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COMMUNICATION

Highly enhanced performance of spongy graphene as oil sorbent

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This work demonstrates a brand-new spongy graphene with a highly enhanced performance as oil sorbent. The absorption capacity of the new spongy graphene to chloroform reaches 616 times of its own weight, which is approximately 8 times higher than that in previous reports. The absorption capacity towards other organic chemicals is also greatly improved.

Introduction

Graphene-based three-dimensional carbon macrostructures, including 3-D porous structures, have attracted attention for their physical/chemical properties including ultrahigh surface area.¹⁻³ Such materials have been studied in solar cells,^{4,5} lithium-ion batteries,⁶⁻⁸ various sensors,⁹⁻¹² supercapacitors,¹³⁻¹⁶ and in other systems.¹⁷ We recently reported a 3-D carbon macrostructure based on self-assembly of graphene-based nanosheets, namely “spongy graphene”, as a selective and efficient absorbent of oils and organic solvents.¹⁸

Leakage of oil as well as toxic or flammable chemicals is an environmental problem. The materials tested for mitigating oil pollution in marine environments include natural products,^{19,20} expanded graphite,²¹⁻²⁴ carbon nanotube structures^{25,26} and polymeric sorbents,²⁷⁻³¹ among others. However, these materials suffer from problems such as low capacity, high cost, inconvenient to use, or potential safety issues.

3-D graphene and its derivatives are low-cost, recyclable, and safe alternative oil sorbents. In our previous report, a 3-D macrostructure based on graphene nanomaterial produced by chemical exfoliation and reduction, i.e., SG, has been proposed as an efficient and recyclable oil sorbent.¹⁸ Details on the improved performance of this SG is described in the present paper. The absorption capability improved by 8 times to over 600 times the weight of SG.

Results and discussion

Graphene oxide (GO) was obtained following an improved Hummer's protocol.^{32,33} GO bulks were then fabricated by freeze-casting technique. Heat treatment up to 1000 °C in an inert atmosphere enabled the reduction of GO to SG. Finally, SG bulks were placed on the flame of an alcohol burner or wax candle for several seconds to obtain the final form of SG. Figure 1 shows a schematic of SG fabrication. SGs without

flame treatment are abbreviated as SG-R, whereas flame-treated SGs are called SG-F (Experimental Section). The SG density was measured to be $\sim 0.9 \text{ mg cm}^{-3}$ based on Archimedes' theory, which indicated that the percentage of air-containing cavity was $>99.9\%$ (the theoretical density of pure, solid graphite bulk was believed to be $>2.2 \text{ g cm}^{-3}$).

Microscopic structures of SG-R and SG-F were identified by scanning electron microscopy (SEM) (Figs. 2a and 2b). Unlike the SG in our previous report, no obvious flaky, cabbage-like structure was observed in SG-R and SG-F. Instead, denser, cross-linked pores 10 μm to 50 μm in diameter were observed. More combined homogeneous pores with lower density were also observed, which indicated that the graphene nanosheets used to construct SG-F were thinner, thereby directly affecting the shapes of sponges from GO rather than those from graphene by freeze casting. The dispersive ability of GO in aqueous solution was better than that of reduced GO because GO was more hydrophilic, which indicated that the sponge had smaller and denser porous structures. In the subsequent reduction, the GO sponge was chemically reduced into SG-R without changing the structural appearance. Therefore, the as-proposed protocol further reduced the density while increasing the cavity percentage, which resulted in greater absorptive efficiency.

A serious problem occurred when SG-R was used for oil absorption. Although SG-R had a lower density and a larger air-containing volume, water permeated into the SG-R body at a slow rate. Despite the hydrophobicity of the graphene nanosheets, the high cavity content and appropriate pore size of SG-R caused bulk water absorption, which deviated from the initial aim and rendered oil absorption pointless. Various efforts have been exerted to avoid this unwanted phenomenon. Flame treatment has been adopted because it is simple and the effect is sufficiently stable. Incomplete combustion candle or alcohol produces amorphous carbon nanoparticles (CNPs) on top of the flame. The soot is also composed of various types of CNPs.^{34,35} The flame soot treatment can be used as an effective strategy for surface modification because CNPs strongly adhere (Fig. S1, Supporting Information) onto the interior region of a bulk material and modifies SG-R into SG-F, which completely repels water. Figure 2b demonstrates the adhesion of CNPs onto graphene nanosheets. Compared with SG-R (Fig. 2a), the graphene sheets in SG-F (Fig. 2b) had a rougher surface with homogeneously adhered CNPs from the

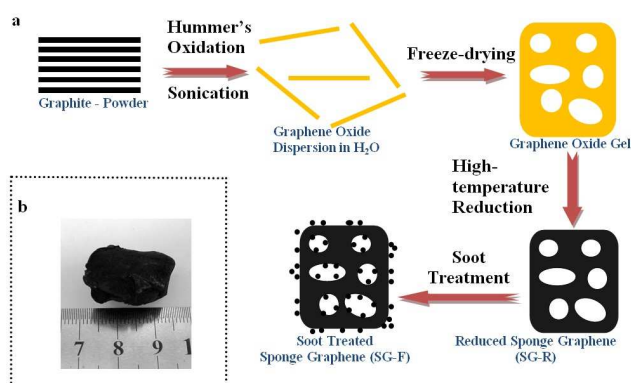


Figure 1. Fabrication and macroscopic appearance of spongy graphene (SG). a) Fabrication of SG. The components are intentionally drawn not into scale. b) Macroscopic image of SG bulk.

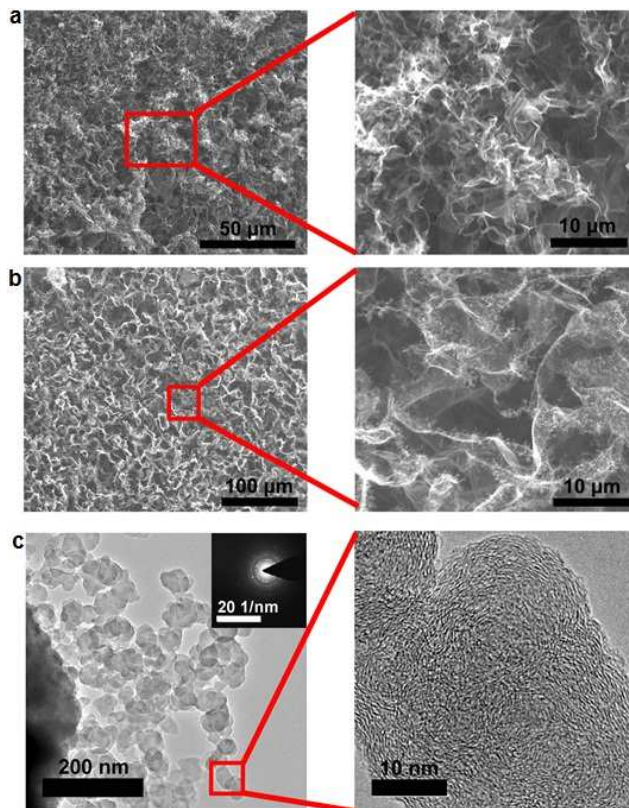


Figure 2. Microscopic analysis of the structure of SG. a) SEM images of SG-R. Scale bar: 100 μm and 10 μm , respectively; b) SEM images of SG-F. Carbon nanoparticles (CNPs) could be observed on the surface of graphene nanosheets. Scale bar: 100 μm and 10 μm , respectively; c) TEM image of CNPs observed in b) and the corresponding high-resolution image. Inset: Micro-zone diffraction pattern of CNPs, indicating the part crystallization of the nanostructure.

combustion soot of a candle, even at the center of the cross-section. The detailed structure of these CNPs was characterized by transmission electron microscopy (TEM). As shown in Fig. 2c, the partly crystallized CNPs were composed mainly of 30 nm to 50 nm-diameter nanospheres. As mentioned above, although SG-R was hydrophobic, its surface still slowly absorbed water (Fig. 3a), whereas the CNP structure made the external surface of SG-F water resistant (Fig. 3b). In addition, both SG-R and SG-F had similar backbone structures composed of graphene nanosheets (Figs. S2, S3, and S4, Supporting Information), which indicated that soot treatment did not change the overall microstructure of SG. We also found that the surface of SG-F was self-cleaning, wherein water droplets completely slipped when the surface was inclined at several degrees (Fig. S5, Supporting Information). The mechanism was similar to that of lotus leaves, as discussed in detail elsewhere. By contrast, a water drop stuck onto the surface of SG-R even when tilted to 60° (Fig. S6, Supporting Information). Therefore, the self-cleaning ability of a sponge when tilted was an indicator of effective soot treatment and quality of water-resistant SG sorbent. The absorption of SG-F toward various types of alkanes, fats, and organic solvents was examined, and Figs. 3c and 3d show the absorption of crude oil (dark brown) (Movie S1, Supporting Information) and phenixin (underwater, stained with Sudan red 5B) by SG-F (Movie S2, Supporting Information), respectively.

SG-F still functions even at the bottom of a container when it is used to absorb a substance with density higher than water. We found that the sponge can repel water by forming a protective air shell on its outer surface caused by its superhydrophobicity while maintaining its oil absorbing capacity (Fig. 3d). Submerged SG-F absorbed phenixin by releasing the air bubbles from its surface until it was fully saturated (Movie S2, Supporting Information). This commendable property indicated the possibility for environmental applications in absorbing floating pollutants and those underwater.

Figure 4 shows the absorption capacities of SG-F on various organic liquids (black bars), including alkanes, fats, and organic solvents. The absorption capacity was evaluated by weight gain, i.e., the ratio of total mass after absorption to

the initial mass of SG. Weight gain dramatically improved compared with our last report (shown in red bars).¹⁸ The absorption capability of SG was generally >100× its own weight. For instance, the absorption toward chloroform was close to 616×, whereas only ~86× has been previously found. To the best of our knowledge, this absorption capacity was one of the highest among all absorbents reported to date for oils and organic solvents (Table S1, Supporting Information). For example, in pump oil and chloroform, the absorption capacity corresponding to 30% to 40% of the pore volume was filled with the absorbates. The inner bone structure of graphene nanosheets also had sufficient mechanical strength that can bear a load 100× its own weight, which can be attributed to the superior mechanical properties of cross-linked graphene material.

Conclusions

Table 1 compares the SG-F fabricated in the present and previous studies.¹⁸ In a typical procedure, the fabrication process was improved to fabricate SG with lower density and porosity. A new surface treatment, flame soot treatment, was used to regulate the hydrophobicity of the outer surface of SG. The graphene nanosheets had CNPs that formed hierarchical carbon structures. This unique structure exerted a lotus leaf-like effect on the surface of SG, i.e., superhydrophobicity and

self-cleaning ability. Given the lower density of the current

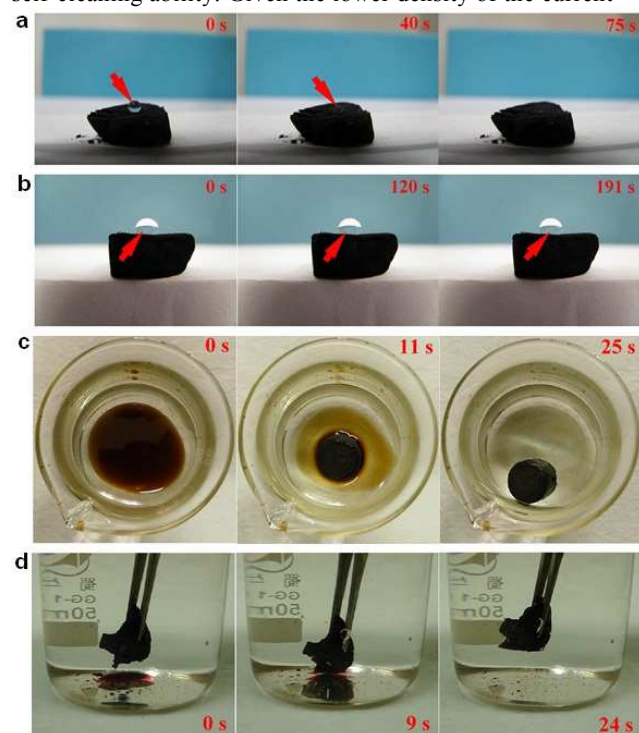


Figure 3. Water and oil absorption of graphene sorbent. Series of digital photos showing the water / organic chemicals absorption by the graphene sorbent. a) A water drop was completely absorbed by SG-R (without soot treatment) after 75 seconds; b) SG-F, the sorbent treated with candle soot, shows excellent water resistance, indicating that the carbon nanoparticles generated by the soot play a critical role on deciding the performance of the spongy graphene; c) The SG-F absorbs crude oil (dark brown, thick liquid) floating on the water; d) The SG-F absorbs phenixin (dyed with red color) from the bottom of the water.

Table 1. Improvements of the new SG-F compared to previously reported SG.

	<i>SG-F</i>	<i>SG (old)</i> ¹⁸
Fabrication Process	GO-Freeze casting-High-temperature Reduction	GO-Liquid-phase Reduction-Freeze casting
Density	< 1 mg cm ⁻³	5-12 mg cm ⁻³
Morphology	Porous, dual microstructure with CNPs adhesion	Cabbage-like structure
Hydrophobicity (e.g. Contact Angle)	155 °	115 °
Absorption Performance (e.g. Weight Gain towards Chloroform)	max. 616.4	max. 86.1

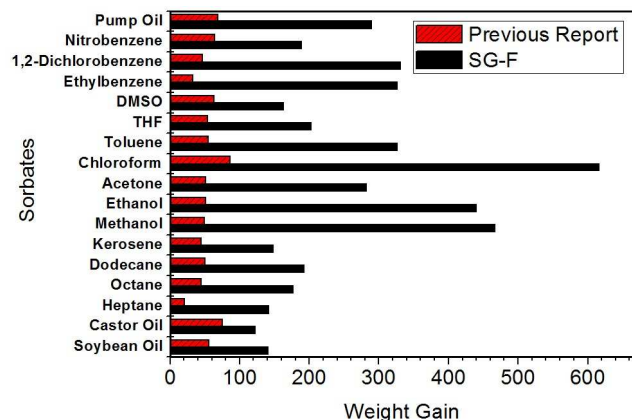


Figure 4. The capacity of graphene sorbent towards various organic chemicals. Absorption capacity of SG-F, the soot-treated graphene sorbent, towards various organic chemicals. Black bars: performance of SG-F studied in this report. Red bars: corresponding performance of SG prepared elsewhere.¹² A maximum of 616 times of the own weight of graphene sorbent can be absorbed when using chloroform as the target substance, which is ~ 8 times higher than previous report.

SG, the absorption capability significantly increased to 8 to 10 times of a previously reported SG. Results not only indicated the fabrication of highly absorptive nanomaterials but also helped improve the fabrication of other mesoporous structures. Apart from the application of the new SG material in oil absorption in environmental protection or chemical industries, this material also has potential value in energy storage and chemical sensors because of its light weight and highly porous structures.

Experimental

Preparation of GO

GO was prepared by oxidizing expandable graphite powders through a modified Hummer's method.^{18,32} Graphite flakes (2 g, purity, >99.7%; Qingdao Chemical Reagent Co. Ltd., China) and sodium nitrate (1 g) were mixed with sulfuric acid (46 mL, 98 wt%) in an ice bath. Potassium permanganate (6 g) was very slowly added to the mixture to maintain the temperature below 20 °C. The reaction was then kept at 35 ± 1 °C for 8 h, and during this time, gas was released. Deionized water (92 mL) was gradually added to the mixture, which produced violent effervescence. The temperature of the water bath was increased to 98 °C and maintained for 15 min to increase the degree of oxidation of the produced GO. The bright-yellow suspension was diluted with deionized water (280 mL) and further treated with H₂O₂ (30%, 6 mL). Finally, the mixture was separated by centrifugation and washed seven times with 5% hydrochloric acid solution until no sulfate ion can be detected with BaCl₂. The product was then washed seven times with distilled water to remove chloride ions and dried overnight in an oven at 60 °C. The characterization of GO has been described elsewhere.¹⁸

Fabrication of SG-R and SG-F

GO dispersions in water (3 mg mL⁻¹ GO concentration) were placed in a sealed container that can hold vapor pressure. The container was first frozen using liquid nitrogen for 5 min and then

transferred to a freeze dryer (LGJ-10D, Beijing Sihuan Scientific Ltd., China) for drying. The dried, brownish GO gel was placed in an air oven and heated to 1000 °C for 20 min under N₂ protective atmosphere. Shiny black SG-R was formed after cooling to room temperature. The SG-R bulk was placed on the flame of a wax candle and carefully rotated for 3 s. Direct contact between the material and flame envelope was ensured. The surface of SG-F was prepared for SEM (FEI Quanta 200) and TEM (FEI Tecnai G20) imaging (Fig. 2).

Oil absorption test

A drop of absorbate (~20 μL, including water) was added dropwise onto the horizontal surface of SG to determine the absorption of SG. In case of repulsion, the surface of SG was tilted to investigate the self-cleaning ability of the surface. After determining the absorption behavior, dry SG bulk was weighed and then the absorbate was added dropwise onto the sponge until the SG bulk was saturated, as indicated by slight moisture on the entire SG surface. SG was weighed again upon saturation. The absorption capability (weight gain) was then calculated according to the wet-to-dry weight ratio. Liquid absorption on water was performed in a glass beaker. The absorbate was stained with Sudan red 5B (final concentration = 1 mg mL⁻¹) and poured onto a container with water. SG bulk was thrown and stirred gently at the air-liquid interface (in most cases) or submerged (e.g., phenixin) depending on the absorbate density. The experiments were documented (images and videos) using a commercial digital camera.

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Notes and references

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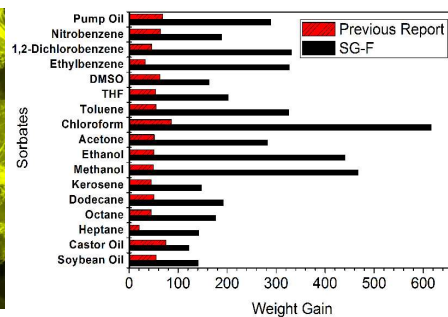
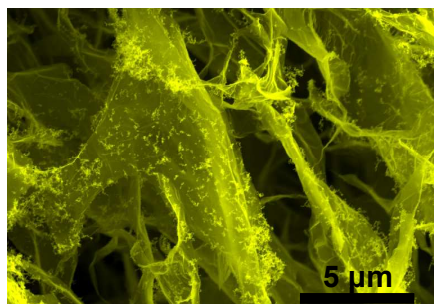
Electronic Supplementary Information (ESI) available: the morphology and wettability of SG-F, the Raman spectrum of SG-R and SG-F, IR spectra of SG-R and SG-F, X-ray photoelectron spectroscopy of SG-R and SG-F, the adhesive performance of SG-R and SG-F, the dynamic adsorption process, and comparison of various sorber materials. See DOI: 10.1039/b000000x/

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A brand-new spongy graphene treated with flame soot has a highly enhanced performance as oil sorbent, which is 616 times its own weight towards chloroform (8 times higher than the previously reported literature).