Metal-Organic Frameworks as Precursor for Metal Oxide Nanostructures Part I: MOF-Derived Copper Oxide Embedded in Carbon Matrix

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A R T I C L E   I N F O

A B S T R A C T

Three isostructural metal-organic framework materials (MOFs) formulated as M[(HBTC)(H$_2$O)]·H$_2$O(M = Cu for **1**, Zn for **2** and Ca for **3**) constructed with 1, 3, 5-benzenetricarboxylate (BTC) were synthesized under hydro/solvothermal conditions. The three compounds were characterized on the basis of infrared and UV-Vis spectroscopy and the structure of **3** elucidated with the help of single-crystal x-ray crystallography. The UV-Vis spectrum of **1** exhibited a unique band at 511 nm. In the region 520 – 534 nm, the band splits into two moderately intense peaks at 527 and 531 nm. These absorption peaks along with other bands at 629 and 638 nm were assigned to d-d transitions of the copper (II) ion with distorted square planar geometry. The infrared spectra of the three compounds revealed that the ligand, BTC anion coordinated in a chelating and / or bridging mode to the metal center. The presence of absorption bands at 1699 cm^{-1} in **1** and **2**, (1681 cm^{-1} in **3**) can be attributed to protonated HBTC for **1-3**. Single-crystal X-ray crystallographic studies of compound 3 revealed well-ordered structure with BTC ligand linking the individual chains to form a network structure. On heating Cu(HBTC)(H$_2$O)·H$_2$O up to 400°C, a copper-oxide embedded in carbon matrix was obtained with uniform particles of 10 -100 nm size.

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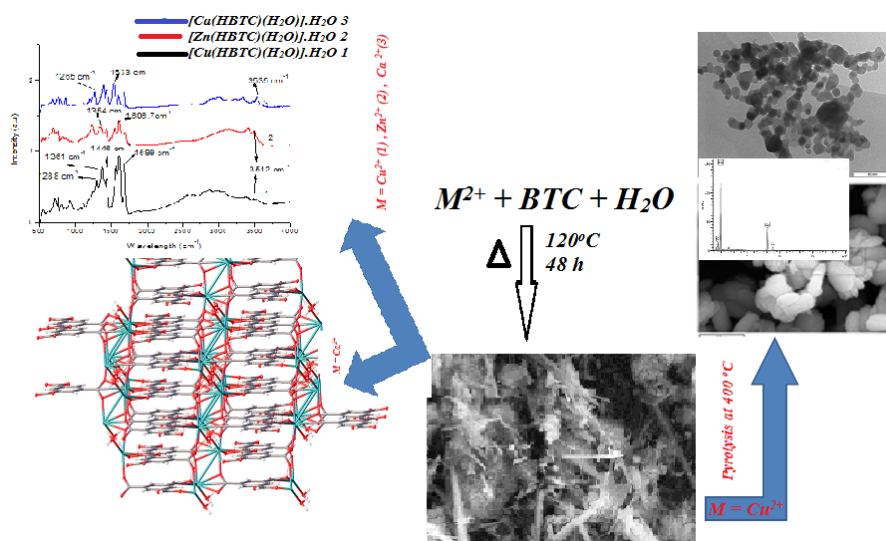
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Introduction

Nanotechnology involves the study of the synthesis, characterization, and properties of nanomaterials [1]. The emergence of nanotechnology has led to innovations in many areas of electronics, energy management, structural materials, functional surfaces, construction, information technology, pharmaceuticals, and medical devices. The largest share of the manufacturing and application market among the different nanomaterials belongs to metal oxide nanomaterials, they are already used in some consumer products, such as TiO_2 in paints and ZnO in sunscreen products [2]. Metal oxides play a very important role in many areas of chemistry, physics and materials science [3-6]. The metal elements are able to form a large diversity of oxide compounds. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysts. In the emerging field of nanotechnology, the goal is to make nanostructures or Nano-arrays with special properties with respect to those of bulk or single particle species [7-9]. Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites.

The first requirement of any novel study of nanostructured oxides is the synthesis of the material. Different synthetic protocols which have been developed in the synthesis of nanostructured metal oxides include amongst others co-precipitation, sol-gel and micro-emulsion techniques, solvo/hydrothermal as well as using MOFs as a precursor and/or template to prepare metal or metal oxide nanoparticles inside carbon framework [10, 11].

In spite of the extensive research work on the preparation of metal or metal oxides nanostructures, aggregation of the particles is still a major challenge. In order to resolve the aggregation issue, a new strategy has been developed in which these nanoparticles are dispersed into carbon matrices such as porous carbon, carbon nanotubes and graphenes [12]. The carbon matrices, in addition to preventing aggregation of the nanoparticles, can also modify their properties [13].

In the design of metal–organic frameworks, versatile carboxylate ligands, such as 1,4-benzenedicarboxylic acid, 1,3,5-benzenetri-carboxylic acid, 1,2,4,5-benzenetetracar-boxylic acid or pyridine-2,4-dicarboxylic

acid, are usually employed under hydrothermal and/or solvo thermal conditions owing to their abundant carboxylate groups, with high affinity to metal cations [14, 15]. Metal-organic framework materials (MOFs) have been known for their applications in the area of gas storage and separation owing to their large surface area [16, 17]. In addition, MOFs have also been used in recent times, as a precursor for metal/metal oxide nanoparticle-embedded carbon frameworks [18-22, 28]. The subject has become of particular interest for functional applications such as catalysis, gas storage materials, anode materials for lithium-ion batteries, etc. After the report on the carbonization of MOF-5, various methods have been reported to synthesize materials that contain metal/metal oxide nanoparticle-embedded porous carbon matrix from MOF precursors. In this work, Ca-, Zn- and Cu-carboxalye-framework solids have been prepared and characterized. The Cu-carboxylate framework was then heated under air to convert it to copper oxide nanostructures embedded in the carbon matrix. Herein, we report the copper oxide nanoparticles derived from copper carboxylate-frameworks.

Experimental

Materials

The syntheses were carried out in Ace pressure tubes (15 cm^3), purchased from Aldrich Chemical Co., and heated in programmable ovens. The reagents used for syntheses: 1, 3, 5-benzenetricarboxylic acid, 4, 4-bipyridine (Bipy), Cu $(NO_3)_2 \cdot 2.5H_2O$, [Zn $(OOCCH_3)_2 \odot \odot \cdot 2H_2O$] and $CaCl_2 \cdot 2H_2O$ were obtained from Aldrich and used without further purification. The common laboratory apparatus used were chemical balance, magnetic stirrer, pipettes of different dimensions, filter papers, beakers and petri dishes.

Methods

Synthesis of MOFs

The hydro/solvothermal method was used for the synthesis of the compounds. In a typical synthesis, Cu $(NO_3)_2 \cdot 2.5H_2O$ (0.236 g, 1.0 mmol) was stirred together with benzene tricarboxylic acid (BTC) (0.210g, 1.0 mmol) in 10 cm^3 of distilled water. This was followed by the addition of 0.030 g of 4, 4-bipyridine and the pH of the solution was adjusted to 6.0 by the addition of 4.0 cm^3 of 0.5 M NaOH. The resulting mixture was homogenized for 30 min at room temperature before being transferred into a reaction vessel and heated at 120 ^{o}C for 48 h. The bluish green crystalline product was filtered under vacuum, washed with distilled water and air dried. Similar

procedure was used for compounds **2** (Zn (OOCCH$_3$)$_2$·2H$_2$O:0.238 g, 1.0 mmol) and **3** (CaCl$_2$·2H$_2$O:0.221 g, 1.0 mmol). The products were characterized with the help of infrared and UV-Vis spectroscopic techniques. Compound 1 was further characterized using SEM and TEM while the structure of compound **3** was determined using single-crystal X-ray crystallography.

Conversion of [Cu (HBTC) (H$_2$O)].H$_2$O to CuO nanoparticles

The copper-oxide nanostructures embedded in carbon matrix was carried out by direct calcination of the synthesized CuMOFs as precursor. In a typical process, [Cu (BTC) Bipy] (0.147 g) was taken into crucible and heated in a tube furnace from room temperature to 400 °C under air to carbonize the MOF. The products were cooled to room temperature and were further characterized by SEM / EDAX and TEM.

Characterization

Electronic absorption spectra were recorded at ambient temperature on a "Thermo Scientific Evolution 201 UV-Vis spectrophotometer. A portion (1 cm^3) of methanolic solution of the compounds (0.1 g of solid dissolved in 5 cm^3 of methanol) was taken out and dispersed in 5 cm^3 of distilled water for the UV-Vis measurement. The Infrared spectra were recorded on a

Shimadzu IR affinity-1 from 400– 4000 cm^{-1}. The surface morphology of the as synthesized compound **1** and the derived copper oxide nanoparticles embedded in carbon matrix were determined using a Hitachi S-4800 microscope at a voltage of 15 kV. The elemental composition of the CuO was determined with the help of energy dispersive analysis by x-ray attached to the scanning electron microscope. Transmission electron microscopy (TEM) measurements were performed on a JEOL 1010 instruments at 200 kV.

Results and Discussion

In the synthesis of MOFs, 1, 3, 5-benzenetricarboxilic acid (BTC) has been used as an organic linker with different metal ions. For instance, Copper (II) ions in combination with BTC form several different materials depending on the protonation state of the incorporated linker [29, 30]. One of the major challenges within the field of MOFs is the control of dimensionality [31-35]. When polyfunctional ligands are employed low dimensionality will be formed due to ancillary ligation of the water or other solvent molecules [36]. For example, in the reaction between Cu^{2+} and BTC one dimensional chain polymers [Cu(BTC-H)(H$_2$O)$_3$]n or [Na Cu(BTC)(H$_2$O)$_5$] are formed from alcoholic solutions at room

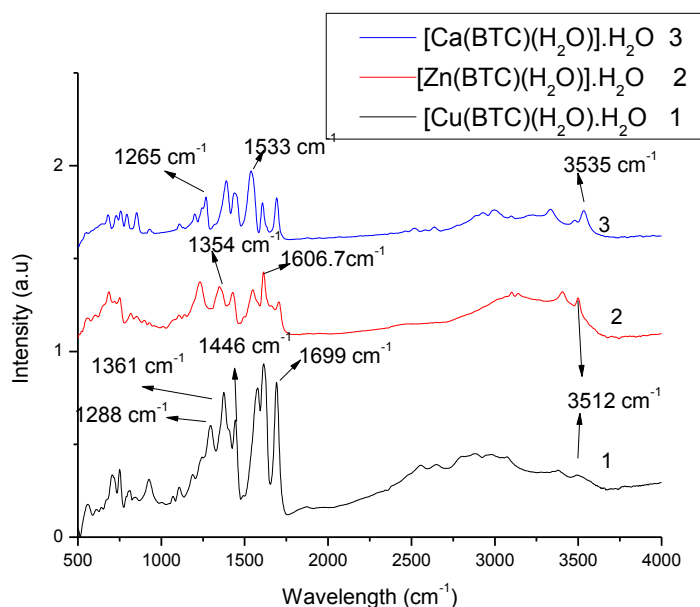temperature (RT). The same reaction in ethanol resulted in producing 3D HKUST-1 at higher temperatures [37].

When it comes to STAM-1 the same conditions made a 2D solid with the only difference being the choice of alcohol, from ethanol to methanol. Since the original synthesis of HKUST-1, there have been many variants on the preparative procedure and it is clear that the facile synthesis of HKUST-1 is one of its advantages. Mohideen [38], was able to isolate a new MOF with unique properties by small modification to the synthesis procedure   of HKUST-1. The common solvent used for the preparation of HKUST-1 is 50:50 ethanol: water. However, changing the solvent to a 50:50 methanol:

water mix resulted in the formation of a new material with the composition Cu ($C_{10}H_6O_6$) (H_2O).1.66 H_2O, and named as STAM-1 (St Andrews MOF-1). In this study, BTC was used as an organic linker to complex with three different metal ions namely: Cu^{2+}, Zn^{2+} and Ca^{2+}. In a typical synthesis of **1**, the molar composition: Cu (NO_3)$_2$: BTC: 4, 4-Bipy: NaOH: H_2O was utilized. In the case of compounds **2** and **3**, the compositions were ZnOAc: BTC: 4, 4-Bipy: H_2O and $CaCl_2$ .H_2O: BTC: NaOH: 2, 2-dipyridyl: H_2O: n-Butanol, respectively. It is worthy of note that the 4, 4-Bipy and 2, 2-dipyridyl were not incorporated in the final products formed, but assisted the formation of crystals.

Table 1. Infrared vibrational frequencies of the as-synthesized compounds **1-3** (cm^{-1})

	$\nu_{(O-H)}$	$\nu_{sym}(C-H)$	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	Δ $\nu_{asym}(CO_2) - \nu_{sym}(CO_2)$ / Bonding mode	δ(C-H) In-plane	δ(C-H) Out-of-plane	$\nu_{(M-O)}$
1	3512	3080	1699	1446	253 Bridging	1186	923	555
		2889	1606	1361	245 Bridging	1094	705	
			1573	1288	285 Unidentate			474
2	3512	3109	1699	1425	274 Unidentate	1136	893	597
		3097	1606	1354	252 Bridging	1099	682	
			1544	1244	300 Unidentate			478
3	3535	3064	1681	1435	246 Bridging	1199	927	472
		2980	1606	1386	220 Chelating	1112	678	
			1533	1265	268 Unidentate			435

Figure 1. Infrared spectra of as-synthesized compounds M [(HBTC) (H₂O)] ·H₂O
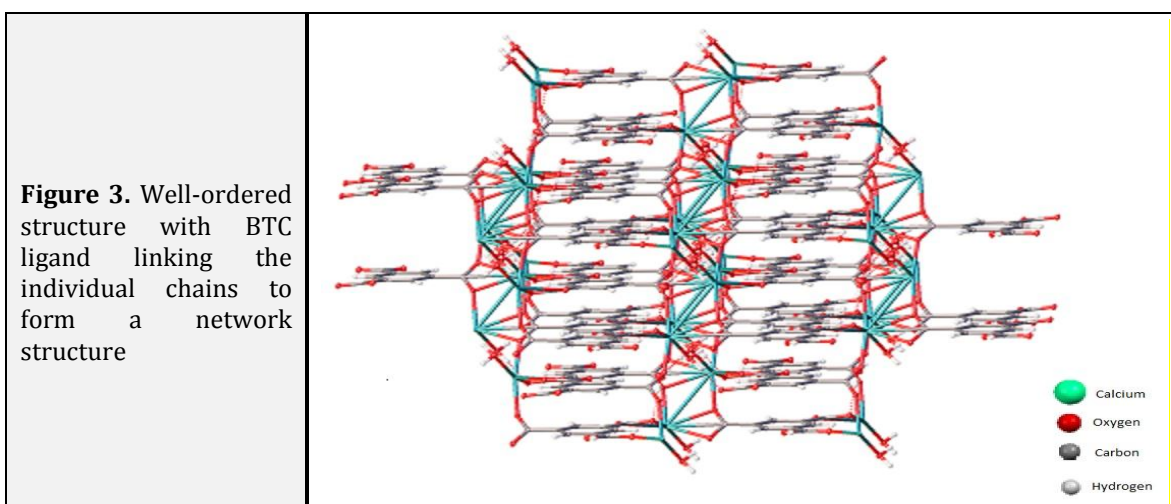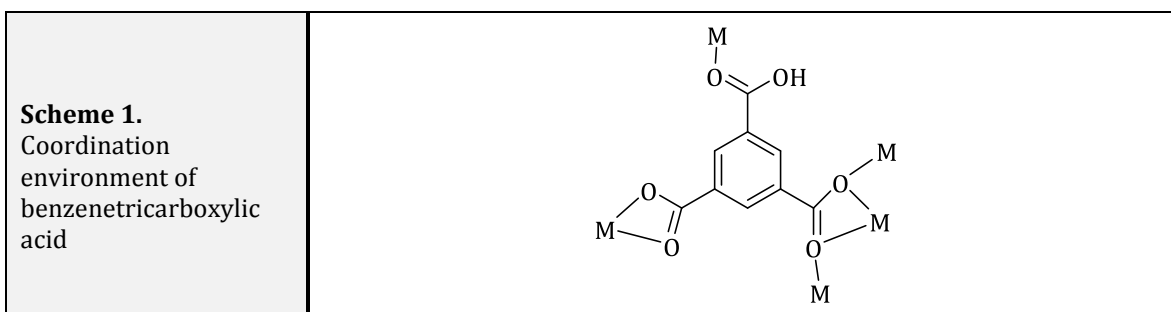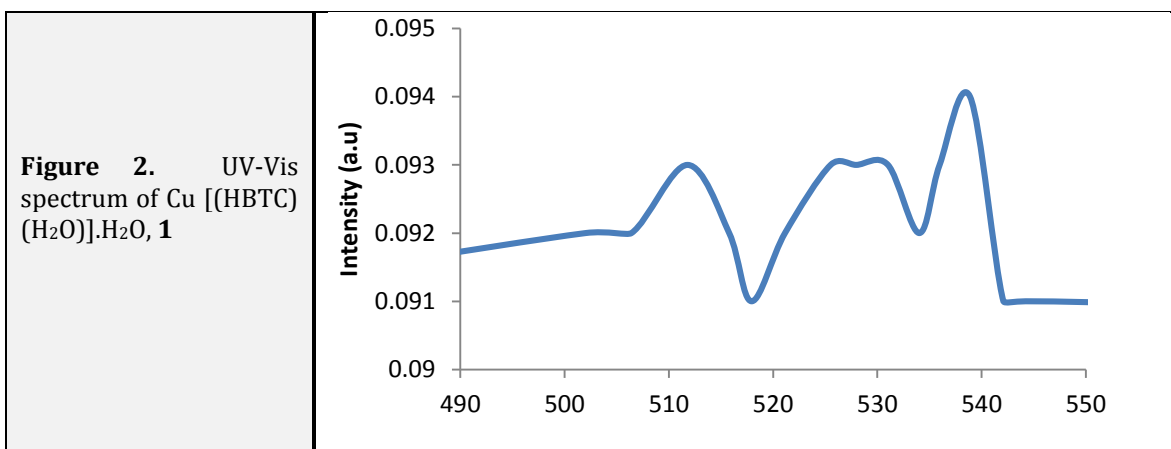
The infrared vibrational frequencies of the three compounds are shown in Table 1, while their FTIR spectra are presented in Figure 1. The bands for the carboxylate ligand at 1699-1573 (1), 1699-1544 (2) and 1681-1533 cm⁻¹ (3) for asymmetric vibrations and 1446–1288 (1), 1425-1244 (2) and 1435-1265 cm⁻¹ (3) for the symmetric vibrations having separation $\Delta[\nu_{asym}(CO_2^-) - \nu_{sym}(CO_2^-)]$ values of 245-285 cm⁻¹ (1), 252-300 cm⁻¹ (2) and 220-268 cm⁻¹ (3) are higher compared to the free carboxylate group and is a good indication that the carboxylate is coordinated with metal atom in a unidentate, chelating and/or bridging fashion [39]. The bands at 1288, 1244 and 1265 cm⁻¹ for compounds 1, 2 and 3, respectively, are assigned to symmetric stretching unidentate O-C-O vibrations. The presence of absorption bands at 1699 cm⁻¹ in 1 and 2, (1681 cm⁻¹ in 3) can be attributed to -COOH of the tricarboxylates. The bands at 3080-2889 cm⁻¹ in 1, 3109-3097 cm⁻¹ in 2 and 3064-2980 cm⁻¹ in 3 are due to C-H stretch of the benzene ring. The *in-plane* C-H bending vibrations of the 1, 3, 5-trisubstituted benzene ring are observed at 1186-1094 cm⁻¹ in 1, 1136-1099 cm⁻¹ in 2 and 1199-1112 cm⁻¹ in 3, while the *out-of-plane* C-H bending vibrations appeared in the region 923-705 cm⁻¹, 893-682 cm-1 and 927-678 cm⁻¹ for compounds 1, 2 and 3, respectively. Bands in the region 555-474 cm⁻¹ in 1, 597- 478 cm⁻¹ in 2 and 472- 435 cm⁻¹ in 3 are due to M-O vibrations. The bands at 3477, 3495 and 3523 cm⁻¹ for 1, 2 and 3, respectively, are attributable to O–H stretching vibrations.

The electronic spectrum of [Cu (HBTC) (H$_2$O)].H$_2$O **1**, in methanol solution presented in Figure 2, exhibits a unique band at 511 nm. In the region 520 – 534 nm, the band splits into two moderately intense peaks at 527 and 531 nm. These absorption peaks along with another band at 538 nm are assigned to d-d transitions of the copper (II) ion. This type of d-d spectrum is typical of a distorted square planar arrangement around the copper (II) ion [40, 41].
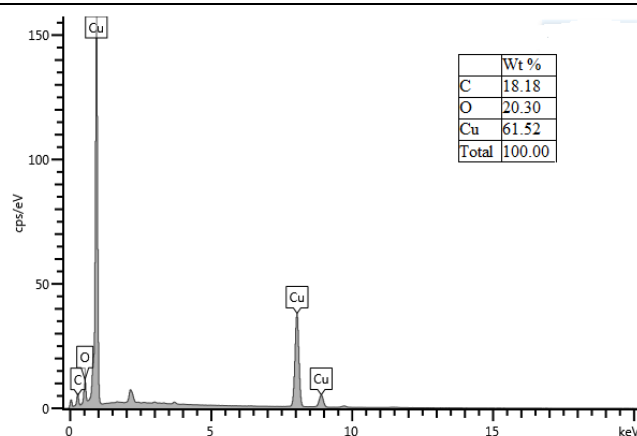

Figure 2. UV-Vis spectrum of Cu [(HBTC) (H$_2$O)].H$_2$O, **1**

Scheme 1. Coordination environment of benzenetricarboxylic acid

Figure 3. Well-ordered structure with BTC ligand linking the individual chains to form a network structure

Single-crystal x-ray crystallographic studies of [Ca(HBTC)(H$_2$O)]·H$_2$O, **3,** revealed that it crystallizes in a triclinic crystal system with the following cell dimensions: a= 6.8325(13) b=8.9345(17), c=9.9752(19) Å, α= 102.119(2), β=100.791(2), γ=109.701(2) ^{o}. The asymmetric unit consists of one crystallographically independent calcium (II) ion, a BTC^{2-} anion, aqua ligand and lattice water. Calcium is coordinated to seven carboxylate oxygen atoms from one BTC ligand and one oxygen from aqua ligand to form a CaO$_8$ polyhedra. The BTC ligand is heptadentate coordinating to Ca atom *via* O1 and O2 in a chelating and bidentate bridging fashion, through O3 and O4 in a chelating mode and through O5 in a unidentate mode (Scheme 1). The edge-sharing of CaO$_8$ polyhedra along *a*-direction gives rise to inorganic chain that are connected by the BTC ligands to form a three dimensional framework with water molecules in the channels (Figure 3). The Ca-O bond distances are in the range of 2.4030 (3) -

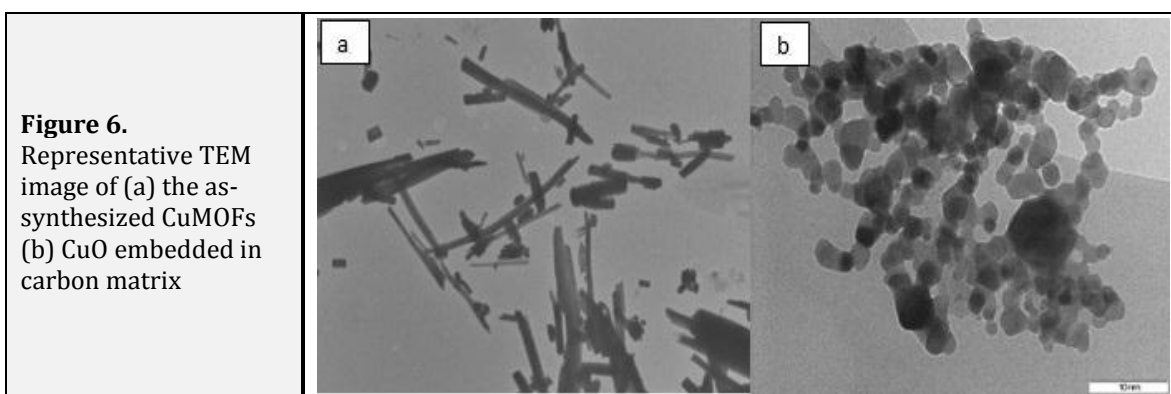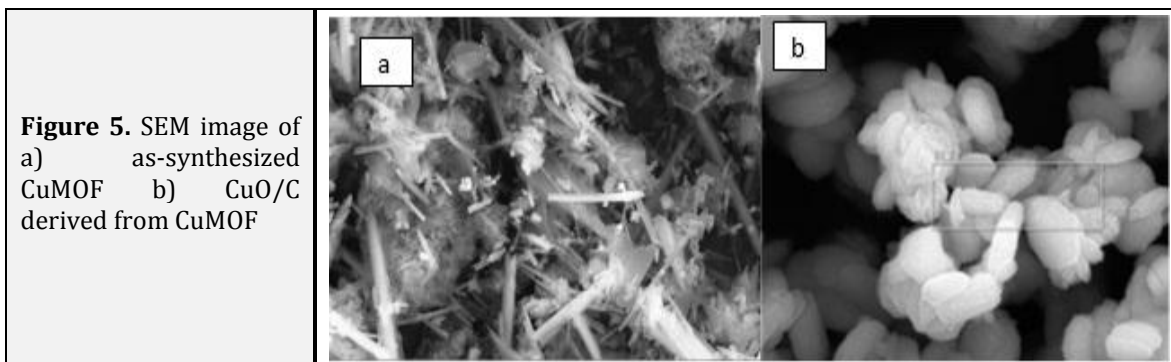2.5655(4) Å and are consistent with similar compounds in the literature [38, 39, 41].

The copper-based MOF, compound 1, was converted into copper oxide nanostructures embedded in carbon matrix by heating to a temperature of 400 °C in air. The energy dispersive analysis of the calcined product (Figure 4) gives the composition of copper, oxygen and carbon as 61.52, 20.30 and 18.18%, respectively.

The representative SEM image of the CuMOFs and CuO nanostructures are presented in Figure 5. The image of copper-based MOFs shows the presence of rod-like crystals whereas the copper oxide derived from the MOFs consists of microspheres with average size of 2.5 μm, The TEM images of the as-synthesized MOF and the CuO Nano are presented in Figure 6. The TEM image of the as-synthesized CuMOFs reveals the presence of Nano-rod crystals, while the image of the derived copper oxide shows uniform Nano spheres of 10 -100 nm size.

Figure 4. EDX spectrum of CuO embedded in the carbon matrix

	Wt %
C	18.18
O	20.30
Cu	61.52
Total	100.00

Figure 5. SEM image of a) as-synthesized CuMOF b) CuO/C derived from CuMOF

Figure 6. Representative TEM image of (a) the as-synthesized CuMOFs (b) CuO embedded in carbon matrix

Conclusion

Three metal-organic framework materials: M [(HBTC) (H$_2$O)] ·H$_2$O (M = Cu, Zn and Ca) constructed with 1, 3, 5-benzene tricarboxylate have been synthesized under hydro/solvothermal conditions and characterized using spectroscopic techniques and x-ray diffraction method. Using Cu-MOF as a precursor material, copper oxide nanoparticle embedded in carbon matrix has been synthesized by simply heating in air to 400 °C. The SEM, TEM, and EDS measurements confirmed that copper oxide nanoparticles have been formed in the carbon matrix. Research is underway on the properties and applications of the MOF-derived metal-oxide nanomaterials as catalysts and sensors and will be published elsewhere.

Acknowledgement

Single-Crystal X-ray crystallographic data.

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