

A CONVENIENT APPROACH FOR INDUCING CONDUCTIVITY IN COPPER-BASED METAL ORGANIC FRAMEWORKS

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Abstract

Copper-based Metal Organic Framework (MOF) hybrids intercalated with conductive graphene-like layers were synthesized and carefully characterized in order to define their morphological, structural, textural and electrical properties. HKUST-1 was selected as MOF component and graphene-like layers were obtained by a two-step oxidation/reduction wet treatment of carbon black. The structure of the hybrids resulted dominated by the structural features of HKUST-1 but a uniform incorporation of graphene-like layers was found. dc experiments, confirmed the insulating character of HKUST-1 and revealed that the incorporation of graphene-like layers drastically changes the conductivity of hybrids. Intriguing perspectives about the application of copper-based MOF-graphene like hybrids as gas sensors and electrode materials for supercapacitors have emerged.

Introduction

Metal-organic frameworks (MOF) are crystalline microporous materials obtained by the assembly of metallic centres and organic linkers through strong coordination bonds. MOF are typically synthesized, under mild conditions, by a self-assembly reaction between various metal ions and organic linkers. Optimization of the pore structure, surface functions, and other properties can be achieved by choosing appropriate building blocks. The large variety of possible linker and metal units and the possibility to modify MOF after their synthesis makes the number of imaginable structures very huge [1]. Scientific community is considerably attracted by MOF because of their unique structural properties: high surface area, high porosity, and low crystal density. MOF, as porous material, are suitable adsorbents or membrane materials for gas storage and separation, and industrial applications of these materials in those fields are currently growing. The use of MOF in heterogeneous catalysis and in sensoristics is emerging too.

The principal limitations of MOF are: the poor stability in presence of humidity, the air- and moisture sensitivity and a lower chemical and thermal stability with respect that of zeolites and other porous inorganic solids [1]. The preparation of hybrid materials combining MOF and carbonaceous materials (carbon nanotubes [2], graphite oxide [3]) has been proposed as a solution to these weak points of MOF and to expand their field of applications.

This paper describes the synthesis and the properties of copper-based MOF hybrids intercalated with conductive graphene-like layers. HKUST-1, a water-stable MOF, containing Cu²⁺ dimers coordinated to the oxygen atoms of benzene tricarboxylate (BTC), has been selected as MOF component [1]. Graphene-like layers used to intercalate the MOF structure were obtained by a two-step oxidation/reduction wet treatment of a high surface carbon black (CB) [4]. Four hybrids were prepared with a different carbon loading (5, 15, 30, 45 wt.%, respectively).

These hybrids, as well as the parent material were carefully characterized in order to define morphological, structural, textural and electrical properties.

Experimental

Sample preparation

HKUST-1 was prepared applying the solvothermal procedure reported by Petit [3]: 1 g of copper nitrate hemipentahydrate and 0.5 g of 1,3,5 benzenetricarboxylic acid (BTC, 0.5 g) were mixed in 8.5 mL of N,N dimethylformamide under stirring and sonication (5 min). 8.5 mL of ethanol were then added to the mixture, which was stirred and sonicated 5 minutes more. Finally, 8.5 mL of deionized water were added too and the mixture was kept under stirring and sonication for 30 min. The mixture was then heated at 85 °C for 21 h under stirring. After cooling, the crystals were recovered by filtration, washed and immersed in dichloromethane for three days and finally collected by filtration.

CB (Phillips Petroleum Co.) was oxidized according to the procedure reported by Kamegawa [5]: 500 mg of CB powder were treated with 10 mL of nitric acid (67%) at 100 °C under stirring for 90 hours. The oxidized carbon nanoparticles were recovered by centrifugation, washed twice and named CNP.

The CNP reduction was performed applying the procedure with hydrazine hydrate proposed by Stankovich [6]. CNP in aqueous suspension (1mg/ml) was treated with hydrazine hydrate (50%) and heated at 100 °C for 24 h under stirring. At the end of the reaction the excess of hydrazine was neutralized with nitric acid and the resulting black solid recovered by centrifugation and named CNPR.

The CNPR neutral aqueous suspension was used for the preparation of the hybrid. CNPR was added to the well dissolved MOF precursors and solvent mixture during the final step in substitution of the volume of pure water. Four hybrids were prepared with a different CNPR loading and named MGL-1, MGL-2, MGL-3, MGL-4 (5, 15, 30, 45 wt.% of CNPR, respectively).

Methods

Elemental composition was estimated by a Perkin–Elmer 2400 CHNSO elemental analyzer. The thermal stability was evaluated by thermogravimetric analysis (TGA) on a Perkin–Elmer Pyris 1 Thermogravimetric Analyzer heating the samples in inert environment (N₂, 40 mL min⁻¹) from 30 °C up to 750 °C at a rate of 10 °C min⁻¹. Infrared spectroscopy was performed on a Nicolet iS10 spectrometer using the attenuated total reflectance (ATR) method by using a germanium crystal. The spectra were acquired on the powdered samples without KBr addition. BET area

and pore size distribution were evaluated using a Quantachrome Autosorb 1-C by Ar adsorption at 87 K [7]. The samples were outgassed under vacuum at 110 °C before the analysis. Adsorption or desorption data were processed according to NLDFT method which allows an accurate analysis over the complete micro and mesopore size range. X-ray diffraction (XRD) analyses were carried out using a Philips PW1710 diffractometer operating between 5° 2θ and 60° 2θ with a Cu Kα radiation. A diffraction experiment was run on standard glass slide for the background correction. The samples morphology was evidenced by Scanning Electron Microscopy (SEM) using a FEI Inspect SEM. Each scanning was performed on a powdered sample previously dried and sputter coated with a thin layer of gold to avoid charging. Conductibility was estimated through dc electrical measurements (I-V measurements, van der Pauw method [8]) on thin pellets (100-200 μm height) obtained by pressing MOF powders.

Results and Discussion

CNP and CNPR samples were fully characterized and more details are reported in [4]. The severe oxidation step lead to the demolition of the pristine CB backbone structure with the formation of small graphene-like nanoplatelets (4-10 nm). Oxygenated functional groups (mainly hydroxyl, carboxylic, carbonylic) are introduced, as testified by the significant increase of the oxygen content from 0.5% (CB) to 44% (CNP). The chemical reduction of CNP with hydrazine reduces the CNP hydrophilicity by partially transforming the oxygenated functionalities in hydrazones leading to an increase of nitrogen percentage from 1.12% (CNP) to 6.09% (CNPR). Is it noteworthy that the oxygenated functionalities are not completely removed upon the chemical reduction. The H/C ratio kept constant (0.27-0.32) suggesting that the size of the graphitic units remains rather unchanged. Figure 1 reports the X-ray diffraction patterns of the parent materials as well as the hybrids. In the case of CNP, a single peak around $2\theta = 23^\circ$ is observed. The HKUST-1 diffraction pattern is in accordance with the one reported in the literature [9] and it is similar to those of the hybrids indicating the existence of the well-defined MOF units in the samples. This finding indicates that the CNPR are rather well-dispersed in the materials and do not form densely packed agglomerates. The SEM images, also reported in Fig. 1, provide information about hybrids morphology. HKUST-1 presents typical octahedral crystals [9] of different sizes with relatively smooth surface. In MGL-1 (corresponding to wt. 5% of incorporated CNPR) well-defined crystals of octahedral shape are still observable. With the increasing quantity of CNP in the hybrid, the octahedral shape typical of HKUST-1 tends to disappear. In the case of the MGL-4 (45 wt. % of CNPR loading) small agglomerates are observable in which the octahedral shape of the pristine HKUST-1 crystal is not discernible.

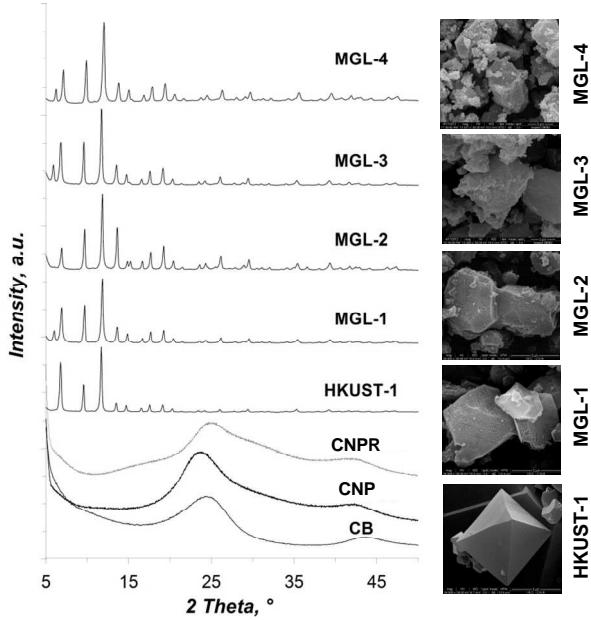


Figure 1. XRD and SEM images of the parent materials and the hybrids.

The ATR-IR spectra of CNP, CNPR, HKUST-1 and of the hybrids are plotted in Fig. 2a in the 700-2000 cm⁻¹ wavenumber region, baseline corrected and shifted for clarity.

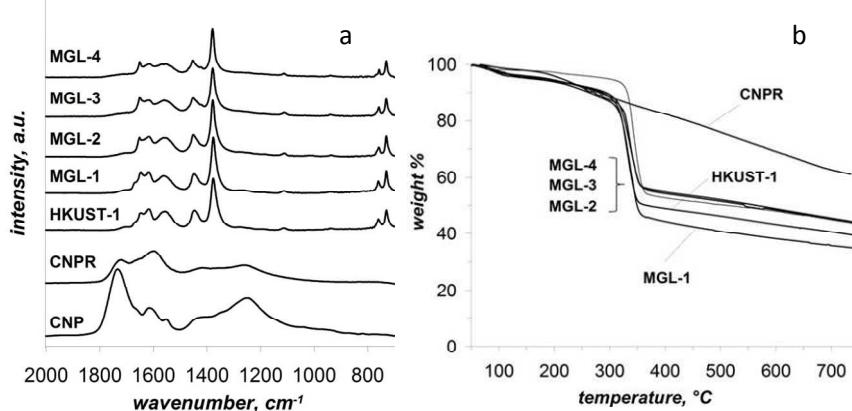


Figure 2 a) FT-IR spectra of CNP, CNPR, HKUST-1 and hybrids. b) Thermal analyses in inert environment (nitrogen) of CNPR, HKUST-1 and hybrids.

Both CNP and CNPR exhibit broad shaped spectra as a consequence of the complex carbon network with bands at 1650-1750 cm⁻¹ (C=O stretching modes of carbonyl and carboxylic groups) and 1500-1600 cm⁻¹ (skeletal vibrations of the sp² graphitic domains). The CNP spectrum presents an enhanced broad band in the

1300- 1100 cm⁻¹ region ascribable to the overlapping of C-OH and C-O stretching vibrations. The intensity of the C=O band and of the C-O broad band significantly decreases in the CNPR spectrum as a consequence of the partial removal of carboxylic-carboxylic functionalities upon the reductive treatment.

The ATR spectrum of HKUST-1 is very similar to those reported in literature [3]. The bands at 1645 and 1590 cm⁻¹ and at 1450 and 1370 cm⁻¹ correspond to the asymmetric and symmetric stretching vibrations of the carboxylate groups in BTC, respectively. The FT-IR spectra of the hybrids exhibit features similar to those of HKUST-1 spectrum. The absence of the C=O bands in the hybrids suggests that the carboxylic functionalities of the CNPR have reacted with the copper dimers and chemical interactions are involved in the formation of the hybrids.

The TGA profiles obtained in inert environment for the CNPR and the hybrids are reported in Fig. 2b. The TG plot of CNPR presents a progressive weight loss between 150 and 500 °C (20-40% weight loss) corresponding to the decomposition of oxygenated functionalities (carboxylic/carboxylic). The TGA curves of HKUST-1 and the hybrids exhibit a high weight loss at 300 °C corresponding to the complete collapse of the structure accompanied by the release of CO₂ [3]. The thermal behaviour of the hybrids is similar to those observed for HKUST-1 indicating a good dispersion of the CNPR into the hybrid structure.

In Table 1 the BET surface areas are listed along with the porosity distribution of each sample. HKUST-1 has a BET surface area of 1989 m² g⁻¹ which is in the range of the values reported in the literature [2, 3]. The surface area of the hybrids is lower than the HKUST-1 suggesting that the presence of CNPR cause distortion in the porous structure of the materials. HKUST-1 shows the typical bimodal micropores distribution with maximum centered at about 5 and 7 Å. In addition to micropores, representing the dominant type of pores, HKUST-1 is characterized also by some mesopores in the region 40-60 Å and few larger pores around 160 Å. The mesopores contribution is quantitatively less significant (<10% total pore volume) for HKUST-1, whereas it accounts for 40-50% total pore volume of the hybrids, confirming the disturbance of the micropore structure and the formation of mesopores, probably related to the formation of interparticles spaces.

Table 1. BET surface area, porosity distribution and conducibility of HKUST-1 and hybrids.

Sample	BET area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Conducibility σ (S m ⁻¹)
HKUST-1	1989	0.98	< 1 E-9
MGL-1	906	0.74	8.18 E-8
MGL-2	709	0.67	1.28 E-7
MGL-3	582	0.62	9.31 E-7
MGL-4	570	0.45	7.67 E-3

The electrical conducibility of MOF hybrids is a macroscopic characteristic governed by both the hybrid microstructure (i.e. crystal dimensions, intercalation degree) and chemical composition. On HKUST-1, no current was detected (with

applied voltages up to 10 V) within the sensitivity of our instruments, confirming the insulating character of the material [10]. The incorporation of CNPR (whose conducibility has been estimated to be 0.167 S m^{-1} [4]) changes the conducibility of the samples by several orders of magnitudes as shown by the values reported by the table 1.

Conclusions

A new class of copper-based MOF/graphene-like hybrids was produced starting from the HKUST-1 MOF. The hybrids were produced by varying the carbon nanoparticles loading and carefully characterized in order to define their morphological, structural, textural and electrical properties. It was found that the features of HKUST-1 in the hybrids are dominant and a good dispersion of the graphene-like layers into the hybrid structure is demonstrated. The interaction of the HKUST-1 units with the carboxylic functionalities of CNPR does not interfere with the HKUST-1 crystal growing. The values measured for dc resistance and resistivity confirmed the basically insulating character of HKUST-1 while those estimated for the hybrids revealed that the incorporation of graphene-like layers changes the conductivity by several orders of magnitudes. These results open intriguing perspectives about the application of hybrids as gas sensors and material electrode for supercapacitors.

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