A 2D Layer Copper(II) Coordination Polymer with 3-Nitrophthalic Acid: Synthesis, Crystal Structure and Copper 3-Nitrophthalate Metal-organic Framework-graphene Oxide Nanocomposite[①]

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ABSTRACT A 2D layer Cu(II) coordination polymer $[Cu(npth)(H_2O)]_n$ (**1**) was crystallized from a mixture of 3-nitrophthalic acid and $Cu(OAc)_2 \cdot H_2O$ in water under room temperature and structurally characterized by single-crystal X-ray diffraction, FT-IR and TGA. Compound **1** was applied to make a nanocomposite with graphene oxide (GO). A highly dispersible and stable nanocomposite of Cu(npth)-GO was successfully synthesized by a simple ultrasonication method. SEM, TEM, UV-vis, FT-IR and TGA were used to characterize the morphology and structure of the prepared composite. In accordance with the characterization results, we suspected that the binding mechanism of Cu(npth) and GO was assigned to be the cooperative interaction of Cu–O coordination, π-π stacking and hydrogen bonding.

Keywords: copper 3-nitrophthalate metal-organic framework, crystal structure, graphene oxide, nanocomposite; DOI:10.14102/j.cnki.0254–5861.2011–2970

1 INTRODUCTION

Metal-organic frameworks (MOFs) known as coordination polymers or coordination networks have attracted increasing attention in recent years because of their intriguing architectures[1], coupled with their fascinating properties resulting in potential applications in various fields, such as magnetism, composite material, gas adsorption and separation, catalysis, electrochemistry and so on[2-7]. Recently, the applications of MOFs have been focused on electrochemical field owing to the electroactivity of metal ions. On the other hand, a pathway for electrons could be afford by ligands in MOFs[8, 9]. Nevertheless, the straight utilization of single-phase MOFs is still restricted in electrochemistry in some aspects, such as their poor electrocatalytic ability, inferior electronic conductivity and low mechanical stability[10]. Therefore, MOFs generally associate with other greatly conductive and mechanically durable materials in practice, forming MOFs-based composites[11-13].

Graphene has aroused great interest in the past decades. The preeminent physical and chemical properties make graphene and its derivatives as a superb candidate widely used in various fields[14]. In order to combine the unique properties of both MOFs and graphene/GO for diverse applications, a lot of efforts were taken to prepare MOFs-graphene/GO composites[15-18]. A remarkable example was reported by Wang et al., in which the nanocomposite of Cu(tpa)-GO was transformed into Cu(tpa)-EGC and it was used to detect ACOP and DA[15]. Liu et al. proposed the selective isolation of Hemoglobin by a LaMOF-GO₃ composite, which broadens the applications of MOFs and graphene/Go in the field of biological separations[16]. Yang et al. developed a facile one-step method to prepare a Cu-MOF-GN and it was used for constructing H_2O_2 and ascorbic acid sensors, showing excellent electrochemical response, wide linear range and long-term stability[17]. Our group is interested in the study of coordination chemistry with multi-hydroxyl/carboxylate ligands in recent years[19, 20].

In this work, we have used 3-nitrophthalic acid and copper(II) to synthesize a novel 2D layer framework at room temperature, namely [Cu(npth)(H$_2$O)]$_n$ (**1**). And it has been utilized to prepare a new hybrid nanocomposite of copper 3-nitropathalate MOF-graphene oxide (Cu(npth)-GO) by a simple and effective method. The gained composite was highly dispersible and stable in aqueous solution. The structure and morphology of the composite were investigated by UV-vis, Fourier transform infrared (FT-IR), thermo-gravimetric analysis (TGA), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

2   EXPERIMENTAL

2. 1   General materials and methods

All of the reactants were reagent grade and used as purchased. IR spectra were measured on a PerkinElmer Spectrum 100 FT-IR spectrometer. Thermogravimetric analysis (TGA) measurements were carried out using a DSC/TG pan A1203 system in N$_2$ flow at a heating rate of 10 ℃/min. Elemental analyses were performed (C, H, N) by Thermo Scientific FLASH 2000 elemental analyzer; Cu was analyzed on a Varian (720) ICP atomic emission spectro-meter. Scanning Electron Microscope (SEM) images were acquired by using a Hitachi S-4800 microscope working at 5 kV. Atomic Force Microscopy (AFM) images were acquired under ambient conditions using SPM nanoscope IIIa multimode working on a tapping mode with a RTESPA tip at a working frequency of ~235 Khz.

2. 2   Synthesis of [Cu(npth)(H$_2$O)]$_n$ (1)

A mixture of Cu(OAc)$_2$H$_2$O (199 mg, 1 mmol) and 3-nitrophthalic acid (211 mg, 1 mmol) was dissolved in water (10 mL), and gradually added in NaOH (4 mL, 1 M) while stirring. The mixture was stirred at room temperature for 6 h. Then the resulting blue-green solution was filtered and the filtrate was left undisturbed at ambient temperature. After several days, the green crystals were obtained by filtration, washed with MeOH and dried under vacuum. The yield is 68% based on copper. Anal. Calcd. for C$_8$H$_9$CuNO$_9$: C, 29.38; H, 2.75; Cu, 19.44; N, 4.29%. Found: C, 29.29; H, 2.64; Cu, 19.50; N, 4.32%. IR (KBr, cm^{-1}): 3518 s, 3463 s, 2745 w, 2534 w, 2365 w, 2141 w, 1600 s, 1560 m, 1487 m, 1374 s, 1142 m, 1086 m, 875 m, 776 s, 707 m, 650 m, 566 m, 510 w.

2. 3   Crystal structure determination

A green block single crystal of **1** with dimensions of 0.28mm × 0.25mm × 0.30mm was selected and mounted on a glass fiber. Data collection was performed at 296 K on a Smart Apex II CCD with graphite-monochromated Mo*K*α radiation (*λ* = 0.71073 Å). The structure of **1** was solved by direct methods and refined by full-matrix least-squares method on F^2 using the SHELXTL-97 crystallographic software package[21]. More details on the crystallographic studies as well as atomic displacement parameters are given in the CIF files. All carbon-bonded hydrogen atoms were placed in geometrically calculated positions; hydrogen atoms in water molecules were not assigned or directly included in the molecular formula. Compound **1** crystallizes in monoclinic *C*2/*c* space group with *a* = 24.8556(19), *b* = 10.7781(7), *c* = 8.4579(6) Å, *V* = 2264.4(3) Å^3, *Z* = 8, C$_8$H$_9$CuNO$_9$, *M$_r$* = 326.71, *D$_c$* = 1.917 g/cm^3, *F*(000) = 1320, *μ*(Mo*K*α) = 1.975 mm^{-1}, the final *R* = 0.0286 and *wR* = 0.0735 (*w* = 1/[$σ^2(F_o^2)$ + (0.0391*P*)^2 + 0.4206*P*], where *P* = (F_o^2 + 2F_c^2)/3), *S* = 1.043. Selected bond lengths are listed in Table 1.

Table 1.   Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
Cu(1)–O(1)	2.220(1)	Cu(1)–O(2)	1.985(5)	Cu(1)–O(3)	1.958(3)
Cu(1)–O(7)	1.990(8)	Cu(1)–O(8)	1.975(3)		
Angle	(°)	Angle	(°)	Angle	(°)
O(1)–Cu(1)–O(2)	54.52(6)	O(1)–Cu(1)–O(8)	75.03(8)	O(1)–Cu(1)–O(3)	127.05(3)
O(1)–Cu(1)–O(1)	142.75(3)	O(1)–Cu(1)–O(7)	96.37(2)	O(2)–Cu(1)–O(7)	90.72(0)
O(2)–Cu(1)–O(8)	88.39(7)	O(3)–Cu(1)–O(8)	90.78(7)	O(1)a–Cu(1)–O(7)	100.43(9)

2. 4   Preparation of Cu(npth)-GO nanocomposite

The graphene oxide (GO) was synthesized from natural graphite powder (99.95%, 45 μm) by a modified Hummers' method[22]. The Cu(npth)-GO nanocomposite was prepared by adding 1 mg of Cu(npth) to 1 mg/mL aqueous GO under stirring, followed by sonication at 100 W for 1 h to obtain a homogeneous dispersion.

3   RESULTS AND DISCUSSION

3. 1   Crystal structure

The single-crystal X-ray diffraction study reveals that complex **1** crystallizes in monoclinic space group $C2/c$. The crystal structure of $[Cu(npth)(H_2O)]_n$ is constituted of Cu^{2+}, 3-nitrophthalate and H_2O. As shown in Fig. 1a, each Cu(II) atom surrounded by six O atoms has a distorted octahedral coordination environment. For Cu(1), the basal plane of the octahedron is defined by four carboxylate-oxygen atoms (O_1 and O_3) belonging to three different npht ligands. The apical coordination sites are occupied by two oxygen atoms (O_7 and O_8) of other two H_2O molecules. The Cu–O bond lengths range from 1.958 to 2.222 Å (Table 1). The two carboxylate groups of npht ligand coordinate to the Cu(II) center in one distinct mode: one carboxyclate group chelating one Cu(II) ion, and the other bidentate bridging two Cu(II) ions (Fig. 1b). In this way, the Cu(1) center bridges three npht ligands, and one npht ligand links to three Cu centrals. The [Cu(npth)(H_2O)] structural units consist of a centrosymmetric metallocycle and the metallocycle extends to form a 2D-layered structure along the a-axis direction (Fig. 2).
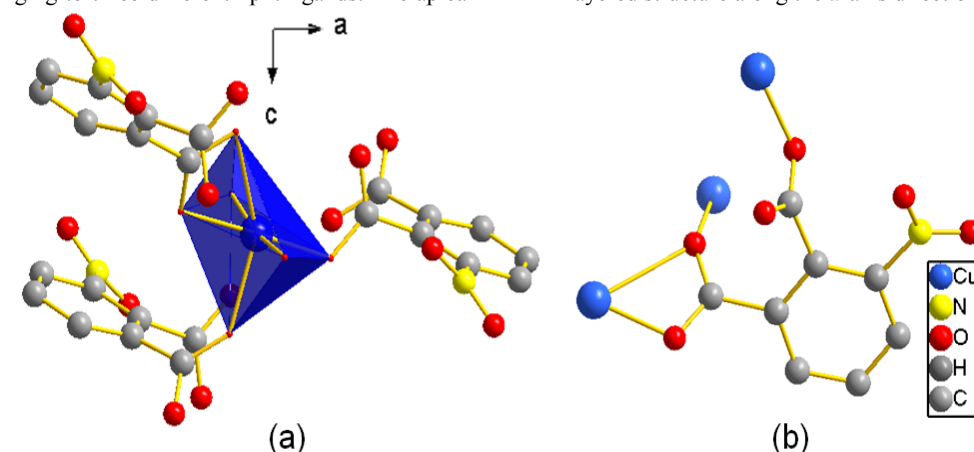

Fig. 1.   (a) A ball-and-stick representation of Cu^{2+}, 3-nitrophthalate and H_2O in 1 along the b-axis. The Cu(II) center is represented by a octahedron. (b) Schematic views of coordination mode of the 3-nitrophthalate ligand in 1. Color scheme: Cu, blue; N, yellow; O, red; C, gray
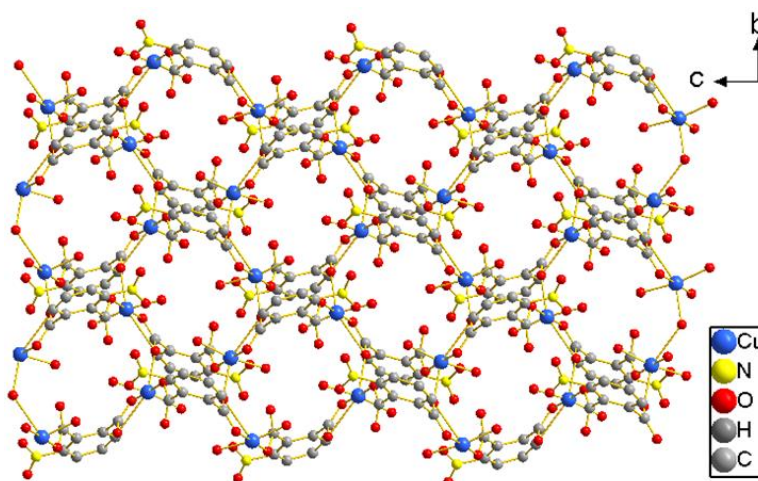

Fig. 2.   View of the 2-D structure of 1 along the a-axis. Color scheme: Cu, blue; N, Yellow; O, red; C, gray

3. 2   Materials characterization

Fig. 3a shows the SEM image of the synthesized Cu(npth) particles, in which most particles were irregular. It indicates that the yield of Cu(npth) MOF is high. Fig. 3b displays the SEM image of the Cu(npth)-GO composite. By virtue of the cooperative interaction of Cu–O coordination, hydrogen bonding and π-π stacking between Cu-MOF and GO, the Cu-MOF had been coated well with GO host. The buck Cu(npth) and its combination with GO could be further observed through the TEM images of Cu(npth) (Fig. 3c) and the Cu(npth)-GO composite (Fig. 3d).
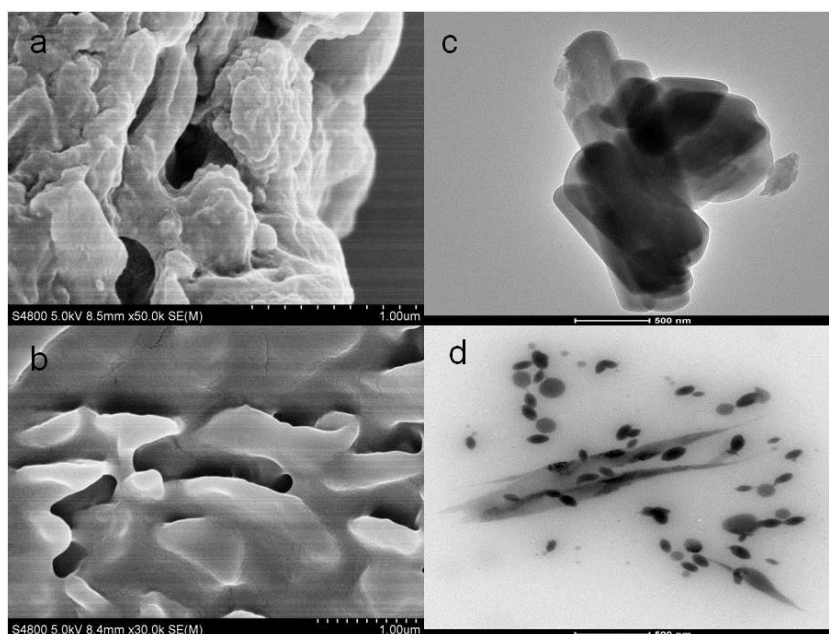
Fig. 3.　SEM images of Cu(npth) (a) and Cu(npth)-GO (b), TEM images of Cu(npth) (c) and Cu(npth)-GO (d)

The UV-vis spectroscopy was further performed to confirm the binding mechanism of the composite material between Cu(npth) and GO. As can be seen in Fig. 4A, a broad absorption peak around 231 nm and a weak shoulder peak at 300 nm could be assigned to the GO in water (curve a), in accordance with the previous research of GO[23]. A sharp absorption peak of Cu(npth) in water at about 202 nm was belonging to the characteristic absorption peak of benzene rings in 3-nitrophthalate ligands (curve b). The Cu(npth)-GO in water showed a new band at 234 nm and a red-shift in absorption bands compared to Cu-MOF at 204 nm (curve c) due to the presence of GO in Cu(npth)-GO creating a new band at 234 nm. It was assigned to the π to $\pi\alpha$ transitions of aromatic domains in GO and a red-shift in the absorption bands was characteristic of charge or energy transfer interaction between the poly aromatic scaffold in GO sheets and MOF[18].

For further investigating the interaction between Cu(npth) and GO, the composite was characterized by FT-IR spectroscopy, as shown in Fig. 4B. For GO (curve a) as reported in the literature[15], four absorption bands at 3427, 1746, 1219 and 1052 cm^{-1} were ascribed to the characteristic vibrations of O–H, C=O, C–OH and C–O–C (epoxy) bonds, respectively, while for Cu(npth)-GO, the O–H, C=O and C–O–C peaks of GO shifted to 3146, 1733 and 1044 cm^{-1} (curve c). More importantly, the peak at 1219 cm^{-1} (C–OH)

disappeared and a new absorption peak at 1395 cm^{-1} was found, which can be attributed to the benzene ring of Cu(npth). These changes testified that the interactions between the two species were π-π packing and hydrogen bonding[24]. Furthermore, the peaks of Cu(npth) such as 1388 and 1619 cm^{-1} (curve b) were observed in the FT-IR of Cu(npth)-GO (curve c), indicating that the composites were incorporated with Cu-MOF successfully.

The thermal stability of GO, Cu(npth), and Cu(npth)-GO was examined by thermogravimetric analysis (TGA). In Fig. 4C, the GO underwent first weight loss below 100 °C because of the removal of its physically adsorbed water molecules. Then the mass loss gradually appeared with the increase of temperature (curve a). Cu(npth) began to lose weight at 160 °C, and the second weight loss step presented from 200 to 260 °C. As the temperature went up to 260 °C (curve b), a sharp increase in the weight loss occurred, indicating the decomposition of the ligand in Cu(npth). The TGA curve of Cu(npth)-GO composite showed the expected thermal behavior (curve c). The first loss is found below 100 °C attributable to the adsorbed water of GO, and then the second and third losses were observed at 190 and 215 °C, respectively. These changes were fairly consistent with the combined thermal decomposition behaviors of GO and Cu(npth).
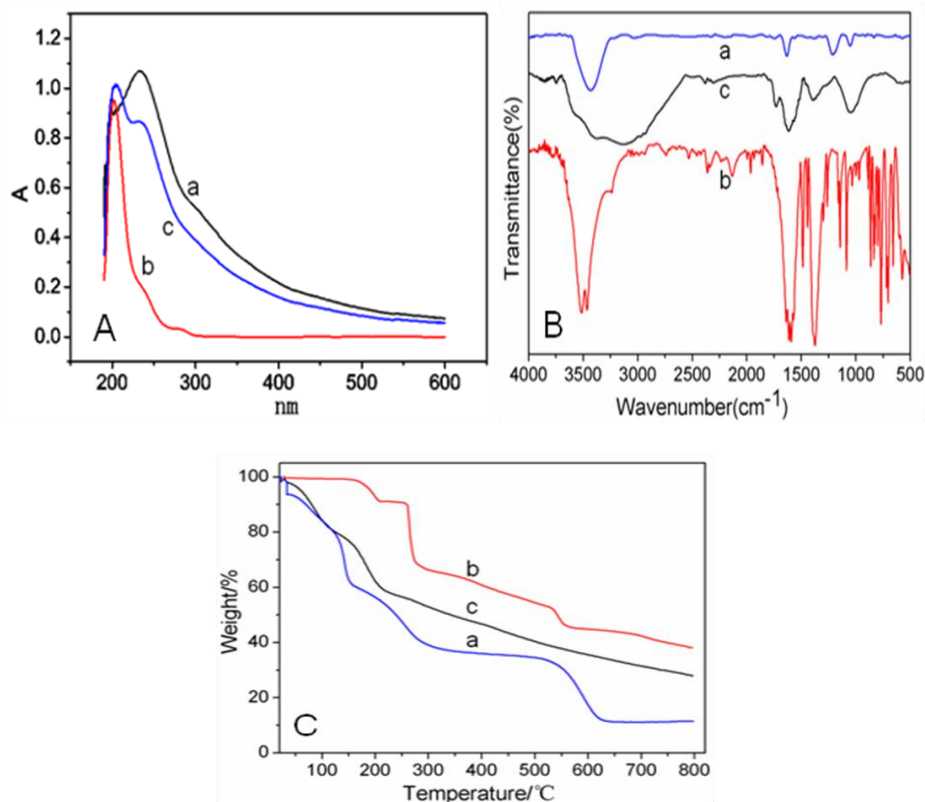
Fig. 4. UV-vis absorption spectra (A), FT-IR spectra (B), and
TGA curves (C) of GO (a), Cu(npth) (b), and Cu(npth)-GO (c)

4　CONCLUSION

In this work, a novel 2D layer copper(II) coordination compound based on 3-nitrophthalic acid was synthesized. Structures of the compound were characterized by X-ray, FT-IR and TGA. Furthermore, we have demonstrated a facile method for preparation of a Cu(npth) MOF-based composite using GO and Cu(npth). SEM, TEM, UV-vis, FT-IR and TGA were performed to characterize the structure and composition of this composite. Due to the high hydrophilicity of GO and its interaction with Cu(npth), the composite shows excellent dispersibility and stability in water. The work to apply this composite in electrochemistry and catalysis is in progress.

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