



# Nanocomposites formed by in situ growth of NiDOBDC nanoparticles on graphene oxide sheets for enhanced CO<sub>2</sub> and H<sub>2</sub> storage

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## ABSTRACT

A hybrid composite containing NiDOBDC [Ni-MOF-74 or Ni<sub>2</sub>(dobdc)] and graphene oxide (GO) was successfully synthesized using a facile method for enhanced CO<sub>2</sub> and H<sub>2</sub> storage. Additional porous spaces were created when the nanocomposite material with a three-dimensional (3-D) architecture was constructed with two-dimensional (2-D) graphene oxide sheets and microporous NiDOBDC nanoparticles. The analysis of gas storage performance reveals that the generation of new porosity resulted in enhanced CO<sub>2</sub> and H<sub>2</sub> adsorption. In particular, the NiDOBDC/GO composite with 10 wt% GO loading exhibited the highest CO<sub>2</sub> and H<sub>2</sub> storage values, up to 10.5 mmol/g (298 K, 20 bar) and 1.39 mmol/g (298 K, 20 bar), respectively, values that are significantly higher than those of the Ni-DOBDC metal-organic framework. Besides, enhanced CO<sub>2</sub>/N<sub>2</sub> selectivity was also observed for NiDOBDC/GO composite due to the additional storage sites for CO<sub>2</sub>. The strategy demonstrated in this work can also be applied to other microporous materials to enhance their gas adsorption properties.

## 1. Introduction

Since the 19th century, the massive release of carbon dioxide (CO<sub>2</sub>) from anthropogenic sources has been the major contributor to the increased concentration of greenhouse gases in the atmosphere, which in turn is one of the major contributors to global warming [1,2]. Between 1880 and 2012, the reported global average surface temperature has increased by 85%, with the temperature increment increasing from 0.65 °C to 1.06 °C [3]. It has been projected that such a rapid increase in surface temperature could lead to severe snowballing effects such as extreme weather events and a rise in sea level, as well as a decrease in habitable space for the ecosystem. Therefore, effective ways of reducing the massive emission of greenhouse gases are required to address this long-standing issue. In addition to developing materials that can absorb CO<sub>2</sub> effectively so as to mitigate the release of greenhouse gases into the atmosphere, the increased demand for clean energy with the use of hydrogen (H<sub>2</sub>) has attracted much attention because H<sub>2</sub> typically does not release any greenhouse gases [4]. Hence, an effective method to store CO<sub>2</sub> and H<sub>2</sub> plays a significant role in fulfilling these targets.

Through the years, various approaches had been developed for effective gas storage, such as storage in typical high-pressure vessels or under cryogenic temperatures and storage via chemical adsorption. Among them, solid adsorption using adsorbents based on nanoporous materials has demonstrated its usefulness in gas storage technology for

industrial applications. Several advantages of storing gases using nanoporous materials have been highlighted in numerous journals. First, the addition of a nanoporous material into a typical storage cylinder can increase the gas storage density as compared to storage in a typical cylinder without the incorporation of a nanoporous material. Second, storage of gases using nanoporous materials is much safer because a reasonable capacity can be captured without subjecting the cylinder to extraordinarily high pressure. Third, because the storage of gases using nanoporous materials is typically constant with respect to temperature and pressure, the required space to store such materials can be easily predicted and estimated [5]. Therefore, such an approach would be relatively cost-effective and energy-saving.

To date, many adsorbents have been investigated for potential application in CO<sub>2</sub> and H<sub>2</sub> storage, including zeolites [6–9], mesoporous silica [10,11], carbon materials [12–18], porous organic polymers [19,20], and metal-organic frameworks (MOFs) [21–29]. Among them, MOFs have recently grown to be competitive candidates because of their high surface area, high porosity, low density, and reasonable thermal and mechanical stability [30–32]. Substantial MOFs have been extensively studied, such as MOF-2 [33], MOF-5 [22], MOF-177 [34], MOF-505 [29], Cu<sub>3</sub>(BTC)<sub>2</sub> [35], HKUST-1 [36], ZIF-8 [37], and XDOBDC (X = Mg, Ni, Zn, Co) [21,38] for CO<sub>2</sub> and H<sub>2</sub> adsorption at various temperatures and pressures. In comparison, XDOBDC MOFs show extraordinarily high CO<sub>2</sub> uptake, particularly at low partial

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pressures, and reasonable H<sub>2</sub> storage capacities, and thus they have attracted interest from many researchers. These characteristics are attributed to the presence of coordinatively unsaturated open metal sites that allow reversible interaction with CO<sub>2</sub>, together with large accessible surface areas that allow effective H<sub>2</sub> storage.

A series of XDOBDc MOFs that incorporate several open metal sites has been studied. For example, NiDOBDc [Ni-MOF-74 or Ni<sub>2</sub>(dobdc)] exhibits a reasonably high CO<sub>2</sub> storage capacity. It is also generally true that MgDOBDc has the best storage performance of all XDOBDc analogs; nonetheless, its sensitivity to air and moisture makes it incapable of conducting full regeneration, even though the samples are regenerated under high temperature and strong vacuum conditions. Thus, practical realization of MgDOBDc in industrial applications is still a long way off. However, NiDOBDc is highly favorable for gas storage application owing to its high surface area, high gas uptake capacity, and reasonable stability as compared to MgDOBDc [39]. Also, numerous synthesis protocols of NiDOBDc with various forms have been developed, particularly in nanocrystalline form [38]. Downsizing NiDOBDc to nanocrystals has made it possible to create polymer-based composite materials for various applications, including mixed-matrix membranes for molecular separation. In addition, the nanocrystalline form of NiDOBDc could possibly be used as building blocks for novel nanocomposite materials with a three-dimensional (3-D) architecture.

Graphene oxide (GO) is a two-dimensional (2-D) lattice of carbon atoms that contains hydroxyl, epoxy, and carboxylic groups, and its atoms are linked by strong covalent bonds [40]. In recent years, GO has been used in several applications, particularly in gas separation, because of its high aspect ratio, tunable surface functionality, and good thermal and mechanical properties [41–43]. The use of GO as a component in MOF composites has drawn great attention because the properties of both materials can effectively create a 3-D architecture. Bandoz et al. [44–46] first reported several MOF/GO composites that were prepared by dispersing MOF particles into a GO suspension for applications in gas adsorption and sensors. Meanwhile, Kumar et al. [47] synthesized hybrid composites of ZIF-8 and GO by in situ growth of MOF crystals on the GO surfaces. Xia et al. [48–51] successfully designed a series of MOF/GO composites using Cu-BTC, MIL-101, and MOF-505 that showed larger surface areas than pristine MOFs. However, previous studies thus far have used MOF particles larger than 50 nm or non-uniform crystals with a broad size distribution, which can cause the development of irregular structures in the resultant MOF/GO composites. Small MOF nanocrystals with uniform size and morphology are highly desirable to design a well-defined 3-D architecture with extra pore spaces for storage of gases.

In this study, 30-nm NiDOBDc nanocrystals with uniform size distribution were grown and sandwiched between GO sheets to form a GO/NiDOBDc nanocomposite with 3-D architecture. As exemplified in Scheme 1, the incorporation of GO could reduce the aggregation effects and create additional storage sites for gas molecules, resulting in increased gas storage capacity [52,53]. The synthesis method used is

facile and scalable. By optimizing the proportion of GO in the composites, we could maximize the CO<sub>2</sub> and H<sub>2</sub> storage capacity at room temperature.

## 2. Experimental

### 2.1. Materials

Nickel(II) nitrate hexahydrate [Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O], graphene oxide (GO) powder, methanol, ethanol, N,N'-dimethylformamide (DMF), and triethylamine (TEA) were purchased from Sigma-Aldrich. 2,5-Dihydroxy-1,4-benzenedicarboxylic acid (H<sub>4</sub>DOBDc) was purchased from Tee Hai Chem Pte. Ltd. These chemicals were used as received without further purification.

### 2.2. Synthesis of nanocrystalline NiDOBDc

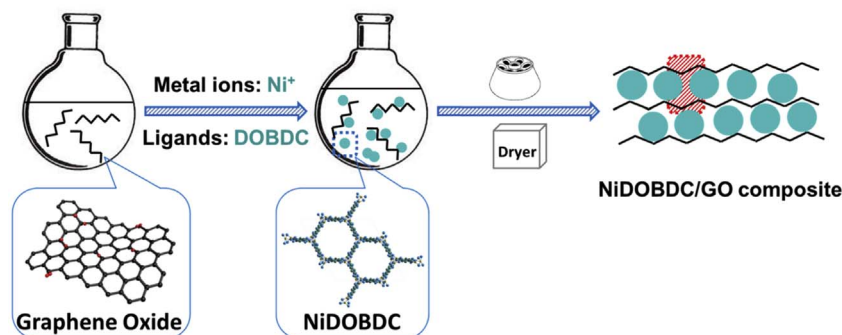
Nanocrystalline NiDOBDc was prepared as described in a previous report [38,54] with substantial modification. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (5.46 mmol, 1.5877 g) and H<sub>4</sub>DOBDc (1.7 mmol, 0.3368 g) were first dissolved in 135 mL of DMF. A separate solution of water/ethanol/TEA (9/9/1 mL) was prepared, which was then poured rapidly into the first solution. The resulting solution was subjected to 2 h of vigorous agitation at room temperature. The resulting precipitate was collected by repetitive centrifugation and washing with DMF. To ensure that the resulting crystals were free of impurities, the MOF crystals were re-dispersed in DMF and heated at 100 °C for 2 h. This process was repeated further by replacing the solvent with methanol without heating. The whole process was repeated twice. Before the necessary analysis and characterization, the residual solvent was removed in a vacuum at 60 °C for 24 h, from which red-brown nanoporous MOF crystals were collected.

### 2.3. Synthesis of NiDOBDc/GO composites

The synthesis of the NiDOBDc/GO composite was conducted in a manner similar to that described in Section 2.2, where graphene oxide (5, 8, and 10 wt%) was added to Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and H<sub>4</sub>DOBDc in 135 mL DMF. After completion of the synthesis, the precipitate was similarly redispersed first with DMF and then with methanol, with the exception that the process was conducted at 60 °C overnight because of the sensitivity of graphene oxide at elevated temperatures [55].

### 2.4. Characterization

Powdered X-ray diffraction (PXRD) patterns were measured using a Bruker D2 phaser diffractometer equipped with Cu Kα source in the 2θ range from 5° to 50°. Raman spectra were determined using Renishaw InVia Reflex Raman Spectrometer with a 633-nm incident laser source. The samples were observed using field emission-scanning electron



Scheme 1. Reaction and structural schematic of the NiDOBDc/GO nanocomposites.

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