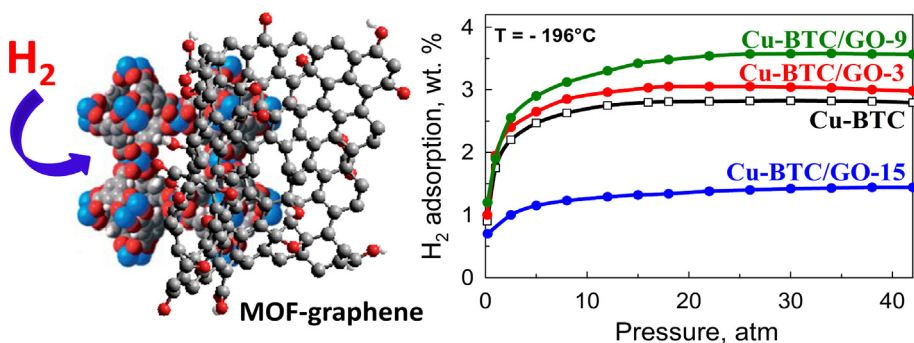


Feature Article

Gas adsorption properties of hybrid graphene-MOF materials

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GRAPHICAL ABSTRACT



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ABSTRACT

Nowadays, hybrid porous materials consisting of metal-organic frameworks (MOFs) and graphene nanosheets become more and more attractive because of their growing applications in adsorption, catalysis and related areas. Incorporation of graphene oxide into MOFs can provide benefits such as increased water resistance and thermal stability as well as enhanced surface area and adsorption properties. Graphene oxide is one of the best additives to other materials owing to its two main virtues: high atomic density and large amount of surface functional groups. Due to its dense array of atoms, graphene oxide can significantly increase dispersion forces in graphene-MOF materials, which is beneficial for adsorption of small molecules.

This work presents a concise appraisal of adsorption properties of MOFs and graphene-MOF hybrids toward CO₂, volatile organic compounds, hydrogen and methane. It shows that the graphene-MOF materials represent an important class of materials with potential applications in adsorption and catalysis. A special emphasis of this article is placed on their adsorption applications for gas capture and storage. A large number of graphene-MOF adsorbents has been so far explored and their appraisal could be beneficial for researchers interested in the development of hybrid adsorbents for adsorption-based applications.

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1. Introduction

Currently, there is a continuous increase in energy demand, which leads to a rapidly growing depletion of available fossil fuels. Additionally, serious environmental concerns such as global warming and related effects, for example, melting of glaciers and rising ocean levels require immediate solutions. One of them is the implementation of safe energy conversion and storage technologies, which use clean energy carriers such as hydrogen and methane. Hydrogen is considered to be the most ecological energy carrier because the product of its combustion is pure water vapor, whereas methane is naturally abundant fuel and its combustion produces mainly carbon dioxide and water vapor without hazardous substances. Taking advantage of recent developments in the area of porous materials, it is possible to use these materials for energy storage. Moreover, it could be also desirable to capture harmful gases that are produced in large quantities by the industry and other human activities. Therefore, the development of new advanced adsorbents for gas storage and capture is essential.

Various kinds of porous materials have been proposed for the above-mentioned tasks, with particular focus on activated carbons [1–3], zeolites [4–6], ordered silicas [6–8] and carbons [9–11], metal-organic frameworks [12,13] and graphene materials [14–20]. In comparison to conventional inorganic materials, metal-organic frameworks feature well-developed porosity, organic-inorganic nature with a homogenous dispersion of components and controlled pore sizes. Additional advantages of these materials are their suitability for modifications and coupling with other classes of materials [21–26]. Furthermore, pyrolysis of MOFs at high temperatures results in new inorganic structures such as porous carbons, metals, metal oxides or complex materials [22,27–30]. Thanks to such modifications and processing, the potential usage of MOFs grows exponentially. Many researchers are inspired by remarkable adsorption properties of MOFs, their composites and derivatives that have been reported in literature, which refer to their various applications ranging from automotive industry, fuel cells to stationary power stations [31–35].

This work presents a concise and comparative appraisal of adsorption properties of graphene-MOF hybrids and the corresponding MOFs. These materials have been explored for capture of CO₂ and volatile organic compounds as well as for hydrogen and methane storage. It is expected that the presented hybrid materials and the cited literature will stimulate a further research in the development of new MOFs and first of all, their composites. First and foremost, the aim of this work is to present graphene-MOF composites of the best properties for gas adsorption and storage.

2. Structure of graphene-MOF composites

Due to the fact that metal-organic frameworks are crystalline materials consisting of metal ions/clusters and organic linkers, their structure and, consequently, properties can be relatively easily tailored by using suitable metal ions/clusters and organic

linkers. In addition, a wide range of modifications of MOFs is already known and applied in both the synthesis and post-synthesis modification. Up to now, over 20,000 different MOFs have been reported with various pore sizes ranging from a few angstroms to 50 nm [36,37]. Fig. 1 shows the selected MOFs, including their specific surface areas and pore sizes, because these parameters are important indicators of their adsorption properties. Usually, organic linkers are polycarboxylates: 1,3,5-benzenetricarboxylate (Cu-based HKUST-1, Al, Cr or Fe-based MIL-100), 1,4-benzenedicarboxylate (Zn-based MOF-5; V(IV)-based MIL-47; Al, Cr, Fe or Ga-based MIL-53; Cr, Fe-based MIL-101) or 1,3,5-benzenetribenzoate (Zn-based MOF-177). Most of them can be easily synthesized in larger quantities, e.g., MOF-5, HKUST-1, MIL-100, MIL-101, MOF-177, Mn₃[(Mn₄Cl)₃(BTT)₈] (BTT – 1,3,5-benzenetris-tetrazolate) [38–45].

Although MOFs feature many advantages, many of them have also substantial drawbacks such as susceptibility to slow degradation even at ambient conditions, low water and light resistance, and also poor electrical conductivity and mechanical strength [46–48]. Due to the fact that MOFs can possess high surface areas (up to 7000 m²/g [48]) and they are mainly composed of organic compounds, they can be easily transformed into nanoporous carbons (NPCs) via simple carbonization [27,28,49–56]. Carbons acquired in such a way can feature not only large surface areas and pore volumes but also good mechanical and chemical stability (comparable to activated carbons). For instance, carbonization of Zn-fumarate MOF allowed obtaining a nanoporous carbon with surface area of 4800 m²/g and pore volume of 4.0 cm³/g [49]. In general, in the synthesis of NPCs from MOFs (often with additional carbon sources), parameters such as carbonization temperature, temperature ramp, crystal size or the presence of additional components in MOF determine the main characteristics of the obtained carbons such as their porosity, functionality and stability. As opposed to the most activated carbons obtained by direct carbonization and activation of organic precursors, NPCs usually feature uniform distribution of porosity. This is particularly important in applications where highly selective adsorbents are needed. It is also possible to obtain other functional materials from MOFs, for example, graphene ribbons consisting of 2–6 graphene layers [30,57–62]. An interesting approach to obtain NPC-graphene composite was reported by Chen et al. [54]. They firstly carbonized Zn-containing MOF (ZIF-8) at 900 °C achieving a microporous carbon, next they doped this material with sulfur and wrapped it with graphene sheets (Fig. 2). However, synthesis of MOF derivatives, e.g., NPCs, metals or metal oxides is associated with high energy consumption because carbonization is carried out for several hours at high temperatures (700 °C–1100 °C) [50,52]. The synthesis cost of MOFs should also be considered, because in many cases it would be a limiting factor for their usage. Therefore, further research would be desirable to make the synthesis of MOFs feasible and inexpensive.

As it was already mentioned, one of the key disadvantages of MOFs is their low stability, above all, their low water resistance, which results in the gradual deterioration of their crystalline

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