Synthesis and characterization of conductive copper-based metal-organic framework/graphene-like composites

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HIGHLIGHTS

- A new class of HKUST-1/graphene-like composites was produced.
- High amount of graphene-like does not interfere with the HKUST-1 crystal growing.
- Composites exhibit a new porosity.
- Strong increase of the dc conductivity as a function of graphene-like content.

GRAPHICAL ABSTRACT
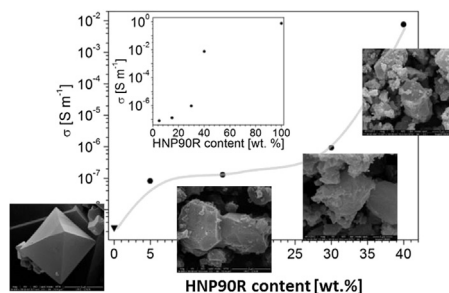
ABSTRACT

Metal-organic framework (MOF) incorporating conductive graphene-like layers were synthesized and characterized. The selected MOF, HKUST-1, combines high surface area, water stability, simple preparation and low costs. Graphene-like layers incorporated into the MOF structure were obtained by a two-step oxidation/reduction wet treatment of a high surface carbon black. MOF composites were produced at different carbonaceous layers content. It was shown, through a wide characterization of the samples, that the composites preserve the main features of the parent MOF, additional exhibiting a tunable electrical conductivity.

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1. Introduction

Metal-organic frameworks (MOF) are coordination networks characterized by a high crystallinity and uniform porosity, obtained by the assembly of metallic centers and organic linkers through strong covalent bonds. MOF attracted in the last years a great attention due to their high surface area (up to 4500 m^2 g^{-1})

[1] and the possibility to vary their metallic centers and organic functionalities [2] in order to tune chemico-physical and textural properties for a large array of specific applications. Because of such features (large internal surface area and high porosity and crystallinity) MOF are often compared with zeolites: similarly to zeolites, MOF have been utilized in some applications including adsorption and separation of specific gases [3], gas storage [4–8], heterogeneous catalysis [9] drug delivery [10] and chemical sensors [11]. The principal disadvantages of MOF are the tendency of reversible binding of water, the air- and moisture sensitivity and a lower chemical and thermal stability compared to zeolites

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and other porous inorganic solids [1]. The electrical properties of MOF were very rarely studied due to their insulating nature. The preparation of composites combining MOF and carbon-based materials (carbon nanotubes, CNT [12], graphite oxide, GO [13], graphite [14]) has been proposed as a solution to overcome the weak points of MOF and to expand their field of applications. Studies on a zinc-based MOF (MOF-5) show that MOF-5 intercalated with graphene decorated at the basal plane with carboxylic groups exhibit new electrical properties [15]. These composites combine the properties of carbonaceous surfaces and MOF. The introduction of carbonaceous material into MOF structure potentially leads to an enhancement in non-specific adsorption improving the kinetics of adsorption. Moreover, the conductivity and high specific surface area of graphene can strongly affect the dielectric and conducting properties of host materials, which could fulfill the recently highlighted request for MOF with conducting properties for several applicative purposes [15–16].

This paper focuses on the synthesis and description of the structure of MOF in which conductive graphene-like layers are embedded. We chose a copper-based MOF containing Cu^{2+} dimers as the metallic units linked to oxygen atoms from benzene tricarboxylate (BTC) [17–18], and referred in literature as HKUST-1 or MOF-199. HKUST-1 combines high surface area, water stability [19], simple preparation (anhydrous conditions are not required) and low costs (precursors are easily available and not expensive). Graphene-like layers used to prepare the composites were obtained by a two-step oxidation/reduction wet treatment of a high surface carbon black (CB), according to the procedure described in Alfè et al. [20]. This procedure offers high reproducibility and control of the results and it is extremely inexpensive. In this work we show, through a wide characterization of samples with several carbonaceous layers content, that the obtained composites preserve the main features of the parent MOF, additionally exhibiting a tunable electrical conductivity.

2. Experimental section

2.1. Sample preparation

HKUST-1 preparation. The MOF HKUST-1 was prepared applying the synthetic procedure reported by Petit[13]: 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 (DMF) under stirring and sonication (5 min). 8.5 mL of ethanol were then added to the mixture, which was stirred and sonicated 5 min 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. All chemicals were purchased from Sigma–Aldrich of the purest quality and used without further purification.

Graphene-like (GL) layers preparation. GL layers in water suspension were prepared according to a two-step procedure proposed in Alfè et al. [20]. Briefly, CB (Phillips Petroleum Co., furnace carbon black, 15–20 nm primary particles diameter, specific BET area 151 $m^2 g^{-1}$) was oxidized with nitric acid (67%) at 100 °C under stirring for 90 h. The oxidized carbon nanoparticles were recovered by centrifugation and named HNP90. The product had a dark brown appearance and it was not as opaque black as the pristine CB. The HNP90 was dispersed in water and treated with hydrazine hydrate (50%) at 100 °C under reflux for 24 h. 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

HNP90R. The HNP90R mass yield was 55%. It is noteworthy that the dried HNP90R resulted to be insoluble in water and in the most common organic solvents, both polar and apolar (water, ethanol, *N*-methyl pirrolidinone, dichloromethane, heptane, DMF) [20]. This was attributed to an increase of hydrophobicity of the material caused by a decrease in the polar functionalities on the surface and consequent intimate self-assembling interaction between the restored graphitic planes leading to the formation of a graphene-like assembling. For this reason freshly prepared HNP90R in water suspension was readily used for the preparation of the composites.

MOF/GL (MGL) preparation. HNP90R suspension was added to the well-dissolved MOF precursors and solvent mixture during the final step of the MOF preparation, in substitution of the volume of deionized water. The synthesis conditions were kept the same as those used for the preparation of the HKUST-1. Four MGL composites were prepared with a different HNP90R loading and named MGL-1, MGL-2, MGL-3 MGL-4 (5, 15, 30, 40 wt.% of HNP90R, respectively). In all cases the liquid phase recovered after the filtration of the crystals resulted colorless, indicating a complete incorporation of the GL material into the MOF structure. The percentage of the incorporated GL was checked by elemental analysis and inductively coupled plasma mass spectrometry (ICP-MS).

2.2. Methods

Elemental composition of the samples (C, H, N) was estimated by a Perkin–Elmer 2400 CHNSO elemental analyzer. The quantitative determination of the Cu was obtained by an Agilent ICP-MS 7500ce spectrometer. For the ICP-MS measurements, 50 mg of the powdered sample was suspended with 5 mL of deionized water and digested with 5 mL of HNO_3 (65%) and 1 mL of H_2O_2 (30%) for 30 min by microwave heating. The digested sample was filtered to remove any particulate or solid contaminant which may interfere with the analysis, diluted with deionized water and analyzed. The quantitative determination of copper was achieved extrapolating from a four point calibration curve. Each measurement was repeated thrice.

The thermal stability of the samples was evaluated by thermogravimetric analysis (TGA) on a Perkin–Elmer Pyris 1 Thermogravimetric Analyzer. The samples were heated both in oxidant (air) and in inert (nitrogen) environment (30 mL min^{-1}) from 30 °C up to 750 °C at a rate of 10 °C min^{-1}.

Fourier Transform Infrared (FTIR) spectra were recorded 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 specific surface area and pore size distribution of the samples were evaluated using a Quantachrome Autosorb 1-C by Ar adsorption at 87 K in order to limit the p/p_0 range in comparison to N_2, requiring lower p/p_0 value for adsorption into micropores [21]. The samples were outgassed under vacuum at 110 °C before the analysis. Data of the adsorption branch of the complete isotherm were processed according to NLDFT method to evaluate the pore size distribution and pore volume.

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 ($\lambda = 1.54056$ Å). The sample powder was grounded and then loaded into a glass holder and leveled with a glass slide before mounting it on the sample chamber. A diffraction experiment was run on standard glass slide for the background correction.

Scanning electron microscopy (SEM) was performed on a FEI Inspect™ S50 Scanning Electron Microscope. SEM was performed