



# Graphene-based porous materials with tunable surface area and CO<sub>2</sub> adsorption properties synthesized by fluorine displacement reaction with various diamines



Baoyin Li<sup>a</sup>, Kun Fan<sup>a</sup>, Xin Ma<sup>a</sup>, Yang Liu<sup>a</sup>, Teng Chen<sup>a</sup>, Zheng Cheng<sup>a</sup>, Xu Wang<sup>a,\*</sup>, Jiaying Jiang<sup>b</sup>, Xiangyang Liu<sup>a,\*</sup>

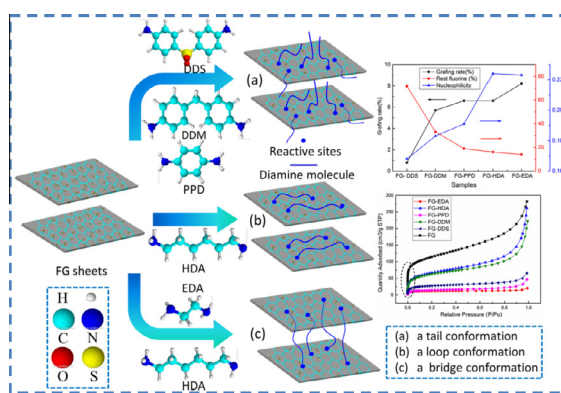
<sup>a</sup> College of Polymer Science and Engineering, State Key Laboratory of Polymer Material and Engineering, Sichuan University, Chengdu 610065, People's Republic of China

<sup>b</sup> School of Materials Science and Engineering, Shanxi Normal University, Xi'an 710062, People's Republic of China

## HIGHLIGHTS

- Graphene porous materials were constructed by intercalating fluorinated graphene.
- Both amino end groups of diamines during intercalating show a different reactivity.
- The porous properties depend on the size and structure of diamine intercalants.
- The intercalation of ethylenediamine shows excellent CO<sub>2</sub> adsorption performance.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 25 April 2016

Revised 27 May 2016

Accepted 30 May 2016

Available online 30 May 2016

### Keywords:

Fluorinated graphene  
Intercalating  
Reactivity  
Conformation  
Nanoporous

## ABSTRACT

A mild, operationally simple and controllable protocol for preparing graphene-based porous materials is essential to achieve a good pore-design development. In this paper, graphene-based porous materials with tunable surface area were constructed by the intercalation of fluorinated graphene (FG) based on the reaction of reactive C–F bonds attached to graphene sheets with various amine-terminated molecules. In the porous materials, graphene sheets are like building blocks, and the diamines covalently grafted onto graphene framework act as pillars. Various diamines are successfully grafted onto graphene sheets, but the grafting ratio of diamines and reduction degree of FG differ greatly and depend on the chemical reactivity of diamines. Pillared diamine molecules chemically anchor at one end and are capable of undergoing a different reaction on the other end, resulting in three different conformations of graphene derivatives. Nitrogen sorption isotherms revealed that the surface area and pore distribution of the obtained porous materials depend heavily on the size and structure of diamine pillars. CO<sub>2</sub> uptake capacity characterization showed that ethylenediamine intercalated FG achieved a high CO<sub>2</sub> uptake density of 18.0 CO<sub>2</sub> molecules per nm<sup>2</sup> at 0 °C and 1.1 bars, and high adsorption heat, up to 46.1 kJ mol<sup>-1</sup> at zero coverage.

© 2016 Elsevier Inc. All rights reserved.

\* Corresponding authors.

E-mail addresses: [wx19861027@163.com](mailto:wx19861027@163.com) (X. Wang), [lxxy6912@sina.com](mailto:lxxy6912@sina.com) (X. Liu).

## 1. Introduction

Graphene-based porous materials with designed porous nanostructure and high surface area are the most promising carbonaceous materials with potential applications such as catalytic supports and selective adsorbents because of their unique molecular structure and many exciting properties such as high mechanical strength, good chemical stability, large accessible surface area, and tunable porosity [1–3]. Recently, graphene-based porous materials have been widely developed such as N-doped porous graphene-based materials, which were mostly prepared by high temperature carbonization [4–7]. However, porous materials obtained in this way generally exhibit an uncertain chemical structure and a poor controllable or tailored pore structure due to the complicated decomposition process under such high temperature [8–10]. Therefore, a mild, operationally simple and controllable protocol for preparing graphene-based porous materials is essential to achieve a good pore-design development and a clear chemical structure.

Changing the interlayer spacing in few-layer graphene to generate novel porous materials would be an attractive alternative to develop new adsorbents with tailored properties for gas capture applications [11], since the simplicity of these reactions allows for the facile control over the physicochemical characteristics of the derivatives [12,13]. Modification of graphene oxide (GO) through intercalation or covalent linking with amines has been attempted to produce easy-to-design bridged or pillared graphene nanostructures [14,15]. However, the diversity of oxygen-containing groups on GO makes grafting reaction process uncontrollable and limits grafting sites, making GO not an ideal candidate for preparing porous materials with a tailored pore structure [16].

As a prominent member of the graphene derivatives, fluorinated graphene (FG) is a two-dimensional layered nanomaterial, which can be capable of undergoing one-dimensional expansion along its *c*-axis. FG can be prepared by fluorinating graphene or chemical/mechanical exfoliation of graphite fluoride [17,18]. Importantly, its properties can be tuned by adjusting the degree of fluorination [19,20]. As was previously reported, the fluorinated carbon backbone of these structures can serve as an activated precursor for diverse post-synthetic substitution reactions such as substitution reaction with amine-terminated molecules [21,22], providing essentially infinite possibilities to precisely fabricate graphene derivatives with desired properties [23–25]. A very recent paper describing the preparation of thiofluorographene from FG supports this idea [26]. Furthermore, unlike with GO, fluorination provides a single reactive C–F bond (F/C ratio up to above 1.0) instead of an ensemble of functional groups, thereby greatly simplifying the chemistry [27,28]. Therefore, FG can serve as an ideal precursor for preparing a variety of graphene derivatives with desired chemical structures and specified properties.

The purpose of this article is to prepare graphene-based porous materials via a mild chemical method as well as to elucidate the chemical reactivity of FG. In this work, we present an easy and controllable method to construct graphene-based porous materials via chemical modification of fluorinated graphene sheets with various organic diamines. Several different sizes of diamines ranging from inert aromatic diamines to active aliphatic diamines and computational simulation methods have been used with the objective of controlling the surface area and pore volumes by varying the size and structure of intercalants as well as assessing the reactivity of these functional groups in the intercalated structures. The results show that the intercalated difunctional molecules chemically anchor at one end and are capable of undergoing a different reaction on the other end. Furthermore, the obtained materials exhibit

different porogenic behavior that is sensitive to the size and molecular structure of the intercalants. CO<sub>2</sub> adsorption characterization suggests that the large CO<sub>2</sub> uptake is due to a combination of high-density strong basic sites and narrow microporosity.

## 2. Experimental

### 2.1. Materials

The F<sub>2</sub>/N<sub>2</sub> (10 vol% for F<sub>2</sub>) mixture with purity up to 99.99% were obtained from Chendu Kemeite Fluorine Industry Plastic Co., Ltd. Ethylenediamine (EDA), hexamethylenediamine (HDA) and *p*-phenylenediamine (PPD, 97%) were obtained from Chengdu Kelong Chemical Reagent Co., Ltd. 4,4'-diaminodiphenylmethane (DDM, 99%) and 4,4'-diaminodiphenyl sulfone (DDS, 98%) were purchased from Chengdu Best Reagent Co., Ltd. The detailed information of the above diamines including their chemical structure, charge density of nitrogen atom and molecule size is presented in Fig. 1 and Fig. S1 (see Supporting Information file). All other chemical reagents were commercially analytical grade and used without further purification.

### 2.2. Preparation of fluorinated graphene

Fluorinated graphene was prepared using previously reported direct heating fluorination method [29]. The spongy graphene oxide (GO) prepared by modified Hummer's method was placed in one container filled with the chemical reducing agent hydrazine (80 wt% water solution, 5 mL) and kept at room temperature for 72 h. Then the product was dried at 100 °C, and called as reduced spongy GO [30,31].

The fluorination was carried out in a Teflon lined autoclave using F<sub>2</sub>/N<sub>2</sub> mixture (10 vol% F<sub>2</sub>). An amount of reduced spongy GO (50 mg) was placed in the Teflon liner, and the autoclave was evacuated and filled with F<sub>2</sub>/N<sub>2</sub> mixture under 0.4 bar pressure. Fluorination proceeded with the temperature increasing from RT to 180 °C at a rate of 4 °C min<sup>-1</sup>, and maintained at this temperature for 1 h. After the completion of reaction, residual F<sub>2</sub> and by-products in the chamber were pumped out, then N<sub>2</sub> gas was carefully introduced into the chamber until atmospheric pressure was reached, at which point the sample could be extracted. The above fluorinated graphene was hereafter referred to as FG.

### 2.3. Preparation of various graphene derivatives

FG (50 mg) was dispersed in ethanol with the aid of ultrasonication for 30 min and then transferred to a one-necked round bottom flask with EDA (1.2 g, 20 mmol) in the presence of pyridine (3 drops) as a catalyst under a nitrogen atmosphere at 80 °C for 5 h [32]. The resultant suspension was diluted with ethanol and isolated by centrifugation to remove the unreacted EDA, and then filtered using a PTFE membrane filter with an average pore diameter of 0.22 μm. The ethylenediaminated FG were further washed in Soxhlet extractor using ethanol at 90 °C under a protection of nitrogen atmosphere in order to remove the physically adsorbed EDA. Finally, samples were dried in a vacuum oven at 60 °C for a minimum of 12 h prior to characterization. The graphene derivative, ethylenediaminated FG, is hereafter referred as FG-EDA.

The subsequent reactions with HDA and aromatic diamines (PPD, DDM and DDS) in the equal molar ratio with EDA were conducted following the same procedure in the case of FG-EDA, denoted as FG-HDA, FG-PPD, FG-DDM and FG-DDS (hereinafter collectively referred as graphene derivatives), respectively. The functionalized FGs with aromatic diamines (such PPD, DDM and DDS) needed be washed in Soxhlet extractor for a longer time

Download English Version:

<https://daneshyari.com/en/article/606228>

Download Persian Version:

<https://daneshyari.com/article/606228>

[Daneshyari.com](https://daneshyari.com)