

Syntheses, Characterizations and Adsorption Properties of MIL-101/Graphene Oxide Composites

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Composites of the Cr³⁺-based metal-organic framework (MIL-101) and graphene oxide (GO) have been synthesized with different ratios of MIL-101 and GO. The composites and the parent material MIL-101 were characterized by X-ray diffraction, scanning electron microscopy and nitrogen adsorption. The results indicated that the incorporation of large amounts of GO (10 and 20 wt%) almost did not prevent the formation of MIL-101 units, but had an obvious impact on the size of MIL-101 crystals. On the contrary, small amounts of GO added (2 and 5 wt%) prevented significantly the proper assembly of MIL-101 units, thus resulting in a pronounced decrease in the porosities of composites.

Keywords MIL-101, graphene oxide, composite, synthesis

Introduction

Recently, metal organic frameworks (MOFs) have attracted extensive attention due to their unusual topologies and potential applications.^[1,2] These materials are usually formed by the self-assembly of metallic centers and bridging organic linkers.^[3] On the other hand, graphene oxide (GO), obtained by oxidation of graphite,^[4] consists of graphene layers bearing various oxygen groups (epoxy, hydroxyl, carboxylic) on the basal planes and the edges of the layers.^[5-7] Indeed, the GO material is a promising precursor for preparing composites, and GO-based composites have been successfully made to date with inorganic nanostructures, organic crystals, polymers, and carbon nanotubes.^[8-10]

It should be noted that examples of MOF-GO composites based on MOFs and GO components are rare. For example, Loh and coworkers have employed benzoic acid-functionalized graphene acting as a structure-directing template to induce the growth of MOF-5 crystals.^[11] Bandosz and coworkers have reported the formation of MOF-GO composites via interactions between the oxygen groups of GO and the metallic centers of MOFs.^[12-14] The new pores created at the interface of the MOF units and the graphene layers were responsible for the enhanced adsorption capacities compared to the parent materials.^[15]

Taking into account the structural variability of

MOFs, it is important to investigate the formation and properties of composites, employing GO and different MOF precursors. In this contribution, we presented new composites of MIL-101 and GO with varying ratios of the two components. Various techniques such as X-ray diffraction, scanning electron microscopy and nitrogen adsorption were carried out to characterize these materials.

Experimental

Preparation of graphite oxide

Graphite oxide was prepared from the natural flake graphite purchased from Qingdao Guyu Graphite Co., Ltd., with a particle size of 150 μm (99.9% purity) according to a modified Hummers method.^[16] In a typical synthesis, 2.0 g of graphite powder was added to 80 mL of cold (0 °C) concentrated H₂SO₄ in an ice bath. Then, NaNO₃ (4.0 g) and KMnO₄ (8.0 g) were added gradually under stirring and the temperature of the mixture was kept to be below 10 °C. The reaction mixture was continually stirred for 4 h below 10 °C. Successively, the mixture was stirred at 35 °C for 4 h, and then diluted with 200 mL of deionized (DI) water. Because the addition of water in concentrated sulfuric acid medium releases a large amount of heat, the addition of water was performed in an ice bath to keep the temperature

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Received June 12, 2012; accepted August 6, 2012.

below 100 °C. After adding all of the 200 mL of DI water, the mixture was stirred for 1 h. The reaction was then terminated by adding 15 mL of 30% H₂O₂ solution. The solid product was separated by centrifugation, washed repeatedly with 5% HCl solution until sulfate could not be detected with BaCl₂. For further purification, the resulting solid was re-dispersed in DI water and then was dialyzed for 3 d to remove residual salts and acids. The suspension was dried in a vacuum oven at 60 °C for 24 h to obtain graphite oxide.

Preparation of MIL-101

MIL-101 was synthesized according to the method reported by Férey and coworkers^[17] using the hydrothermal reaction of 1,4-benzene dicarboxylic acid (H₂BDC) (164 mg, 1 mmol) with Cr(NO₃)₃•9H₂O (400 mg, 1 mmol), fluorhydric acid (HF) (1 mmol), and 4.8 mL H₂O (265 mmol) for 8 h at 220 °C, then cooling down to room temperature at the rate of 10 °C/h, producing highly crystallized green powder. It was then filtered and washed with distilled water and refluxed in NH₄F to remove the unreacted BDC molecules present as needles after synthesis. Then the final product was put into the oven at 60 °C for one night.

Preparation of MIL-GO composites

The composites were prepared by the same procedure as for MIL-101 except that various amounts of GO were added to the mixture of MIL-101 precursors, and the mixture was subsequently sonicated before the heat treatment. The added GO consisted of 2, 5, 10 and 20 wt% of the final material weight. The synthesized products are referred to as MIL-GO2, MIL-GO5, MIL-GO10 and MIL-GO20, respectively.

Instrumentation and measurements

The powder X-ray diffraction measurements were performed on a Shimadzu XRD-6000 diffractometer with Cu K α radiation. Scanning electron microscopy (SEM) was carried out on a JSM-6480 instrument. The nitrogen adsorption isotherms were measured using an automatic volumetric adsorption equipment (ASAP 2020, Micromeritics). Proceeding to gas sorption experiments, samples were outgassed at 120 °C for 24 h. The nitrogen isotherms were measured at 77 K.

Results and Discussion

Structural characterization

The X-ray diffraction patterns of the parent material MIL-101 and composites MIL-GO are presented in Figure 1. The GO spectrum shows a peak at $2\theta=8.8^\circ$, indicating an interlayer distance of about 10.0 Å determined by Bragg's law, compared to 9.5 Å observed in the literature.^[14] The diffraction patterns of MIL-101 are in agreement with those reported previously, and characteristic of this material structure.^[17] It should be noted

that the rather broad d_{002} peak of GO was not observed for MIL-GO composites, which can be attributed to the readily exfoliation/high dispersion of GO in water upon sonication during the synthesis procedure. For the MIL-GO10 and MIL-GO20 composites, the patterns are similar to those observed for the parent material MIL-101, suggesting that the well-defined MIL-101 structure was mainly preserved. In both cases, the graphene layers from GO almost did not prevent the formation of linkages between the Cr³⁺ ions and the BDC bridges.

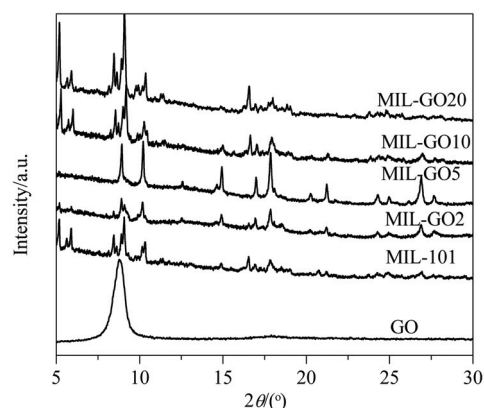


Figure 1 X-ray diffraction patterns of GO, MIL-101 and MIL-GO composites.

For the MIL-GO2 and MIL-GO5 composites, on the contrary, most of the peaks pertaining to MIL-101 were missing. All of these indicated that the carbon layers from GO in both composites prevented significantly the proper assembly of the MIL-101 units. Generally, the oxygen functional groups (especially epoxy groups) in GO are able to coordinated to the metallic sites (the Cr³⁺ ion in this case) of MOFs in the building process of the composites, forming a uniform new material.^[14]

Morphological characterization

From the SEM images (Figure 2) we can see that GO exhibits a dense and disordered arrangement of graphene-based layers. For the MIL-101 material, well-defined uniform octahedral crystals were observed with the size of about 1 μm. The morphologies of the composites showed variations compared to that of the parent material. For the composites with low GO content (2 and 5 wt%), many large blocks were observed with few MIL-101 crystals attaching to the surface. Owing to the fact that the graphene layers from GO with low content can be readily exfoliated in water upon sonication, thus the oxygen functional groups of dispersed GO layers will react with the Cr³⁺ ions, preventing significantly the formation of MIL-101 units. In fact, the yields of both composites are rather low, and the color was gray compared to the green for MIL-GO10 and MIL-GO20 composites. Above results are in agreement with the X-ray diffraction data.

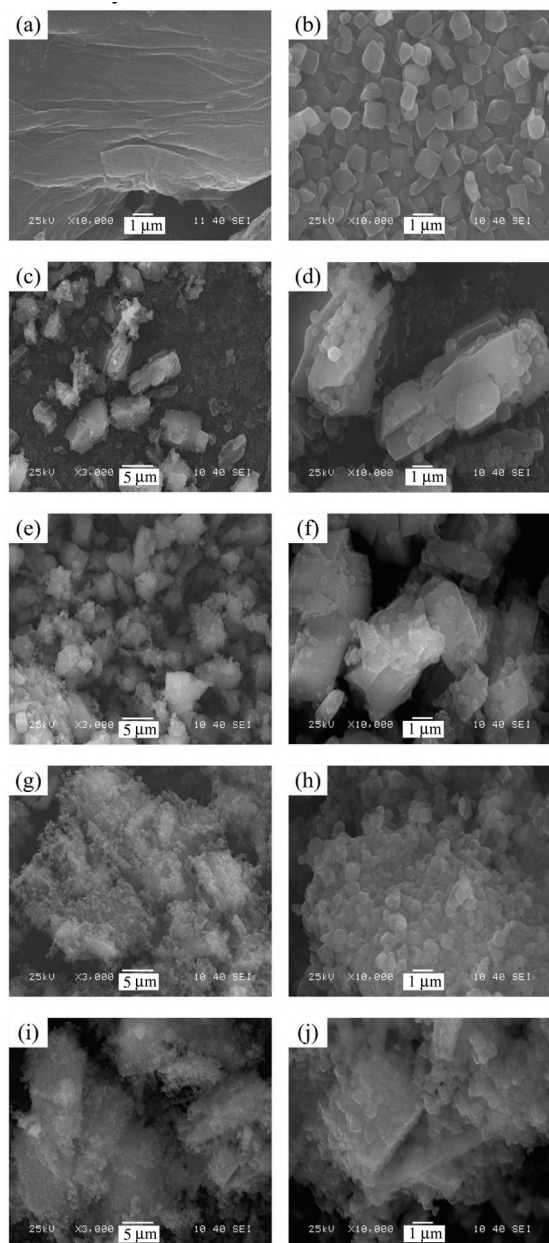


Figure 2 SEM images of GO (a), MIL-101 (b), MIL-GO2 (c, d), MIL-GO5 (e, f), MIL-GO10 (g, h), and MIL-GO20 (i, j) composites.

However, the GO layers were not well-dispersed in composites MIL-GO10 and MIL-GO20 and readily form densely packed agglomerates owing to the high GO content (10 and 20 wt%). In this case, the numbers of oxygen functional groups coordinated to the Cr^{3+} ions are rather smaller than those in composites MIL-GO2 and MIL-GO5. In addition, the size (*ca.* 0.7 μm) of MIL-101 crystals attaching to the surface of agglomerated GO was smaller obviously than pure MIL-101. The similar results were also found in the composite MIL-GO20 except for the more pronounced agglomerated GO features. It should be mentioned here that the presence of the agglomerated GO layers had almost no effect on the formation of MIL-101 units,

except for the size of MIL-101 crystals. These results are in agreement with the X-ray diffraction data.

Nitrogen adsorption

The differences in the structure between the parent material and composites have been also seen from the nitrogen adsorption isotherms, as shown in Figure 3. The GO material showed no nitrogen uptake, and this material generally exhibits no porosity.^[18] The isotherms of the parent material, and composites (MIL-GO10 and MIL-GO20) are of type-I, indicative of the microporous character. The porosities (Table 1) of composites MIL-GO2 and MIL-GO5 are significantly low (BET surface areas of 62 and 135 m^2/g , respectively), owing to the presence of small amounts of MIL-101 crystals caused by the incorporation of GO in composites, as evidenced by XRD and SEM analysis.

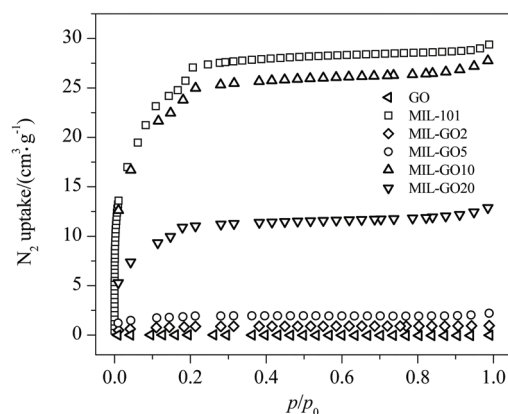


Figure 3 Nitrogen adsorption isotherms of GO, MIL-101 and MIL-GO composites.

Table 1 The surface areas of GO, MIL-101 and MIL-GO composites

Sample	BET surface area/ $(\text{m}^2 \cdot \text{g}^{-1})$
GO	0.94
MIL-101	1946
MIL-GO2	62
MIL-GO5	135
MIL-GO10	1793
MIL-GO20	806

The porosities of the MIL-101 and MIL-GO10 composites (BET surface areas of 1946 and 1793 m^2/g) are lower than that reported by Férey and coworkers for the same synthesis procedure.^[17] The difference in the surface area can be related to the way of outgassing during preparation and thus the completeness of solvent removal.^[19,20] The similar BET value for the composite MIL-GO10 and MIL-101 may be due to the fact that the enhanced porosity induced by the decrease of size of MIL-101 crystals counterbalanced the negative effect of the packed GO layers. However, the situation in the composite MIL-GO20 is different, since the porosity

with BET surface area of 806 m²/g decreased compared to that of MIL-101. In this case, the presence of carbon layers with high GO content was responsible for the decrease in porosity observed, because the incorporation of significantly packed GO started to have an obvious detrimental effect on the porosity compared to the smaller size of MIL-101 crystals.

Conclusions

The composites of MIL-101 and GO were prepared with varying ratios of two components through *in-situ* method. The parent material and composites have been characterized by various techniques and tested for nitrogen adsorption. The incorporation of GO layers has an obvious impact on the formation of MIL-101 units, the size of crystals, and the porosities of composites. The results of this study have presented new directions for achieving new hybrid materials with potential applications between the two highlighted materials such as MOFs and GO. Studies on this line are underway in our laboratory.

Acknowledgement

The authors are grateful for financial support from the National Natural Science Foundation of China (Nos. 51072072, 51102119) and the Natural Science Foundation of Jiangsu Province (Nos. BK2010343, BK2011518).

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