Ultrasonics Sonochemistry 22 (2015) 349–358

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

# Ultrasound and modulation assisted synthesis of {[$Cu_2$(BDC-$NH_2$)$_2$(dabco)]DMF.3$H_2O$} nanostructures; New precursor to prepare nanorods and nanotubes of copper(II) oxide

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ARTICLE INFO

*Article history:*
Received 5 March 2014
Received in revised form 27 April 2014
Accepted 27 April 2014
Available online 9 May 2014

*Keywords:*
Ultrasound
MOF
Modulator
CuO nanotubes and nanorods

ABSTRACT

Nanostructures of *porous coordination polymer* {[$Cu_2$(BDC-$NH_2$)$_2$(dabco)]DMF.3$H_2O$} (**1**) have been synthesized in the presence of acetic acid as a modulator *via* sonochemical method. Different concentrations of metal ions, organic linkers, modulator reagent and also different sonication times were held to improve the quality and distribution of nanostructures. Ultrasound irradiation helps to nucleation step of the oriented attachment of modulation method and nanorods of compound **1** has been prepared. Compound **1** was calcinated at 500 °C to prepare nanorods and nanotubes of copper(II) oxide. Compound **1** and CuO nanostructures were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HR-TEM), X-ray powder diffraction (XRD) and thermal gravimetric analysis (TGA).



## 1. Introduction

Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) can be made from an assembly of organic linkers with metal ions [1–6]. Their porosity and tunable chemical functionality make them applicable in gas storage [7,8], catalysis [9] and separation [10]. Reducing the size of MOFs to nanoscale have been extremely attractive. Recently Kitagawa and coworkers [11] and Zhang and co-workers [12] reported synthesis of MOFs in nanoscale by using the modulator or capping reagents. By the way because of our previous experience [13–17] on using ultrasound irradiation to synthesis of metal oxides, hydroxides and carbonates, it was interesting to coupling the ultrasonic with modulation method to preparation of nano or microstructures of MOFs. Sonochemistry is the research area in which molecules undergo a chemical reaction due to the application of powerful ultrasound radiation (20 kHz–10 MHz) [18]. In recent years many kinds of nanomaterial and nano coordination polymers have been prepared by this method [19–23].

By using acetic acid as a modulator reagent, 1D nanorods of *[Cu(ndc)(dabco)$_{0.5}$]* were prepared by Kitagawa and coworkers [11], where *ndc = 1,4-naphthalene dicarboxylate* and *dabco = 1,4-diazabicyclo[2.2.2]octane*. So to investigate the role of ultrasound irradiation in the presence of modulator on growth mechanism, in this work the preparation of porous coordination polymer, *{[$Cu_2$(BDC-$NH_2$)$_2$(dabco)]DMF.3$H_2O$}* (**1**), nanostructures (where BDC-$NH_2$ = *amino benzene-1,4-dicarboxylate*) is investigated by sonochemical method in the presence of modulator. As prepared *{[$Cu_2$(BDC-$NH_2$)$_2$(dabco)]DMF.3$H_2O$}* (**1**) was calcinated at 500 °C to prepare CuO nano and microstructures. Influence of ultrasound irradiation and modulator reagent on precursor diameter has been affected on CuO nanoparticles dimension and distribution.

In recent years, copper(II) oxide (*CuO*), a p-type semiconductor with a narrow band gap of 1.2 eV, has been studied intensely for its various applications some of which are in catalysis [24], batteries [25], gas sensors [26], biosensors [27], magnetic storage media [28], electronics [29], capacitors [30] and field transistors [31]. In addition, our search in the case of fabrication nanomaterials from metal–organic frameworks, as new precursors, indicates that other nanomaterials such as Cu nanoparticles from the [$Cu_3$(btc)$_2$] (btc = benzene-1,3,5-tricarboxylate) MOF [32], ZnO nanoparticles from $Zn_4O$(1,4-bdc)$_3$ (MOF-5) [33], 1D nano ZnO materials from [ZnF(AmTAZ)]·solvents (AmTAZ = 3-amino-1,2,4-triazole) [34], ZnO nanomaterials from the [$Zn_2$(1,4-bdc)$_2$(dabco)] [35] and PdO nanoparticles from a $Pd^{II}$ MOF, based on tetra-pyridyl porphyrin [36] were prepared.

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http://dx.doi.org/10.1016/j.ultsonch.2014.04.017
1350-4177/

Our searches show that there is no report on synthesis of the MOF nanostructures by coupling of ultrasound and modulation methods. So, this is the first report for synthesis of nanosized *{[$Cu_2$(BDC-$NH_2$)$_2$(dabco)]DMF.3$H_2O$}* (**1**) by coupling of the sonochemical and the modulation methods and there is no report on synthesis of CuO nanostructures from compound **1** as a precursor.

## 2. Experimental

To prepare *{[$Cu_2$(BDC-$NH_2$)$_2$(dabco)]DMF.3$H_2O$}* (**1**) nanopowders, *Cu(OAc)$_2$.$H_2O$*, *aminobenzene-1,4-dicarboxylic acid* and *dabco* with molar ratio of 2:2:1 were added to the one-necked flask that contain DMF as solvent and treated by ultrasound irradiation in ultrasonic bath and yield of nanopowders is 62–86% (Table 1). The obtained green powders filtered through a 0.2 mm membrane filter, washed with DMF several times, and dried using a vacuum pump. To prepare guest free MOFs (*apohost*), obtained powder (*host*) was heated at 150 °C for 15 h. Anal. calc. For *{[$Cu_2$(BDC-$NH_2$)$_2$(dabco)]} (host)*: C, 42.87; H, 5.01; N, 10.7; found; C, 43.84; H, 4.18; N, 9.96%. As it has been seen in Table 1 for two samples acetic acid was used as a modulator reagent to growth nanorods. Ultrasonic generator were carried out on a *SONICA-2200 EP*, input: 50–60 Hz/305W. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer of *Philips Company* with monochromated *Cukα* radiation ($\lambda$ = 0.15405 nm). The samples were characterized with a scanning electron microscope (SEM) (*LEO 1450VP*) with gold coating and also a transmission electron microscope (TEM) (*LEO 912AB*) at an accelerating voltage of 120 kV TEM. High resolution TEM (HR-TEM) images of CuO were taken using a *FEI Tecnai G2 F20* microscope at 200 kV. FTIR spectra were recorded using *Perkin-Elmer 597* and *Nicolet 510P* spectrophotometer. The thermal behavior was measured with *NETZSCH STA*

**Table 1**
Experimental condition to prepare *{[$Cu_2$(BDC-$NH_2$)$_2$(dabco)]DMF.3$H_2O$}* nanostructures.

| Sample | *Cu(OAc)$_2$.$H_2O$* (mmol) | *BDC-$NH_2$* (mmol) | *Dabco* (mmol) | DMF (ml) | $CH_3COOH$ | Sonication time | Yield (%) |
|---|---|---|---|---|---|---|---|
| 1 | 0.9 | 0.9 | 0.45 | 40 | – | 60 | 83 |
| 2 | 0.6 | 0.6 | 0.3 | 40 | – | 60 | 73 |
| 3 | 0.3 | 0.3 | 0.15 | 40 | – | 60 | 76 |
| 4 | 0.3 | 0.3 | 0.15 | 40 | – | 90 | 69 |
| 5 | 0.3 | 0.3 | 0.15 | 40 | – | 120 | 62 |
| 6 | 0.3 | 0.3 | 0.15 | 40 | – | 30 | 62 |
| 7 | 0.3 | 0.3 | 0.15 | 30 | 10 ml (0.3 M) | 60 | 66 |
| 8 | 0.3 | 0.3 | 0.15 | 30 | 10 ml (0.5 M) | 60 | 75 |
| 9 | 0.3 | 0.3 | 0.15 | 30 | 10 ml (0.3 M) | – | 86 |
| 10 | 0.3 | 0.3 | 0.15 | 40 | – | – | 78 |

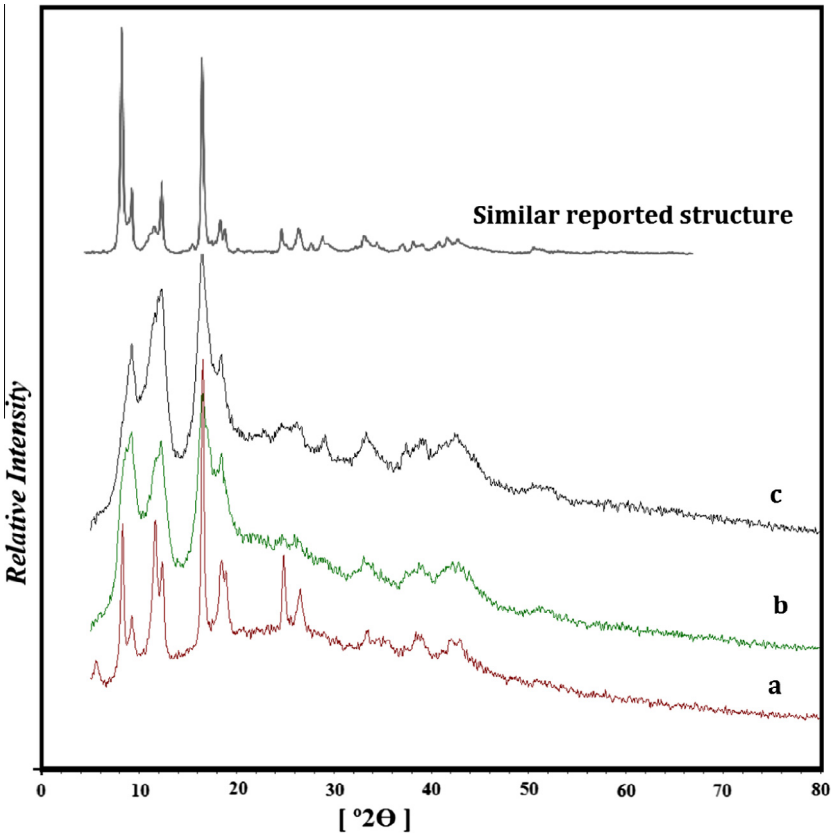


**Fig. 1.** XRD patterns of guest removed samples (apohost) (a) No. 3, (b) No. 6, (c) No. 7 and similar reported structure.