Original Article

Superhydrophobic and superoleophilic graphene aerogel for ultrafast removal of hazardous organics from water

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ABSTRACT

A facile approach to preparing functionalized graphene aerogels (FGAs) with superhydrophobic and superoleophilic properties was developed by modifying graphene aerogels with poly(dimethylsiloxane) (PDMS). The as-prepared FGAs displayed mesoporous structure with a high aspect surface area (157 m²/g), which afforded a high adsorption capacity toward various organic solvents with a remarkable value of 48–96 g/g. In addition, the resultant FGAs also exhibited a high separation efficiency (≥ 99%), ultrafast removal (a few seconds), and good recycling performance (10 cycles, 99% retention) toward multiple hazardous organics (chloroform, dichloromethane, n-hexane, toluene, petroleum ether, etc.) in water. These findings provide a promising material to improve the removal efficiency of hazardous organics for water purification.

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1. Introduction

With the rapid development of industry and economy, wastewater treatment becomes a worldwide challenge due to the ever-increasing discharge of organic chemicals from industrial community, which has triggered severe ecological and environmental problems [1]. In order to protect the clean water supplies from pollution, effective separation approaches are urgently needed. So far, a wide variety of approaches have been developed to remove organics from water, such as biological oxidation [1], adsorption [1], and chemical treatment [2]. Among these approaches, adsorption is one of the most efficient and environmentally friendly approaches for this purpose [3]. Generally, porous materials are considered as good adsorbents that play important roles in wastewater treatment, and thus considerable attention has been paid to the investigation of advanced porous materials, including meshes [4], membranes [5], fabrics [6,7], and sponges [8,9]. In order to endow these porous materials with superhydrophobicity and superoleophilicity, modification with nanoparticles, such as SiO2 [10,11], Fe3O4 [9,12],
Graphene, a two-dimensional monolayer consisted of sp²-hybridized carbon atoms, exhibits high specific surface area, porosity, and thermal stability [18–20], which makes it a superior candidate as absorbent materials. In recent years, graphene aerogel (GA) has been fabricated through constructing three-dimensional interconnected graphene sheets network, which has attracted considerable attention in the field of absorption materials [21–23]. However, because most of GA were prepared from graphene oxide with a lot of structural defects, leading to the hydrophilic nature [24], it is necessary to modify GA to achieve the excellent superhydrophobic and superoleophilic properties. Very recently, Xu et al. prepared a superhydrophobic graphene aerogel by a facile chemical reduction, exhibiting an absorption capacity of higher than 100 g/g for most of organic solvents [25]. Zhou et al. fabricated a polystyrene/Fe₃O₄/graphene aerogel composite through a solvothermal technique [26]. This aerogel composite was used to absorb diesel oil, lubricating oil, and crude oil from wastewater. Specifically, the crude oil absorption capacity was 40 times its own mass after 10 cyclic operations. However, the separation efficiency of the graphene aerogels has been seldom investigated.

In this study, we present a facile approach to the fabrication of functionalized graphene aerogels (FGAs). First, a graphene aerogel was obtained by self-assembly of graphene oxide nanosheets. Then, we deposited polydimethylsiloxane (PDMS) coatings onto the frames of the GAs to convert their wettability from hydrophilic to superhydrophobic. The as-prepared FGAs possessed excellent repellency for water as well as strong affinity with organic solvents, which would be suitable as promising absorbents for ultrafast removal of hazardous organics from water.

2. Experimental

2.1. Materials

Natural graphite powder (99.95%) was obtained from Aladdin Chemicals Co., Ltd. Ethylenediamine (EDA), concentrated sulfuric acid, potassium permanganate, sodium nitrate, hydrochloric acid, hydrogen peroxide (30%), toluene, n-hexane, cyclohexane, petroleum ether, dimethylenzene, chloroform, dichloromethane, methylene blue, and Sudan II were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Poly(dimethylsiloxane) (PDMS) prepolymer (Sylgard 184A) and the curing agent (Sylgard 184B) were supplied from Dow Corning Corporation (Shanghai, China). All the reagents were used as received.

2.2. Synthesis of GA and FGA

Graphite oxide (GO) was prepared via a modified Hummers method. The as-fabricated GO was dispersed into deionized water to form a dark brown suspension (2 mg/ml) by ultrasonication for 30 min. Next, 30 µl of ethylenediamine was added as a reducing agent, and the suspension was treated by ultrasonication in an ice bath for another 1 h. Then, 7.5 ml of the suspension was placed in a 10 ml vial and maintained at 120 °C in a 25 ml Teflon-lined autoclave for 2 h. Afterwards, the autoclave was naturally cooled to ambient temperature to obtain the graphene hydrogel. Then, the hydrogel was frozen at −80 °C for 24 h and then freeze-dried into the graphene aerogel. The FGA was finally achieved by immersing the as-prepared GA in chloroform solution containing 2 wt% Sylgard 184A and 0.2 wt% Sylgard 184B for 2 min and subsequent dried at 80 °C for 2 h.

2.3. Characterization

The contact angle was determined by a SL200B Contact Angle System (Solon Tech. Co., Ltd., China) at ambient temperature, and the drop volume used was 4 µl. At least six parallels were tested and the average value was reported for each sample. The morphology of the samples was observed using an EVO MA15 scanning electron microscopy (Zeiss, Germany). The samples were sputtered with a conductive layer of gold prior to observation. The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Dmax/rA diffractometer (Japan) using copper Kα radiation (λ = 0.15405 nm), operating at 40 kV voltage and 20 mA current. X-ray photoelectron spectroscopy (XPS) was performed on a VG Escalab Mark II spectrometer (Thermo-VG Scientific Ltd., UK), using Al Kα excitation radiation (hv = 1253.6 eV). Fourier transform infrared (FTIR) spectra were obtained on a Nicolet 6700 spectrophotometer (USA) using KBr disk method. Thermogravimetric analysis (TGA) of the samples was measured on a TA Q5000 thermal analyzer (USA) in air atmosphere from 30 °C to 800 °C at a heating rate of 20 °C min⁻¹. N₂ adsorption-desorption isotherms were carried out at 77 K using ASAP 2010 apparatus (USA). The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) method, and the pore-size distribution curves were obtained from the adsorption branch by the Barrett–Joyner–Halenda (BJH) method.

2.4. Oil uptake experiments

The absorption capacity of FGA for various organic solvents was measured by weight gain before and after absorption. Typically, the initial weight of the FGA was recorded as W₀. The FGA was then immersed into organic solvent. Afterwards, the sample was taken out and the surface solvent was removed using a filter paper, the sample was weighed. When its weight was constant with increasing immersion time, this weight was recorded as W. The absorption capacity (Q) was calculated by the following formula:

\[ Q = \frac{W_0 - W_i}{W_i} \]
To regenerate the FGA, the FGA with absorbed organic solvent was dried at 80 °C for 1 h in an oven. Subsequently, the FGA was naturally cooled down to room temperature, and the as-dried FGA was used in the following absorption-drying process.

To determine the separation efficiency of FGA, a mixture of 15 ml water and 5 ml chloroform was poured into the beaker. A piece of FGA was immersed into the mixture for 10 min, and then the chloroform weight in the residual mixture was measured by HPLC. The separation efficiency (η) was calculated using the following formula:

\[ η (\%) = \frac{M_a - M_b}{M_b} × 100 \]

where \( M_a \) and \( M_b \) are the chloroform weight in the mixture after and before separation, respectively.

3. Results and discussion

3.1. Structural characterization

The graphene aerogel (GA) was prepared by a two-step procedure: firstly, the graphene hydrogel was synthesized by self-assembly of graphene oxide into a three-dimensional network with EDA as the reducing agent; then the solvent was removed from the resultant graphene hydrogel by lyophilization to obtain the graphene aerogel. Afterwards, the FGA was produced through a facile dipping GA into poly(dimethylsiloxanes) solution. Fig. 1a gives the digital photograph of the cylindrical FGA. This FGA could stand up on a dandelion without breaking its fluffs (Fig. 1b), implying that the FGA is very light. In fact, its density was only 15.0 mg/cm³. The water contact angle was tested to assess the hydrophobicity of the GA and FGA. The digital and optical photographs of a water droplet on the top-surface and side-surface of GA and FGA are displayed in Fig. 1c and d, respectively. For pristine GA, both the top-surface and side-surface absorbed the water droplets fast, indicating good hydrophilicity. After functionalization by PDMS, FGA converted into hydrophobic materials, and it could be seen that the water droplets remained stable on the top-surface and side-surface of FGA. The water contact angle of the top-surface and the side-surface of FGA were 150.9° and 150.1°, respectively. Therefore, functionalization of GA by PDMS demonstrated to be effective to change its hydrophilic nature to superhydrophobic. Additionally, the organic solvent contact angle including n-hexane and chloroform of the top-surface and the side-surface of FGA were 0°, indicating FGA was oleophilic.

X-ray diffraction was performed to characterize the structural changes before and after the functionalization of GO. The XRD profiles of GO and FGA are presented in Fig. 2. As can be observed, GO exhibited a diffraction peak at 2θ = 10.5°, corresponding to an interlayer spacing distance of 0.84 nm. In contrast, GA displayed no visible peak at 2θ = 10.5° in its XRD profile, indicating the destruction of ordered structure of GO. Instead, GA displayed a quite broad diffraction peak at 2θ = 23.5°, which was attributed to the graphene nanosheets
in FGA were poorly ordered along their stacking direction [27]. After functionalization of GA by PDMS, FGA showed similar XRD profile as GA. No visible peak except a broad one at around 2θ = 23° was observed, implying the formation of disordered three-dimensional networks of graphene sheets.

The FTIR spectra of GO, GA and FGA are displayed in Fig. 3. In the FTIR spectra of GO, some characteristic bands were observed: the C=O stretching vibration in the carboxylic acid groups (1730 cm\(^{-1}\)), aromatic C=C stretching vibration (1620 cm\(^{-1}\)), C=O stretching vibration in the epoxy groups (1225 cm\(^{-1}\)) and alkoxy groups (1053 cm\(^{-1}\)) [28]. Additionally, GO also exhibited a broad band at around 3400 cm\(^{-1}\), originating from the O–H stretching vibration in the absorbed water or C–OH groups. After chemical reduction with EDA, the band intensity at 1730, 1620, 1225 and 1053 cm\(^{-1}\) of the resultant GA decreased notably, indicating that most oxygen-containing functional groups were removed after chemical reduction. Instead, there were two new bands at 1568 and 1185 cm\(^{-1}\), which were assigned to N–H stretching vibration and C–N stretching vibration, respectively. Hence, the amino groups of EDA were bonded covalently to the graphene sheets of GA. Previous literature also reported that the amino groups could be covalently attached to the reduced graphene oxide [29]. Besides these bands in the FTIR spectrum of GA, FGA also displayed another four intensive characteristic bands at 2965, 1262, 1080 and 802 cm\(^{-1}\), which were attributed to –CH\(_3\) stretching vibration in Si–CH\(_3\), –CH\(_2\) deformation vibration in Si–CH\(_2\), Si–O–Si stretching vibration and Si–C stretching vibration in Si–CH\(_3\) [30]. These four bands originated from the PDMS species, demonstrating the successful deposition of PDMS on the graphene sheets of FGA.

X-ray photoelectron spectroscopy (XPS) was also carried out to further verify the change in the chemical composition of GO and FGA. Their C\(_1s\) XPS spectra are shown in Fig. 4. In the case of GO, three different peaks at 284.6, 286.6 and 288.2 eV were detected, which were assigned to the non-oxygenated ring C atoms (C–C/C=C), the C atoms in hydroxyl and epoxy/ether groups (C–O), and the carbonyl C structure (C=O), respectively [31]. The C\(_1s\) XPS spectrum of FGA also exhibits these three peaks, however, the peak intensity of oxygen functionalities (C–O and C=O) was considerably decreased due to the reduction of GO by EDA.

The TGA curves of GO, GA and FGA under nitrogen atmosphere are presented in Fig. 5. GO was thermally unstable and began to lose weight even below 100 °C, which was attributed...
Fig. 5 – TGA curves of GO, GA and FGA under nitrogen atmosphere.

to the loss of physical absorbed water in the samples. The major mass loss (about 30%) occurred in the temperature range from 160 to 250 °C, presumably assignable to the decomposition of the oxygen-contained functional moieties such as epoxy and hydroxyl [32]. GA exhibited similar thermal degradation behavior as GO, but much higher thermal stability than GO beyond 210 °C. The increased thermal stability was ascribed to that part of thermally labile oxygen functional groups were chemically reduced by EDA during the preparation of GA. By comparison, no visible mass loss was observed when the FGA was heated up to 150 °C, implying FGA was repellent to water vapor. Also, FGA showed much higher thermal stability than GO and GA before 620 °C due to the presence of highly thermally stable PDMS coating. However, FGA displayed more mass loss than GA in the range of 620–800 °C, which was basically attributed to the decomposition of organic PDMS species.

The superhydrophobicity of the graphene aerogel related close with their morphological features [33]. The morphology of GA and FGA was examined by field emission scanning

Fig. 6 – SEM micrographs of (a, b) GA and (c, d) FGA in different magnifications. Inset of d: silicon elemental mapping image of FGA.

Fig. 7 – \( N_2 \) adsorption–desorption isotherms and BJH (Barrett–Joyner–Halenda) pore-size distribution plot (inset) of FGA.
electron microscopy (SEM). SEM micrographs of GA in different magnifications are shown in Fig. 6a and b, while those of FGA are presented in Fig. 6c and d. GA exhibited a hierarchical porous structure with interconnected pore sizes ranging from tens to hundreds of micrometers. This porous structure was constructed by the randomly dispersed graphene sheets. In the high magnification SEM micrograph (Fig. 6b), the graphene sheets showed a crumpled surface with size...
of several micrometers. After treatment of GA by PDMS, the roughness of the FGA became more obvious and the pore sizes between graphene sheets became smaller due to the presence of PDMS. To further verify the presence of PDMS, the silicon element distribution mapping of the FGA is provided in the inset of Fig. 6d. The uniform dispersion of PDMS on the surface of graphene sheets was also evidenced by the silicon element distribution mapping.

The porosity and surface area of the as-prepared FGA were examined using N<sub>2</sub> adsorption–desorption measurements. Fig. 7 shows the N<sub>2</sub> adsorption–desorption isotherms and the corresponding BJH pore size distribution plot. The FGA displayed a type IV isotherm with H3 hysteresis loop at high relative pressure, indicating a typical mesoporous material [34]. The surface area of FGA was 157 m<sup>2</sup>/g, which was determined by fitting the isotherms with the Brunauer–Emmett–Teller (BET) model. Its surface area was comparable to that of the graphene aerogel in the previous report [35]. The pore size distribution plot (inset of Fig. 7) exhibited two peaks at ca. 4 and 15 nm, which can be associated to the smaller pores within graphene nanosheets and the larger pores formed between stacked graphene nanosheets, respectively. This mesoporous structure of the FGA enables itself quite suitable to be used as an adsorbent material.

Owing to the simultaneous superhydrophobicity and superoleophilicity, the FGA may find potential application as an adsorbent material for oil/water separation. As shown in Fig. 8a–c and Video S1 (Supporting Information), n-hexane was mixed with water (dyed blue with methylene blue), forming a thin oil layer; then, a piece of the as-prepared FGA was dipped into the mixture. The n-hexane was absorbed quickly within only several seconds (approximately 15 s), with no visible oil remaining in the mixture. Afterwards, the absorbed organic solvent could be removed by squeezing the FGA (Fig. 8d). Furthermore, oil with a higher density than water, such as chloroform, was also applied to determine the separation ability of the FGA. When immersing the superhydrophobic/superoleophilic FGA into the chloroform/water mixture, it could rapidly absorb the chloroform underwater, demonstrating its excellent superoleophilicity (Fig. 8e–g and Video S2). Similarly, the absorbed chloroform could be easily separated by squeezing the FGA (Fig. 8h). Fig. 8i showed the absorption capacity of FGA for a variety of organic solvents, which were in the range of 48–96 g/g. Its absorption capacity is much higher than that of superhydrophobic fabrics [7]: FGA absorbed chloroform, dichloromethane, n-hexane, dimethylbenzene and petroleum ether at rates of 96×, 92×, 51×, 62×, and 48×, respectively, whereas the corresponding values for the superhydrophobic fabrics are 1.4×, 1.3×, 0.7×, 1.1×, and 0.7×. In addition, the as-prepared FGA also exhibited greater absorption capacity than its counterpart, gallic acid based graphene aerogel [36] and was comparable to previously reported spongy graphene [37]. Recyclability is another crucial parameter for an ideal absorbent. The recyclability of FGA was tested in the chloroform/water mixture. As shown in Fig. 8j, the separation efficiency of FGA was still higher than the 99% even after ten absorption-drying cycles. This result demonstrates the excellent recyclability of FGA for removal organics from water.

4. Conclusion

Functionalized graphene aerogel (FGA) with simultaneous superhydrophobicity and superoleophilicity was fabricated by a facile surface modification. The resulting FGA showed ultra-low density, great specific surface area, and high water repellency, which was suitable as an absorption material. The FGAs demonstrated a high absorption capacity (48–96 g/g), high separation efficiency (>99%), ultrafast removal (a few seconds), and good absorption recyclability (10 cycles, 99% retention) toward multiple hazardous organics. The findings reported in this study provide a promising material for water purification.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jmrt.2019.11.008.

Conflicts of interest

The authors declare no conflicts of interest.

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