



# Ultrafast room temperature synthesis of GrO@HKUST-1 composites with high CO<sub>2</sub> adsorption capacity and CO<sub>2</sub>/N<sub>2</sub> adsorption selectivity



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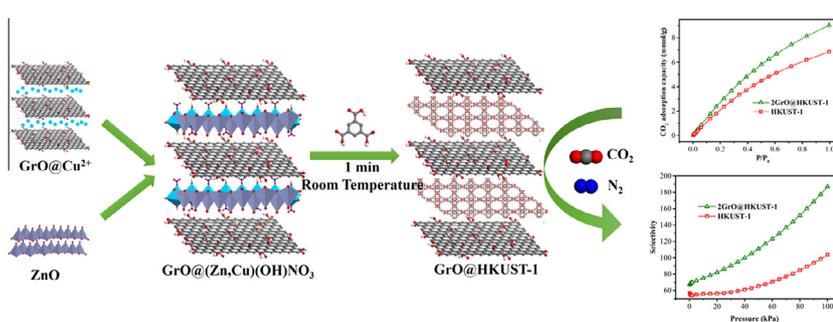
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## HIGHLIGHTS

- The GrO@HKUST-1 composites can be rapidly prepared at room temperature within 1 min.
- The GrO@HKUST-1 composites have a higher surface area compared to its parent HKUST-1.
- Its CO<sub>2</sub> adsorption capacity reached 9.02 mmol/g at 1 bar and 273 K, with an increase of 32% compared to HKUST-1.
- Its CO<sub>2</sub>/N<sub>2</sub> adsorption selectivity reached 186 at 1 bar, 1.8 times that of HKUST-1.

## GRAPHICAL ABSTRACT



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## ABSTRACT

An ultrafast synthesis method is developed for the preparation of composites of graphite oxide and HKUST-1, GrO@HKUST-1. Fast synthesis of GrO@HKUST-1 composites can be quickly achieved at room temperature within 1 min. The synthesized composites were characterized by XRD, SEM, N<sub>2</sub> adsorption, FTIR and TGA. The isotherms of CO<sub>2</sub> and N<sub>2</sub> on the as-synthesized materials were measured and the isosteric heats of CO<sub>2</sub> adsorption were estimated. The CO<sub>2</sub>/N<sub>2</sub> adsorption selectivities were predicted by means of ideal adsorbed solution theory (IAST). Results show that the GrO@HKUST-1 composites have higher BET surface area and pore volume than the parent HKUST-1. The CO<sub>2</sub> adsorption capacity of 2GrO@HKUST-1 (2% of GrO) is up to 9.02 mmol/g at 1 bar and 273 K, giving an increase of 32% in comparison of the parent HKUST-1. The isosteric heat of CO<sub>2</sub> adsorption on 2GrO@HKUST-1 is slightly higher than that of HKUST-1, suggesting the stronger interaction between CO<sub>2</sub> molecules and 2GrO@HKUST-1. The CO<sub>2</sub>/N<sub>2</sub> adsorption selectivity of 2GrO@HKUST-1 is significantly enhanced over pristine HKUST-1. At 1 bar, the CO<sub>2</sub>/N<sub>2</sub> adsorption selectivity of 2GrO@HKUST-1 is up to 186, while that of parent HKUST-1 is only 103. This rapid room temperature synthesis route is promising for new MOF-based composites.

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## 1. Introduction

With a rapidly depletion of fossil fuels since the industrial revolution, extensive amount of CO<sub>2</sub> has been released into the envi-

ronment, causing destructive consequences such as dramatic climate change and melting of polar glaciers [1]. Consequently, developing suitable and effective techniques toward abating the emission of the CO<sub>2</sub> into the atmosphere has becoming an urgent subject and topic. Currently, membrane separation [2], chemical absorption [3] and adsorption [4,5] have been proposed for CO<sub>2</sub> capture. Among them, physisorption-based processes has been

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regarded as one of the most low-energy and cost-effective technologies [6]. In the adsorption process, selection of the efficient adsorbent is crucial.

In the recent years, metal organic frameworks (MOFs) assembled with metal ions and organic linkers are attracting a great deal of attention [7]. MOFs are being considered vastly for their applications in a great variety of fields, ranging from gas adsorption and separation [8–16] to catalysis [17], luminescence [18–20], electronics [21], magnetism [22], drug delivery [23], sensing [24–26] and health science [27]. Up to now, MOFs have been developed as promising materials for CO<sub>2</sub> adsorption owing to ultrahigh surface area and porosity, diverse tunable pores and metal sites. Lin et al. [28] investigated the adsorption of CO<sub>2</sub> on MIL-101, and reported that the adsorption capacity of CO<sub>2</sub> was 1.6 mmol/g at 298 K and 1 bar. Yan et al. [29] measured the isotherm of CO<sub>2</sub> on Cu-BTC, and found that the CO<sub>2</sub> adsorption capacity on this MOFs was up to 6.49 mmol/g at 273 K and 1 atm. Caskey et al. [30] reported that the CO<sub>2</sub> adsorption capacity of Mg-MOF-74 was up to 10.3 mmol/g at 298 K and 1 atm.

Moreover, it was reported that the incorporation of graphite oxide into MOFs can enhance the adsorption performance of the resulting composite. Bandosz et al. [31] reported two types of MOF/graphite oxide (GO) hybrid materials, MOF-5/GO and HKUST-1/GO. It was found that these composites exhibited similar features in crystalline structure and porosity to the parent MOFs, and their ammonia adsorption capacities became higher compared to their parent MOFs due to creation of new pores between the two phases MOF units and GO. A few novel GrO@MOFs composites with higher adsorption capacities than their parental MOFs were recently synthesized. Zhou et al. [32] reported a novel GrO@MIL-101 composite with a CO<sub>2</sub> adsorption capacity of 3.6 mmol/g (298 K, 1 bar), significantly higher than that of MIL-101 (1.6 mmol/g). Ram et al. [33] demonstrated a simple procedure to prepare hybrid GO@ZIF-8 nanocomposites. Their results showed that the composite (ZG-20) exhibited remarkable CO<sub>2</sub> storage capacity (72 wt%) compared to the parent ZIF-8 (27.2 wt%). Liu et al. [34] prepared the composites based on Cu-BTC and graphene layers and reported that the materials obtained exhibited about a 30% increase in CO<sub>2</sub> storage capacity (from 6.39 mmol g<sup>-1</sup> of Cu-BTC to 8.26 mmol g<sup>-1</sup> of CG-9 at 273 K and 1 atm).

Nevertheless, most of the MOF composites were prepared by traditional solvothermal methods, which need high temperature and long reaction time. Rapid room temperature synthesis of MOF composites is highly desired for industrial implementation and commercialization. Li et al. [35] proposed a solvent-free mechanochemical method to rapidly synthesize composites (Cu-BTC@GO) of Cu-BTC and graphite oxide within 30 min, and reported a toluene adsorption capacity of Cu-BTC@GOs up to 9.1 mmol/g at 298 K, having an increase of 47% in comparison with Cu-BTC. While mechanochemical methods can tackle the challenge and reduce the reaction time (e.g. 30 min) and synthesis temperature (e.g. 25 °C), but vast external energy input was required to capacitate the chemical reactions. Therefore, it is desirable to seek for a more gentle and efficient method for the industrial implementation of MOF composites.

Recently, some metal oxides and hydroxides have been reported to act as nucleating agents or sources of cations for rapid synthesis of MOFs [36,37]. Zhao et al. [38] reported an ultrafast room temperature synthesis of MOFs using (Zn, Cu) hydroxyl double salt intermediates. They found that a (Zn, Cu) hydroxy double salt (HDS) intermediate formed in situ from ZnO particles enabled rapid growth (<1 min) of HKUST-1(Cu<sub>3</sub>(BTC)<sub>2</sub>) at room temperature. Synthesis of HKUST-1 was completed within 1 min at room temperature, showing feasibility of fast room temperature synthesis for bulk MOF powders and significant promise for scale-up processing. However, to the best of our knowledge there is no report

about using ultrafast synthesis to prepare composites of MOF and graphite oxide, in short, GrO@MOFs.

Herein, we reported an ultrafast synthesis of GrO@HKUST-1 at room temperature for the first time, and investigated the CO<sub>2</sub> and N<sub>2</sub> adsorption of the resulting composites. The synthesized samples were characterized by XRD, SEM, N<sub>2</sub> adsorption, FTIR and TGA. The CO<sub>2</sub> adsorption isotherms of the composites at different temperature were measured by a volumetric method. The isosteric heat of CO<sub>2</sub> adsorption on the composites was calculated based on the single component of CO<sub>2</sub>. The CO<sub>2</sub>/N<sub>2</sub> selectivities of the samples were predicted by using ideal adsorbed solution theory (IAST). Comparison between GrO@HKUST-1 and the parent HKUST-1 for adsorption of CO<sub>2</sub>/N<sub>2</sub> was made herein.

## 2. Experimental section

### 2.1. Materials

All chemicals were obtained from commercial sources and used as received without further purification. Starting materials include copper nitrate hydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Alfa, 99%), 1,3,5-benzenetricarboxylic acid (C<sub>9</sub>H<sub>6</sub>O<sub>6</sub>, Alfa, 99%), zinc oxide (ZnO, Alfa, 99%), N,N-dimethylformamide (C<sub>3</sub>H<sub>7</sub>NO, Guanghua, 99.8%), ethyl alcohol absolute (C<sub>2</sub>H<sub>5</sub>OH, Fuyu, 99.7%), graphite powder (C, Aladdin, size ≤ 30 μm), sodium nitrate (NaNO<sub>3</sub>, Guanghua, 99%), concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, Guanghua, 98%), potassium permanganate (KMnO<sub>4</sub>, Kaixin, 99.5%) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, Guanghua, ≥ 30.0%).

### 2.2. Solvothermal synthesis of HKUST-1

HKUST-1 was solvothermally synthesized following the modified procedure reported previously [39]. A solution of copper nitrate hydrate (0.725 g) in deionized water (12 mL) was added to a solution of 1,3,5-benzenetricarboxylic acid (0.42 g) in deionized water (12 mL) and ethyl alcohol absolute (24 mL). The mixture was stirred for 10 min and transferred to a 100 mL Teflon-lined autoclave. The oven was heated at 110 °C for 24 h. The resultant blue crystals were filtered, washed with ethanol and chloroform.

### 2.3. Synthesis of graphite oxide (GrO)

Graphite oxide was synthesized following the modified Hummers procedure reported previously [40]. Graphite powder (4 g) and sodium nitrate (4 g) were added to concentrated sulfuric acid (220 mL) and stirred in an ice bath. Then potassium permanganate (24 g) was slowly added to the mixture (below 283 K). The suspension was stirred for 30 min under ice bath, then stirred under room temperature for 48 h. Followed, 368 mL of deionized water was added to the beaker. The mixture was stirred for extra 15 min, and further diluted with 60 °C warm water (1120 mL). Subsequently, hydrogen peroxide (100 mL) was added and the suspension was aged for 12 h. The mixture was separated by centrifugation and washed with water. The remaining particles were transferred to a dialysis tubes. The deionized water should be refreshed frequently until no BaSO<sub>4</sub> precipitated by adding BaCl<sub>2</sub>. Finally, the suspension was spray-dried and fine brown graphite oxide were obtained.

### 2.4. Ultrafast synthesis of GrO@HKUST-1

The ultrafast synthesis of GrO@HKUST-1 composites was performed following the reported procedures [38] with a few modifications. First, ZnO powder (0.293 g) was dispersed in deionized water (8 mL) and sonicated for 10 min to form nanoslurry. Second,

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