



# Magnetic graphene foam for efficient adsorption of oil and organic solvents



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## ABSTRACT

This paper reported the preparation of magnetic graphene foam loaded with magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles and its application for the adsorption of oil and organic solvents. The foam with porous and hierarchical structures was derived from graphene oxide film reduced by gaseous reduction in a hydrothermal system. Drastically different morphologies of Fe<sub>3</sub>O<sub>4</sub> nanoparticles with nanosheet arrays or cubic structures were observed on graphene foam by controlling the reduction degree of graphene oxide under mild conditions. Benefiting from the integration of porous structures and magnetic properties, the graphene foam manifests outstanding oil adsorption capacity, high restoration for adsorbates as well as excellent recyclability and stability under cyclic operations. The simple and effective strategy for the preparation of graphene foams developed in this study may offer a new alternative for scale-up production of graphene materials used for the cleanup of oil spills.

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## 1. Introduction

Pollution by petroleum industry and oil transportation causes severe environmental and ecological problems every year [1–3]. Collection and recovery of oil spills using absorbent materials are promising methods and have got great attention due to their high clean-up efficiency. Various materials, including natural absorbents and synthetic polymers, have been applied to deal with the problems associated with the oil pollution. The natural absorbents, such as wool [4], vegetable fibres [5], perlite [6], are commonly used owing to their micro-porous structures. However, these conventional materials are suffered from the low oil adsorption capacity and poor selectivity, and in most cases water is absorbed in adsorbents together with oil. Polymer foams have been employed thanks to their large surface area and controllable hydrophobic property [7–9]. While they show relative high absorption ability, the materials are limited for wide applications because of their unclear impact to the environmental and ecological systems. Ideal materials for efficient adsorption of oil should have a high specific surface area, an inherently hydrophobic nature and excellent chemical stability. In this context, carbon-based materials are a good candidate for oil adsorption. Currently, many kinds of

carbon-based materials, such as activated carbon [10], expanded graphite [11], carbon fiber [12,13], carbon nanotubes (CNTs) [14], have been developed to remove petroleum products in water.

Graphene, a monolayer of carbon atoms arranged in a two-dimensional honeycomb network, possesses high surface area, excellent electrical conductivity, and high thermal and chemical stability [15–17]. In particular, three-dimensional (3-D) graphene frameworks, such as aerogels, foams and sponges, are an important class of new-generation porous carbon materials with interconnected micro- and macro-porous structures, low density and large surface area [18]. The 3-D materials have both hydrophobic and oleophilic properties, thus attracting much attention as an efficient oil adsorbent [19–23]. In a representative study, Yu et al. [19] reported the selective absorption of oil from water by a graphene-based aerogels prepared by a metal ion induced self-assembly process. Similar selective oil absorption was also reported by Qu et al. [20] using nitrogen-doped graphene framework. The prepared architecture showed an extremely low density ( $2.1 \pm 0.3 \text{ mg cm}^{-3}$ ), and much higher oil adsorption capacity than that of the best carbonaceous materials. Cheng et al. [21] prepared graphene sponges via hydrothermal process, the obtained sponges exhibited high adsorption ability to petroleum products and many organic solvents. Chen et al. [22] described the preparation of graphene foam by a leavening strategy and reported the high selectivity of graphene foams for oil adsorption.

While graphene foams or similar structures have been successfully prepared in recent years using different techniques, there are

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many issues to be addressed to optimize the structural, morphological and functional properties of the materials for oil adsorption. Additionally, the collection and reuse of graphene foams with saturated oil adsorption become a major concern for the practical application of these materials. The integration of magnetic properties in graphene foams offers a possible way to address aforementioned issues due to the facts that: (i) Magnetic foams can be conveniently collected by a magnetic field, and (ii) The plate-like structure of graphene can serve as a robust template for anchoring magnetic nanoparticles to prepare materials with hierarchical structures, offering an attractive roadmap to adsorb and separate hydrophobic materials from water.

This paper is a part of our endeavor in developing materials with multi-functionalities for engineering and environmental applications. Herein, 3-D graphene foams loaded with magnetic nanosheets or nanoparticles were prepared, aiming at overcoming the problems associated with the collection and reuse of graphene foams in real application. The composition and oil adsorption behavior of foams were studied, and the morphologies of magnetic particles controlled by the reduction degree of graphene oxide were presented.

## 2. Experimental sections

### 2.1. Materials

Powder-like graphite (Purity 99.99%, Sinopharm Chemical Reagent Co., China) was used in this study. Multi-walled CNTs were purchased from Nanotech Port Co., Ltd. (Shenzhen, China). The diameter and length of CNTs ranged between 20–40 nm and 5–15  $\mu\text{m}$ , respectively, according to the supplier's specification. CNTs were refluxed in nitric acid at 40 °C for 4 h to purify the raw materials and enhance their dispersion. Iron (II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and ammonia water ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ) (both from Tianjin Fuchen Chemical Reagent Factory, China) were employed as starting materials to prepare magnetic nanoparticles. Hydrazine hydrate and other reagents were purchased from Beijing Chemical Reagent Factory (Beijing, China). Ultrapure water with a resistivity of 18.2  $\text{M}\Omega \text{ cm}$  (Generated by Milli-Q Integral Water Purification System, Merck Millipore, Germany) was used in all experiments. All chemical reagents were analytical grade and used as received without further purification.

### 2.2. Preparation of graphene oxide (GO)

GO was synthesized from natural graphite powder by a modified Hummer's method as described elsewhere [24]. Briefly, 10 g graphite was added into a solution consisting of 50 mL concentrated  $\text{H}_2\text{SO}_4$ , 10 g  $\text{K}_2\text{S}_2\text{O}_8$  and 10 g  $\text{P}_2\text{O}_5$ , and stirred at 80 °C for 4 h. The mixture was diluted with deionized water, filtrated and dried to obtain oxidized graphite. 5 g oxidized graphite was put into 230 mL concentrated  $\text{H}_2\text{SO}_4$ , followed by the addition of 30 g  $\text{KMnO}_4$ . The mixture was stirred for 2 h and diluted with 600 mL water and continuously stirred for another 2 h. Then 50 mL  $\text{H}_2\text{O}_2$  (30 vol%) was added into the mixture, yielding a yellow solution. The solution was centrifuged and the product was washed with HCl solution (10 vol%) and water. GO was achieved by sonicating the product in water for 2 h, and then centrifuged at 5000 rpm for 10 min. Final GO was dried to prepare graphene foams.

### 2.3. Preparation of magnetic graphene foam

Fig. 1 schematically shows the experimental procedure for the preparation of magnetic graphene foam and subsequent removal

for oil. Graphene foam was prepared by the following process: GO (54 mg) was dispersed in water (40 mL) by ultrasonication for 2 h. After adding 6 mg of CNTs, the mixture was sonicated for another 30 min and then filtered by a vacuum filter equipped with cellulose-ester membrane (50 mm in diameter, 0.2  $\mu\text{m}$  pore size) to obtain a GO film. The thickness of film and corresponding foam can be controlled by the concentration and volume of solution. GO film was peeled off from the membrane by immersion method. The freestanding film was placed in an autoclave, followed by the addition of hydrazine hydrate (10 mL) into the autoclave. Graphene foam was obtained by keeping the autoclave at 90 °C for 10 h. During this process, the hydrazine hydrate was gasified and effectively entered into the layered GO films. The CNTs in the film, which serve as the space to effectively inhibit the re-stacking of GO sheets during the filtration. In addition, the introduction of CNTs reinforces the relatively flexible graphene foam and retains its structural integrity. Magnetic graphene foam was prepared by depositing in-site generated magnetic nanoparticles on graphene surface (Route I in Fig. 1). In a typical experiment, the prepared graphene foam was put into a  $\text{FeSO}_4$  solution ( $0.5 \text{ mol L}^{-1}$ ) and transferred into a sampler vial. The pH value of the solution was adjusted by ammonia to 9.5. Then the reaction vessel was placed in an oil bath at 80 °C for 6 h. After cooling down to room temperature, the foam was rinsed with water and dried at 50 °C. For comparison, reduced graphene oxide (rGO) film with magnetic particles was also made by using GO film (Route II in Fig. 1) while other synthetic conditions were kept the same.

### 2.4. Characterization

Various techniques were employed to characterize the elemental composition, surface chemistry and morphology of graphene foam. X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (D8 Advance, Bruker, Germany) with nickel-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ). The morphology of graphene foam was observed using a scanning electron microscopy (SEM, Zeiss Supra55VP, Germany) and a transmission electron microscopy (TEM, JEM-2010F, JEOL, Japan). Magnetic nanoparticles deposited on the surface of graphene-based materials (foam or film) were finely scratched from the substrate and characterized by TEM. Elemental analysis was carried out by the SEM equipped with an energy dispersive spectroscopy (EDS, X-flash-sdd-5010, Bruker, Germany). Raman spectrometry (RM2000, Renishaw, UK) was used to study the integrity of graphene foam. Surface functionalities on graphene were evaluated using an X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250xi, Perkin Elmer, USA). Thermal stability of graphene foam was characterized on a thermalgravimetric analyzer (TGA, STA 449F3, Netzsch, Germany) with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  from 30 to 800 °C in air atmosphere.

### 2.5. Adsorption capacity of magnetic graphene foam

The adsorption capacity of magnetic graphene foam ( $Q$ ) for oil and various organic solvents was calculated according to the following equation:

$$Q = \frac{W_{\text{After}} - W_{\text{Before}}}{W_{\text{Before}}} \quad (1)$$

where  $W_{\text{Before}}$  and  $W_{\text{After}}$  were the weight of magnetic graphene based foams before and after immersing in target liquids for 20 min, respectively.

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