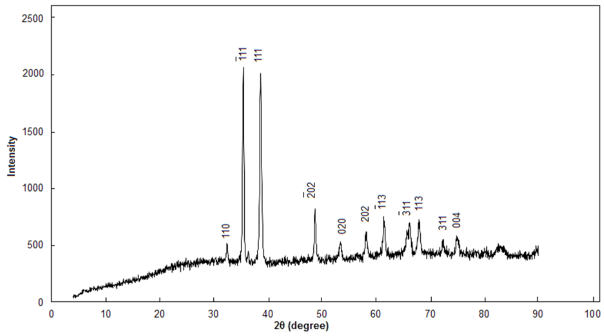


Figure 3: *X-ray diffraction patterns of the CuO nanoparticles with tenorite structure (JCPDS no. 41-0254) by thermolysis of Cu(tpa)(dmf) MOF.*

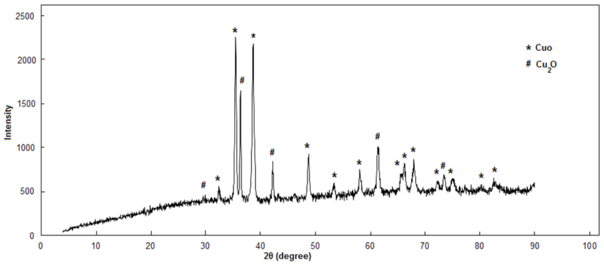
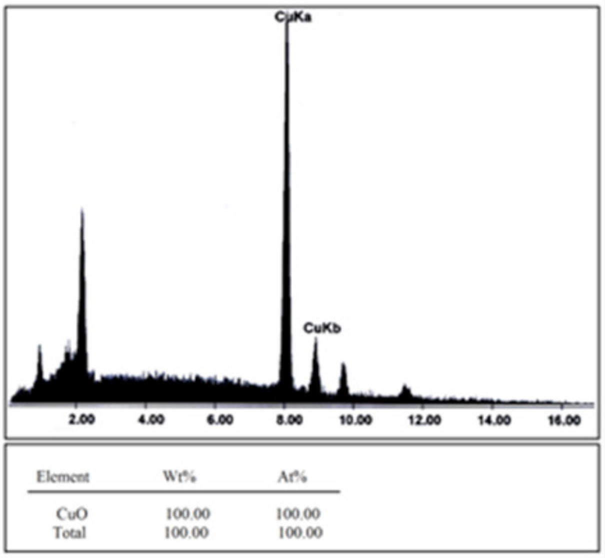


Figure 4: *XRD pattern of as-prepared copper oxide nanoparticles after calcination of* $Cu_3(BTC)_2$*.*



Element	Wt%	At%
CuO	100.00	100.00
Total	100.00	100.00

Figure 5: *EDX analysis of as synthesized products by direct calcination of Cu(tpa)(dmf) at 400 ˚C.*

2.4. Preparation of Copper oxide Nano-Structures

The synthesis reported here, were carried out through solid-state thermolysis in the furnace under air atmosphere. In a typical synthesis, the precursors **1** and **2** were placed in a ceramic boat and calcinated in the furnace at 500 ˚C for 4 h under air atmosphere. After cooling at room temperature, black products were collected. Thermolysis of precursor **1** at other temperatures (400 and 600˚C) followed the above process.

3. RESULTS AND DISCUSSION

Analysis of the resulting materials by X-ray powder diffraction (XRPD) revealed that the solids were pure and compatible with the simulated pattern of solvothermally synthesized MOF crystals structures [17-18], there upon stabilizing the successful synthesis of MOFs (Figures 1 and 2). The structures of the precursors **1** and **2** decomposed to crystalline copper oxide during the heating process under air atmosphere are shown in Figures 3 and 4. For precursor **1**, the peaks appeared in thermolysis at 500˚C correspond to CuO (tenorite; space group C2/c, cell parameters: a = 4.685 Å, b = 3.423 Å, c = 5.132, β = 99.52, JCPDS No. 41-0254) nano-structures and trace amount of Cu_2O.
Moreover, EDX spectrum confirmed formation of CuO nanoparticles from thermolysis at 400˚C (Figure 5). Also, a mixture of CuO and Cu_2O (cuprite; S.G.: Pn3m; with lattice constant a = 4.269; JCPDS file no. 05-0667) resulted for **2,** in major phase. The morphology and size of the as-prepared copper oxide samples were further investigated using scanning electron microscopy (SEM) as shown in Figure 6 and 7. The crystallite size of product resulted from thermolysis of **1** was estimated to be 87, 52 and 175 nm at 400, 500 and 600˚C respectively, and 90 nm for **2** at 500˚C. Particle size histograms can be found in Figure 8 and 9.

4. CONCLUSION

In this study, new simple method was introduced for synthesis of nano-structured copper oxide.

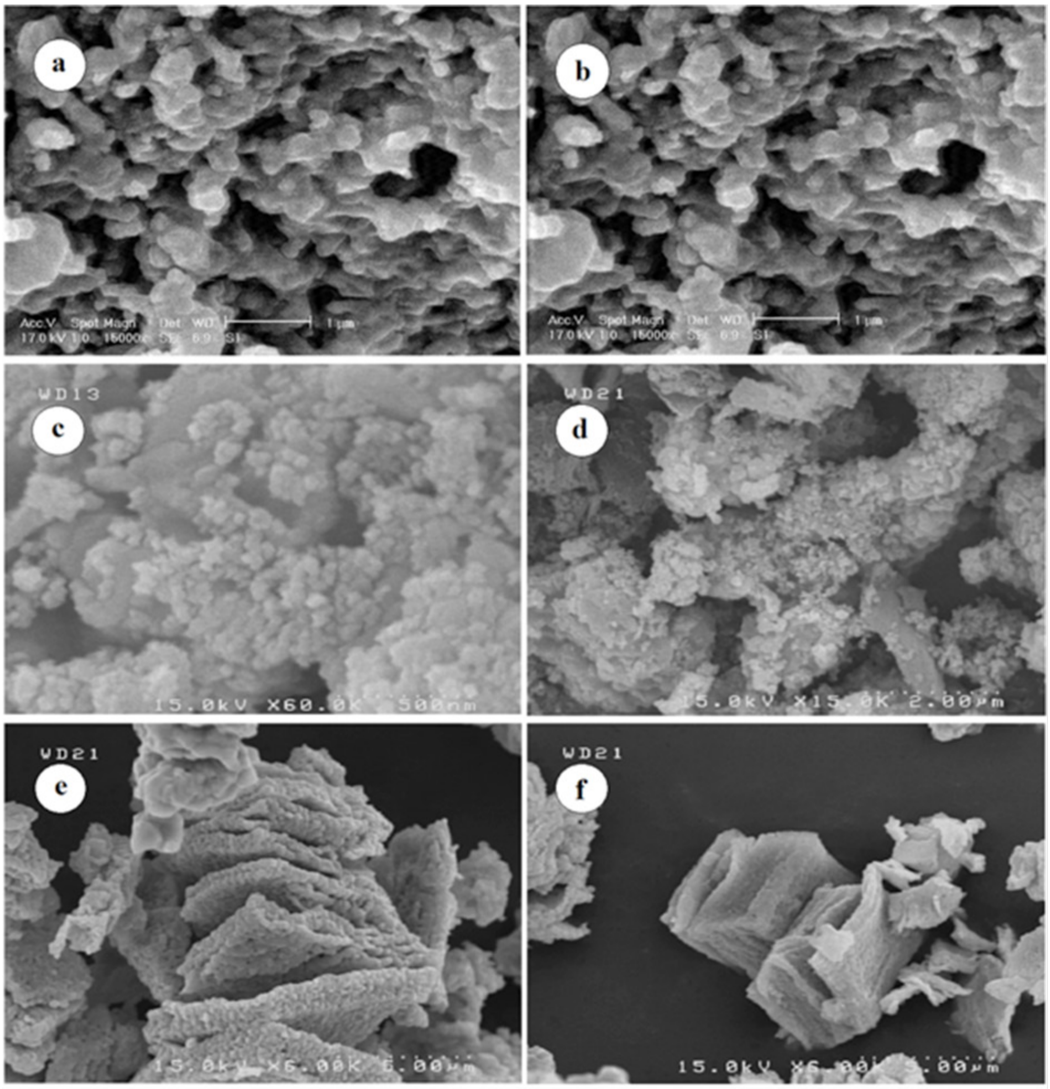


Figure 6: *SEM photographs of CuO nanostructure produced by calcination of compound Cu(tpa)(dmf); (a-b) at 400, (c-d) 500, and (e-f) 600 ˚C, respectively.*

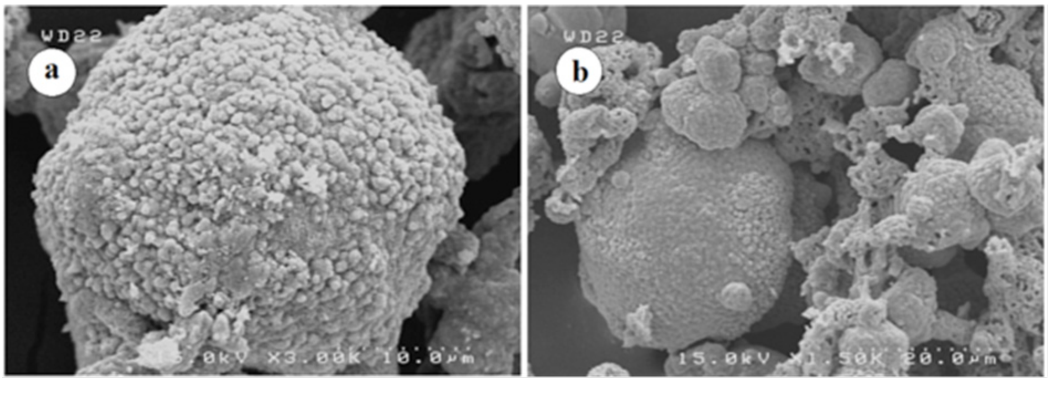


Figure 7: *SEM photographs of copper oxide nanostructure produced by calcination of compound* $Cu_3(BTC)_2$ *at 500 ˚C.*

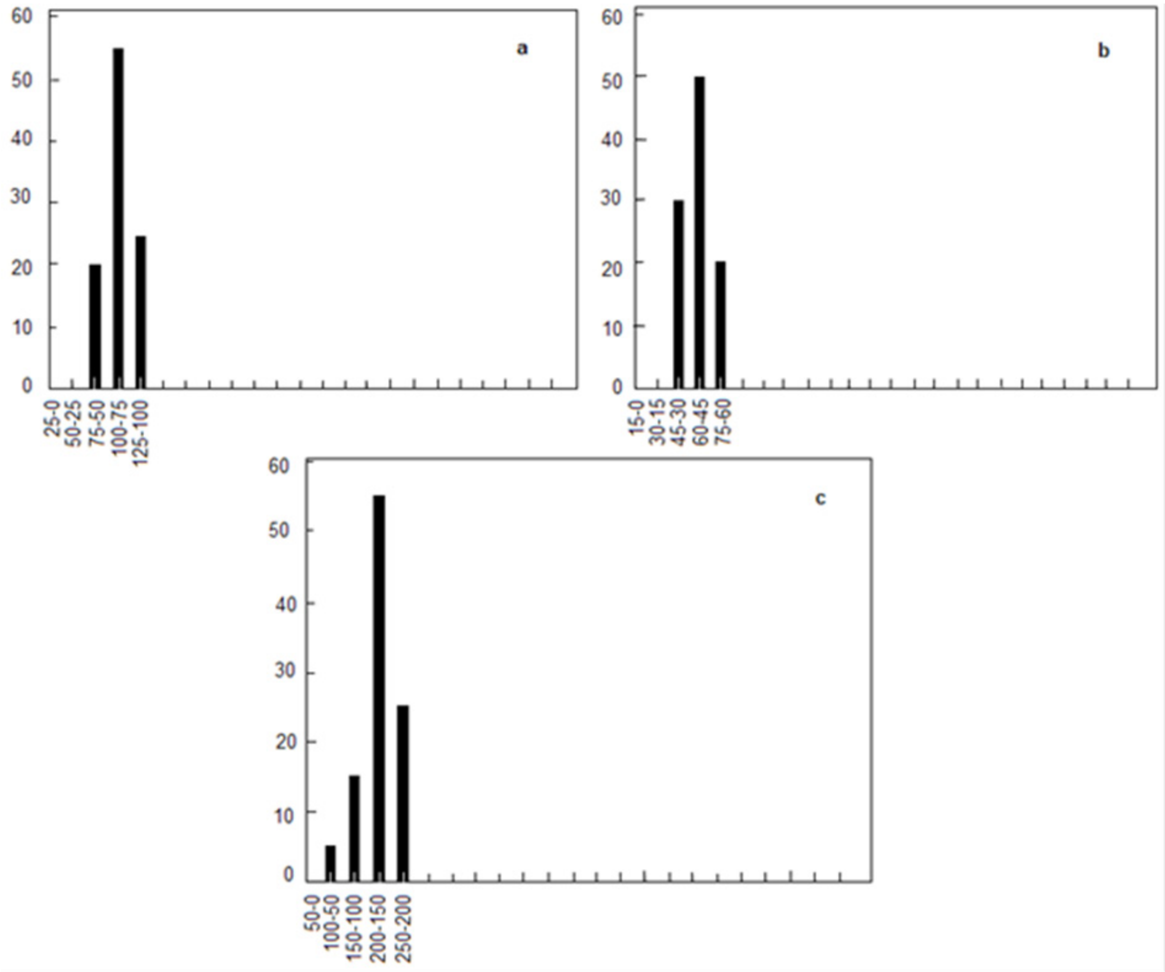


Figure 8: *Particle size histograms of Cu(tpa)(dmf) at (a) 400, (b) 500, and (c) 600 ˚C, respectively.*

Two metal-organic framework precursors were transformated to copper oxide nanoparticles through solid-state thermolysis under air atmosphere. Thermolysis temperature has a great consequence on the size and morphology of the final products and consequently would change them with variation from 400 to 600˚C. The resulting material was characterized by means of XRPD, SEM and EDX. Thus, the thermolysis process of metal-organic frameworks is a facile and promising technique for preparing metal oxide nanoparticles.

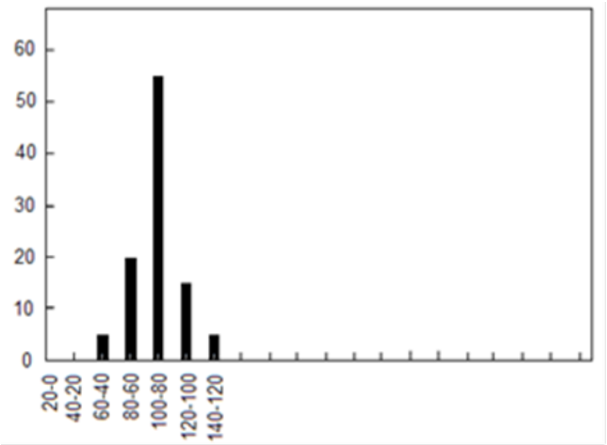


Figure 9: *particle size histogram of $Cu_3(BTC)_2$ at 500 ˚C that estimated 90 nm.*

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