A functionalized graphene aerogel for efficient water purification

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Water pollution has become a worldwide problem due to ever-increasing industrial wastewater. An ideal adsorbing material is able to remove oils, organic solvents and dyes from water efficiently, particularly with a high adsorption capacity and reusability. Herein, the authors report a novel strategy of synthesis of a three-dimensional functionalized graphene aerogel (FGA) with porous structures for effective water purification. The FGA is prepared by a facile one-step hydrothermal method, in which graphene oxide is reduced by ethylenediamine and modified by dodecyltrimethoxysilane to enhance hydrophobicity. When used as an adsorbing material, the FGA exhibits a high adsorption capacity (130–242 g/g for oils and organic solvents, 197–596 mg/g for dyes). Furthermore, the FGA also exhibits high reusability and durability by being reused for organic solvent–water separation for ten cycles without losing its hydrophobicity, which makes it a good candidate for industrial water treatment.

Notation

c_0	initial concentration of the dye
c_1	final concentration of the dye
M	weight after the functionalized graphene aerogel (FGA) has adsorbed the organic solvent
M_0	weight of FGA
m	weight of FGA
Q_e	dye adsorption capacity of FGA
Q_w	adsorption capacity of FGA
V	volume of the aqueous dye solution

1. Introduction

With the rapid development of industrialization, environmental pollution problems have attracted more and more attention. For example, oil spillage and chemical leakage accidents have occurred frequently during exploration and transportation processes, which result in severe environmental pollution.^{1–3} Therefore, many processes, such as chemical precipitation,⁴ physical adsorption,^{5,6} biodegradation method^{7,8} and membrane separation,^{9–12} have been developed to address oil spill pollution. Among these methods, the use of adsorption materials is considered one of the most promising methods for the removal of oils and organic solvents from water. Although traditional adsorption materials, including activated carbon (C),¹³ wool fibers,¹⁴ zeolites,¹⁵ straw¹⁶ and fly ash,¹⁷ have been widely used to remove oil from water, they still suffer from low adsorption capacities and poor recyclability. Thus, it is still a challenge to develop adsorption materials with high adsorption capacity and reusability.

Graphene, a novel two-dimensional (2D) material with remarkable properties,^{18–20} has attracted more and more attention due to its remarkable properties and is used in many fields, such as

sensors,^{21,22} supercapacitors,²³ catalysts^{24,25} and so on.²⁶ To translate the outstanding properties of 2D graphene into a macroscopic perspective, graphene should be assembled into a three-dimensional (3D) porous monolithic material. There are several methods for preparing 3D aerogels, including one-step hydrothermal method,²⁷ chemical vapor deposition,^{28,29} bidirectional freeze-drying approach³⁰ and 3D printing.³¹ Typically, these graphene aerogels (GAs) show a porous structure, a high specific surface area and hydrophobicity, which means that they can be used as adsorbent materials for water purification. Chen *et al.*³² reported a GA prepared by hydrothermal treatment and the freeze-drying method for oil absorption; its absorption capacity could reach 224–522 times its own weight. Hong *et al.*³³ prepared functionalized GA (FGA) by surface modification of GAs for adsorption of oils and organic solvents. Compared with the water contact angle (WCA) of the pristine GA (103°), the WCA of the functionalized GA was higher (144°). Benefitting from the structural features and hydrophobic surface properties, the FGA exhibited excellent absorption performance for oils and organic solvents (capacity up to 112 times its weight). In addition to oils and organic solvents, GAs have also been used to adsorb organic dyes. Chen *et al.*³⁴ prepared GA using the small organic molecule of cysteamine as a covalent cross-linker. The resultant graphene/cysteamine aerogels exhibited a high adsorption capacity for dyes, such as methylene blue (207.8 mg/g) and methyl orange (MO) (70.2 mg/g). Therefore, the GAs with high specific surface areas, high adsorption capacities and hydrophobic surface properties have great potential as recyclable and durable adsorbent materials for water purification.

Here, the authors report an FGA as an efficient and recyclable adsorbent for the removal of oils, organic solvents and dyes from water. Graphene oxide (GO) sheets with numerous oxygen

(O)-containing groups can link with ethylenediamine (EDA) and dodecyltrimethoxysilane (DTMS) through chemical reactions and realize the functionalization of graphene sheets. Benefitting from the hydrophobic nature of DTMS and the porous network of GAs, the FGA exhibits excellent hydrophobicity. The FGA can absorb a wide range of oils and organic solvents with an adsorption capacity of 130–242 g/g. More importantly, the FGA also exhibits excellent recyclability and maintains a high adsorption capacity even after ten cycles through distillation. The authors believe that the FGA with good adsorption performance will have great potential for water purification.

2. Results and discussion

The synthesis process of FGA is illustrated schematically in Figure 1. Firstly, a weak reducing agent (EDA) was introduced into the GO solution to functionalize it and initiate GO sheet assembly into a 3D network. At the same time, DTMS was used to modify the GO sheets, thus improving hydrophobicity. Secondly, after the hydrothermal treatment, the resultant functionalized graphene hydrogel (FGH) was obtained, which exhibited negligible volume shrinkage. Finally, the solvent was removed from the graphene hydrogel by freeze-drying to produce FGA. The reaction mechanism of the DTMS modification is shown in Figure S1 in the online supplementary material. DTMS is hydrolyzed under alkaline conditions, which the alkoxy group is converted to silanol groups.³⁵ Then, the silanol groups react with the hydroxyl group on the GO sheets to form covalent bonds under heating; meanwhile, water molecules are eliminated.³⁶

The interconnected porous structure of FGA with a pore size of several to dozens of micrometers was observed by scanning electron microscopy (SEM) (Figures 2(a) and 2(b)), where the pore walls consisted of partially stacked graphene sheets. In contrast, conventional GA made by the high-temperature hydrothermal method always has thicker pore walls, which are composed of severely stacked graphene sheets (Figure S2 in the online supplementary material). The SEM results indicate that EDA functionalization can suppress the restacking of graphene sheets during assembly, which can effectively improve the specific surface area of FGA. Meanwhile, compared with the smooth surface of pure graphene sheets (Figure S3 in the online supplementary material), the DTMS-modified graphene sheets show increased roughness (Figure 2(c)), which is beneficial for

Figure 1. Illustration of the fabrication process of the FGA

hydrophobicity. The wetting properties of FGA were studied by WCA measurement. When comparing the images in Figure 2(d), the DTMS-modified FGA shows a higher WCA of nearly 135° than that of pure GA (WCA = 106°), which confirms that DTMS modification can enhance hydrophobicity. Thus, the hydrophobic FGA with a porous structure can be used as adsorbing material. The energy-dispersive X-ray spectroscopy mapping of silicon and nitrogen is shown in Figures 2(e) and 2(f), which confirm that DTMS and EDA appear on the surface of GA.

The specific surface area is an important factor for the adsorbing material. Therefore, the specific surface area of the as-prepared FGA was characterized by nitrogen adsorption–desorption at 77 K, and the result is shown in Figure 3(a). The specific surface area calculated from the Brunauer–Emmett–Teller model³⁷ is 141.4 m²/g for FGA. The total pore volume is 0.441 cm³/g by calculation. The high specific surface area of FGA is advantageous in oil adsorption. In addition, Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy and X-ray diffraction (XRD) were conducted to reveal microstructural evolution. FT-IR analysis was further carried out to investigate the variation of the oxygen-containing functional groups in the reaction process. As shown in Figure 3(b), there are numerous oxygen-containing functional groups on GO, including the peak at 3424 cm^{−1} for –OH (stretching vibration),³⁸ at 1733 cm^{−1} for C=O (stretching vibration), at 1623 cm^{−1} for C=C, at 1418 cm^{−1} for carboxy C–O,

Figure 2. (a–c) SEM images of FGA; (d) measurement WCAs of pure GA and FGA; (e, f) elemental mapping showing the presence of silicon and nitrogen on the GA surface

Figure 3. (a) Nitrogen adsorption–desorption isotherm of FGA (STP, standard pressure and temperature); (b) Fourier transform infrared spectra; (c) Raman spectra; (d) X-ray diffraction patterns of GO and FGA

at 1225 cm⁻¹ for epoxy C–O and at 1054 cm⁻¹ for alkoxy C–O.³⁹ In comparison, FGA shows weak spectral intensities, and the peaks located at 1733, 1418, 1225 and 1054 cm⁻¹ almost disappeared. This indicates that GO was reduced by EDA during the hydrothermal process. Moreover, an additional peak appears at 1558 cm⁻¹ for C–N,⁴⁰ which demonstrates that EDA is grafted onto GO.⁴¹ Another new peak, appearing at 1088 cm⁻¹ for C–O–Si, indicates that DTMS reacts with the –OH of GO and forms a covalent bond to cross-link.³⁶ The Raman spectrum shows two peaks located at nearly 1320 and 1590 cm⁻¹, corresponding to the D- and G-bands (Figure 3(c)). The intensity ratio (I_D/I_G) can be used to evaluate the degree of graphitization in the carbon samples.⁴² The I_D/I_G ratio is calculated to be 1.05 and 1.14 for GO and FGA, respectively. The higher I_D/I_G ratio of FGA can be attributed to the EDA and DTMS functional group, which introduces defects to graphene sheets.⁴³ The graphitization degree of the as-prepared samples was also estimated by the using the XRD patterns. As seen in Figure 3(d), the XRD pattern of GO shows a sharp peak at 10.2°, which indicates that the crystallinity of GO is relatively high,^{44,45} corresponding to an interlayer space of 0.87 nm, which can be attributed to the oxygen-containing functional groups on the GO sheets. As for the FGA, the interlayer

space is calculated to be 0.50 nm, which indicates that the oxygen-containing functional groups are removed.^{46,47}

The variation of the elemental composition was determined by X-ray photoelectron spectrometry (XPS) analysis. As shown in Figure 4(a), the intensity of the peak corresponding to carbon located at 284.8 eV⁴⁸ increases from GO to FGA, while the change in the oxygen content (at 532 eV) shows the opposite trend. The XPS analysis further confirms the reduction of GO (the carbon/oxygen atomic ratio is 1.89) to FGA (the carbon/oxygen atomic ratio is 7.39) during the hydrothermal process. As shown in Figure 4(b), the presence of C–N (285.4 eV)⁴⁹ and C–O–Si (285.0 eV)⁵⁰ peaks in the high-resolution carbon 1s spectrum of FGA suggests that EDA and DTMS were grafted onto graphene sheets successfully.

The 3D porous structure and hydrophobicity of the FGA make it an ideal candidate for the removal of oils and organic solvents. When an FGA was placed on the surface of organic solvent–water mixtures, the organic solvent layer (dyed with Sudan Red I) started shrinking and disappeared completely after a few minutes (Figure 5(a)). To determine further the adsorption ability of FGA,

Figure 4. (a) XPS survey spectra of GO and FGA; (b) carbon 1s spectrum of FGA

Figure 5. Adsorption tests of FGA: (a) adsorption process of xylene (stained with Sudan Red I) on the surface of water by the FGA; (b) adsorption capacities of FGA for various oils and organic solvents (DMAC, dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone; DCM, dichloromethane; CTC, carbon tetrachloride); (c) adsorption recyclability of FGA over ten cycles

the authors investigated its adsorption capacities for different oils/organic solvents. The FGA showed excellent adsorption capacities ranging from 130 to 242 g/g. Recyclability is a key requirement in practical applications. Therefore, the authors further evaluated the recyclability of FGA through a simple sorption–distillation cycle by taking xylene as an example (Figure 5(b)). The vapor of the xylene was collected for recovery, and the FGA was regenerated. The sorption–distillation process was repeated ten times to study

the recyclability of FGA. As shown in Figure 5(c), the FGA showed stable sorption performance and no obvious decrease in sorption capacity was observed.

The adsorption mechanism for organic solvents and oils is as follows. There is a relationship between the adsorption of solids to liquids and their surface wettability. Therefore, the wettability of the adsorbent surface is important in oil–water separation.⁵¹

The wettability of a solid depends on its surface energy and morphology, and the wettability of a solid can be changed by adjusting these two factors.⁵² Therefore, the authors choose DTMS with low surface energy as the hydrophobic agent while grafting DTMS onto FGA to reduce surface energy. On the other hand, introduction of DTMS results in a rough surface of FGA. As a result, the FGA possesses hydrophobicity and lipophilicity. Therefore, FGA can adsorb organic solvents and oils from water.

In addition to oils and organic solvents, the FGA also shows high adsorption capability for dyes. As shown in Figures 6(a)–6(c), when FGA (1 mg) was put into aqueous rhodamine B (RB), MO and methyl blue (MB) solutions (8 ml, 20 mg/l) for 12 h, the color of each of the solutions gradually faded. To obtain the maximum adsorption capacity for dyes, an FGA with a mass of 20 mg was

put into the dye solution (50 ml, 1000 mg/l) for 24 h. The maximum adsorption capacities of FGA were calculated to be 197.3, 206.2 and 596.1 mg/g for RB, MO and MB, respectively (Figure 6(d)). These results suggest that the FGA can serve as an adsorbent for organic dyes. The adsorption mechanism for dyes is as follows. After reduction of GO, the π - π conjugate structure is restored between the layers; this conjugate structure interacts with the aromatic or heterocyclic structure of the dyes.⁵³ Therefore, FGA can adsorb dyes from water.

3. Experimental section

3.1 Materials

Natural graphite powder (100 mesh), DTMS and sodium tetraborate were purchased from Shanghai Aladdin Biochemical

Figure 6. Dye adsorption tests of FGA. One milligram of FGA was put into (a) rhodamine B (RB), (b) MO and (c) methyl blue (MB) aqueous solutions for 24 h. (d) Adsorption capacities of FGA for dyes

Technology Co., Ltd. Concentrated sulfuric acid (H_2SO_4), sodium nitrate (NaNO_3), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2) (30%), barium chloride and concentrated hydrochloric acid were provided by Tianjin Chemical Reagent Co. EDA was supplied by Tianjin Damao Chemical Reagent Factory. All reagents were used without further processing.

3.2 Synthesis of GO

GO was synthesized according to a modified Hummers' method as per the authors' previous report.⁵⁴ The procedure involved adding graphite flakes (5 g) into 130 ml concentrated sulfuric acid under constant stirring at 0°C . Then, 2.5 g sodium nitrate was added into the slurry, which was agitated for another 2 h. Afterward, 15 g potassium permanganate was added and stirred for 2 h. Afterward, the suspension was heated to 35°C and reacted for 30 min. After adding 230 ml deionized water dropwise, the temperature was raised to 98°C and held for 30 min. Finally, when the mixture cooled to ambient temperature, 500 ml deionized water and 5 ml hydrogen peroxide were added. The as-prepared slurry was washed by centrifugation several times to remove residual reactant (Figure S4 in the online supplementary material).

3.3 Synthesis of FGA

FGA was prepared through the one-step hydrothermal method. For the typical procedure, GO dispersion at a concentration of 2 mg/ml was prepared by sonication for 3 h. DTMS (60 μl), EDA (60 μl) and saturated disodium tetraborate solution (1 ml) were added to 20 ml GO suspension. Subsequently, the mixture was transferred to a 50 ml polytetrafluoroethylene-lined stainless-steel autoclave and kept at 120°C for 9 h. The obtained FGH was put into a 20% ethanol solution for 48 h to remove residual reagent. Finally, the FGA was obtained by freeze-drying the FGH.

3.4 Characterization

SEM (SU 8010, Hitachi, Japan) was carried out to observe the morphology of aerogels at a voltage of 15 kV. The porosity and specific surface area were measured by using a Quantachrome instrument (ASIQC 050200-6, USA). The elemental maps of aerogels were recorded by XPS (Rigaku, Japan). The functional groups of aerogels were identified by FT-IR using a Thermo Fisher Scientific instrument (USA). XRD was analyzed by using a MiniFlex II X-ray diffractometer (Rigaku, Japan). Raman spectral analyses were performed with a Senterra R200-L apparatus (Bruker Optics) under a 532 nm excitation laser beam in the range of $500\text{--}3000\text{ cm}^{-1}$. WCA measurements were carried out by using a JC 2000C contact-angle-measuring instrument (Powereach, China). The absorbance intensity of the dye aqueous solutions was measured by using a 752 ultraviolet-visible (UV-Vis) spectrophotometer (Spectrum Instruments, Shanghai).

3.5 Absorption capacity measurements

The organic solvent was poured into a beaker. Then, the FGA was immersed in the organic solvent after weighing. When the absorbent reached saturation, it was weighed again. The equation

is listed as follows to calculate the absorption capacity: Q_w is the adsorption capacity of FGA, M is the weight after FGA has adsorbed the organic solvent and M_0 is the weight of FGA.

$$1. \quad Q_w = \frac{M - M_0}{M_0}$$

RB, MO and MB were used to investigate the dye adsorption capacity of FGA. In this experiment, 20 mg FGA was put into the aqueous dye solution (50 ml, 100 mg/l); then, 1 ml solution was taken out for detection after 24 h. A UV-Vis spectrophotometer was used for the measurement of the dye concentration, and the maximum absorbance of each dye is 664 nm for MB, 464 nm for MO and 559 nm for RB. The following equation is listed to calculate the dye adsorption capacity: Q_e is the adsorption capacity; m is the weight of FGA; c_0 and c_1 are the concentrations of the dye initially and finally, respectively; and V is the volume of the aqueous dye solution.

$$2. \quad Q_e = \frac{(c_0 - c_1) \times V}{m}$$

4. Conclusion

In conclusion, FGA with a porous structure was successfully fabricated through a one-step hydrothermal method. With the introduction of EDA reduction and DTMS modification, the FGA shows a large surface area, a structure with abundant pores and high hydrophobicity, which are beneficial for improved adsorption capability. When used as an absorbing material, the FGA exhibits highly efficient and selective adsorption of oils, organic solvents and dyes from mixtures. In addition, organic solvents adsorbed by FGA were easily collected by distillation. Moreover, FGA could be reused for organic solvent-water separation for ten cycles without affecting its oil adsorption performance, demonstrating the great reusability and durability of FGA.

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