

Spongy Graphene as a Highly Efficient and Recyclable Sorbent for Oils and Organic Solvents

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In this work, spongy graphene (SG), a shape-mouldable and nanoporous material with a high specific surface area used as a versatile and recyclable sorbent material, is proposed and studied. SG shows highly efficient absorption of not only petroleum products and fats, but also toxic solvents such as toluene and chloroform (up to 86 times of its own weight), requiring no further pretreatment, which is tens of times higher than that of conventional absorbers. Moreover, SG can be regenerated (>10 times) by heat treatment, yielding the full release of adsorbates (>99%). The present work suggests SG a widespread potential for applications in industry as well as topics regarding environmental protection.

Pollution by crude oil, petroleum products, and toxic organic solvents causes severe environmental and ecological problems each year.^[1–3] New materials that can sequester and remove pollutants are needed. Oil booms, combustion, and oil skimmer vessels have been used but often with poor efficiency while at times also causing other types of pollution during clean-up.^[2] Various natural absorbers such as expanded perlite^[4] and zeolites,^[5] organic materials such as wool fiber,^[6,7] activated carbon,^[6] and sawdust^[7] have all been used because of their microporosity. These conventional materials have low oil loading and absorption of water together with the oil. Microporous polymers have been studied due to their large specific surface area and hydrophobicity.^[8–11] Although they show relative high

absorption ability, the cost to make these kinds of sorbent also increases, and the environmental and ecological risk of these polymers in application remains unclear.

As an alternative to polymer, expanded graphite (EG) has also been used to remove oil. Applying EG as an oil sorbent was first done by Toyoda and Inagaki.^[12,13] EG is a good absorber for crude oil and its petroleum products, but not for many polar solvents, e.g., dimethyl sulfoxide or toluene. Expanded graphite conjugates or composites have thus been designed to enhance absorption of these liquids.^[14,15]

Because of their granular appearance, EG particles and their conjugates or composites are usually wrapped inside plastic bags before being placed in the polluted area, which is inconvenient for both their application and their recycling. Moreover, only 70% of the adsorbates can be retrieved by this method for each use. Therefore, the absorption efficiency of EG declines severely, typically to less than 20% of its initial value after being recycled five times, which makes EG no longer applicable to adsorbates after just a few times of reuse.^[1] Besides EG, there are also other sorbers composed by carbon materials that have been reported, such as nanotubes.^[16] However an extremely high cost limits their extensive application.

Graphene has received considerable attention in different fields of research and has become a “star” material in recent years due to its amazing properties.^[17–26] Reduction from graphite oxide has the potential to produce reduced graphene oxide, a chemically functionalized graphene, in relatively large quantity.^[27,28] In this paper, a new material, termed spongy graphene (SG) has been made by reducing graphene oxide (G-O) platelets in suspension followed by shaping via moulding. SG has a broad-spectrum absorption to petroleum products, fats, alkanes, toluene, as well as other organic solvents, without any further modification or treatment. The absorption efficiency of SG is 20 to 86 times its weight, comparable to or surpassing polymers and EG. SG can be heated to remove adsorbates (>99%) and regenerated more than 10 times. SG thus has better performance than conventionally used materials in removing petroleum products and toxic organic solvents.

In this study, SG was made by reducing a suspension of G-O platelets followed by moulding. The progress of absorption is shown in a series of photos in **Figure 1a** to **Figure 1e** (see Experiments, Figures S1–3, Supporting Information). Photographs were taken every 20 s. In this series 11.8 g dodecane

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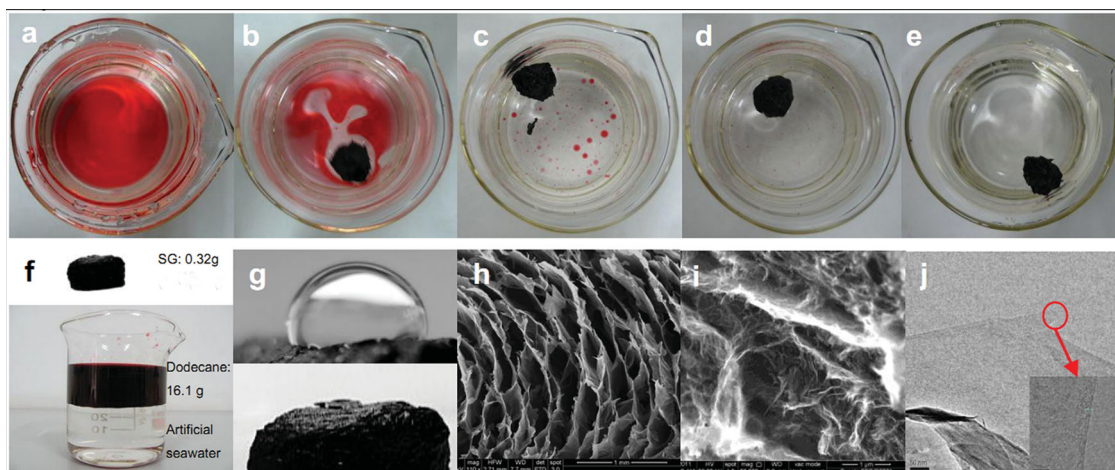


Figure 1. Oil absorption and characterization of SG. a–e) Absorption of dodecane in SG at intervals of 20 s. Dodecane (stained with Sudan red 5B) floating on artificial seawater was completely absorbed within 80 s. f) Efficiency of oil absorption. SG can be molded into any shape. A SG bulk with the shape of a triangular prism was obtained in this case with a mass of 0.32 g. This block absorbed 16.1 g dodecane floating on water, corresponding to a weight gain of 50.3. g) Contact angle of SG surface (upper panel) and fast absorption of dodecane (lower panel). The contact angle to water was $114^\circ \pm 2^\circ$, but dodecane was quickly absorbed without any residue remaining on the surface. h) SEM image of the microporous (fusiform) structure of SG. The scale bar represents 1 mm. SG has a typical specific surface area of $432 \text{ m}^2 \text{ g}^{-1}$. i) SEM image of the graphene skeleton. Scale bar: $1 \mu\text{m}$. j) Transmission electron microscopy image of the graphene skeleton. The scale bar is 50 nm; the scale bar of the inset is 5 nm.

(stained with Sudan red 5B) was absorbed by an SG block (0.26 g, floating on artificial seawater) in 80 s, showing an average absorption rate of dodecane of $\approx 0.57 \text{ g}$ per gram of SG per second. SG appears as a dark sponge (Figure 1f, with the mass of the sponge shown here of 0.32 g). The density of SG was calculated to be $12 \pm 5 \text{ mg cm}^{-3}$, which is comparable to or slightly lower than EG.^[29,30] Conventional materials (especially EG) are stored in apertured containers (e.g., apertured plastic bags) before use; in contrast, SG can be molded into any shape, thus it could be placed directly in polluted areas and dredged intact afterward, making its recovery much simpler. Hydrophobicity was obtained by contact angle measurements performed on the SG-air interface, yielding a contact angle of $114^\circ \pm 2^\circ$. Oils such as dodecane were quickly absorbed (Figure 1g). The microscopic topography of SG was analyzed using scanning electron microscopy (SEM). A microscopic porous structure (fusiform, the average dimension of the long axis was $\approx 570\text{--}620 \mu\text{m}$) was observed (Figure 1h). The sample was characterized by measurements of the nitrogen adsorption isotherm, revealing a specific surface area of $423 \text{ m}^2 \text{ g}^{-1}$ (fitting of the Brunauer-Emmett-Teller (BET) equation). Fine structures, e.g., wrinkles of “graphene” as well as “cottony” and needle-like structures, were found under higher magnification (Figure 1i). The microporosity and such fine structures contribute to the large surface area of spongy graphene. The skeleton of this material was dissected and investigated using transmission electron microscopy (Figure 1j). The combination of Figure 1i,j indicates that the layers which form a foam-like structure in SG are very thin, in contrast to the thick graphitic layers in EG.

The efficiency of oil absorption can be referred to as weight gain, i.e., wt%, defined as the weight of absorbed oil per unit weight of dry SG. Various classes of organic liquids were evaluated in this study, e.g., commercial petroleum products (kerosene and pump oil), fats (vegetable oil), and ketones with

different carbon chain lengths, which are crucial components of crude oil. These materials are common pollutants in both daily life and industry. Organic solvents, such as toluene and dimethyl sulfoxide, alcohols, and acetone were also used for experimentation. SG showed excellent absorption of these liquids (Figure 2). In general, SG could absorb the liquids at 20 to 86 times its own weight. Its absorption efficiency is much higher than that of hydrophobic chemical mechanical planarization (HCMP) polymers.^[7] SG absorbed pump oil, 1,2-dichlorobenzene, and dimethyl sulfoxide at rates of 68 \times , 46 \times , and 63 \times , respectively; the corresponding values for HCMP are $\approx 10\mathbf{x}$, 15.8 \times , and 15 \times . In addition, SG may absorb significantly greater

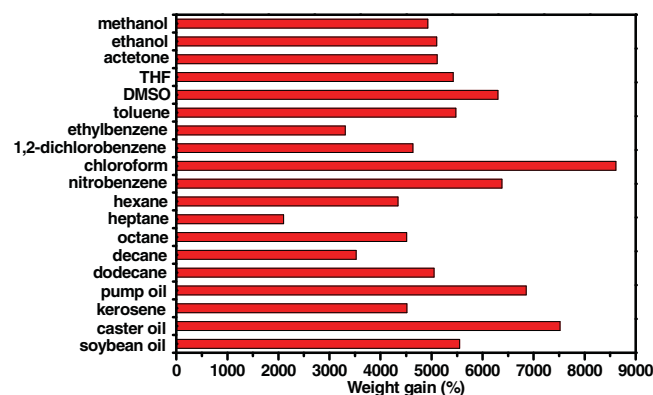


Figure 2. Absorption efficiency of SG. SG efficiently absorbs petroleum products (68.5 \times for lubricating oil), fats (75.1 \times for castor oil), alkanes, aromatic compounds, and commonly used organic solvents, e.g., chloroform (86.1 \times) and toluene (54.8 \times). It also performs effectively with water-soluble alcohols and aldehydes, e.g., methanol (49.2 \times), ethanol (51.0 \times), and acetone (51.1 \times). Weight gain is here defined as the ratio between the mass of the absorbate and the dry weight of SG.

levels of toluene (54.7 \times) than previously reported absorptive materials, e.g., vaseline-loaded EG (<10 \times)^[14] and other composites based on EG.^[31] Absorption occurred quickly; the velocity depends partially on molecular weight, as smaller molecules usually diffuse faster; toluene was hence absorbed faster than dodecane (Figure S3, Supporting Information). SG also absorbed water-soluble organics efficiently, including methanol (49.3 \times), ethanol (51 \times), and acetone (51.1 \times), which hydrophobic polymers and EG could not achieve without pretreatment (e.g., by preloading them with vaseline).

According to the XPS investigation on several cross-sections of SG blocks, the SG still contained \approx 6.3% of oxygen, \approx 9.8% nitrogen, and \approx 0.2% sulfur after being reduced from graphene oxide (see Figure S4, Supporting Information). This result indicates that SG's unique ability to absorb such organic solvents as toluene, alcohols, and ketones was most likely induced by the hydroxyl, carboxyl, amino and hydrosulphonyl residues from the preparation process, SG was used in its hydrophobic state, leading to its highly efficient absorption. In contrast, complete chemical reduction of graphene oxide was almost impossible, due to these functional groups which reduce the hydrophobicity of the graphene surface. However, small amounts of the proper hydrophilic functional groups enhance the interaction between graphene and the molecules of polar solvents. Instead of remaining together as vesicles on the graphene interface, the polar groups could spread on the hydrophobic surfaces in SG, thereby significantly increasing their potential for interaction with such surfaces and their absorption by SG.

Pollution control and environmental protection efforts require that pollutants are not only absorbed and prevented from further harming the environment, but also properly recycled and thus reused, as they are either precious raw materials or toxic, e.g., crude oil and toluene. The recycling pollutants and the regeneration of SG are illustrated in Figure 3. Heat treatment can be applied, instead of solvent extraction which is complicated, incomplete, and more expensive. A recyclability test was performed between SG, toluene (boiling point 110.6 °C), and dodecane (boiling point 215–217 °C). After the liquid had been absorbed by SG, the material was heated to 105 °C to release the vapor of toluene or 200 °C to release dodecane. The temperature required for vaporization can be controlled and kept around the boiling point of the absorbates. The residual mass of dodecane in the SG block was then weighed. This process was repeated 10 times to check the feasibility and completeness of recycling organics from SG, followed by the regeneration of SG. The results are shown in Figure 4.

Less than 1% residual weight remained in the SG after each cycle for both absorbates of toluene and dodecane (as shown in Figure 4a,b, respectively), indicating the highly stable recycling performance. The absorption ability of SG remained essentially identical after 10 cycles of testing. Meanwhile, the absorbed organics could be released by simply heating the material and collecting the condensate. No damage to the SG microstructure was observed after this process (see Figure S5, Supporting Information). No combustion or structural damage occurs in heat treatments at moderate temperatures. Therefore, many pollutants, including heavy oil, could in principle be separated from SG and further reused after heat treatment. Chemical extraction or vacuum treatment is necessary, instead

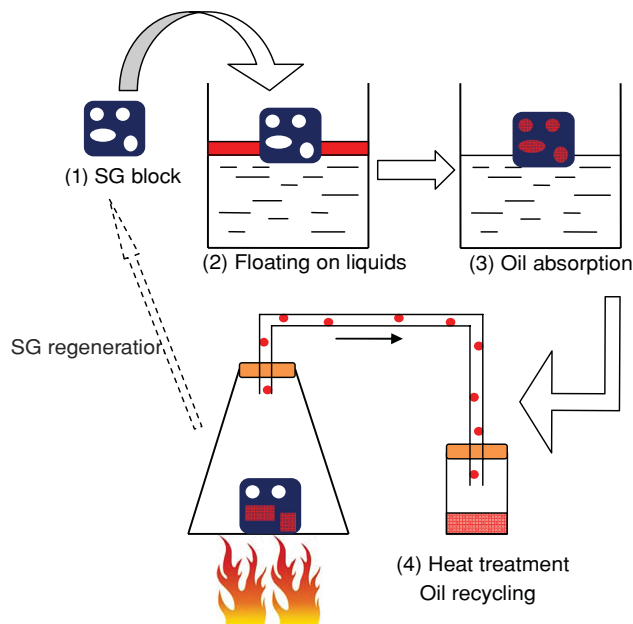


Figure 3. Four-step schematic diagram of SG recycling process. SG can be regenerated and reused without affecting its performance when heated up to the temperature around the boiling point of absorbate. The liquid could be evaporated, condensed, and recollected elsewhere. Simply after heat treatment, the SG material was ready to be used in the next cycle of absorption without further process.

of heat treatment, for polymeric absorbents and EG composites because these are sensitive to heat, resulting in incomplete recycling of pollutants, degradation of materials, and higher costs. Table 1 shows the comparison of SG with various materials reported before.

In conclusion, SG has been fabricated by using facile protocols, and its physicochemical properties have been investigated.

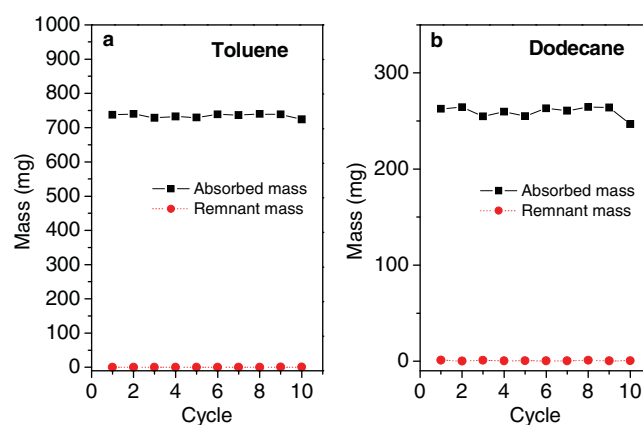


Figure 4. Recyclability of SG. a) An SG repetitively absorbed toluene and released its vapor under heat treatment (105 °C) for 10 cycles. The weight of SG in each cycle was measured before (black line) and after (red dotted line; subtracted by the dormant weight of SG) the heat treatment. The absorbed mass of toluene ranged from 723 to 739 mg, and the SG weighed 13.7 mg. b) Dodecane recycling (200 °C). Conditions were the same as those described in (a). The absorbed mass of dodecane ranged from 246 to 264 mg, and the SG weighed 5.2 mg.

Table 1. Comparison of various sorber materials.

	Natural products	Polymers	Expanded graphite	Spongy graphene
Absorbates	oils and water	oils and organic solvents	oils	oils and organic solvents
Capacity [g g ⁻¹]	n.a. (low)	5–25 (medium)	max. 83 (high, only for oils)	max. 86 (high)
Environmental safety	safe	unknown hazard	safe	safe
Convenience of use	difficult (amorphous fiber or particles)	easy (mouldable)	difficult (worm-like particles)	easy (mouldable to any shape)
Extraction strategy	not possible	squeezing or filtration	vacuum filtration	heat treatment
Restoration of absorbates	n.a.	50%–80%	<70%	>99.9% (high)
Recyclability of the sorber	not possible	n.a.	<5 times (17% capacity remaining)	10 times (>99% capacity remaining)
Cost	medium	high	low	low
Ref.	[4–7]	[8–11,32]	[12–15]	–

Absorption tests of various liquids have been performed, indicating some outstanding features of SG: efficient and quick absorption of oils and organic solvents, mouldable into any shape, high restoration of absorbates, recyclability, and long-life of the sorbent material. The results show that SG has a strong potential to become a versatile, efficient, and safe absorber for hazardous organic liquids with applications in oceanography, environmental protection, and industrial production. The processes to fabricate SG are facile, low-cost, and should be scalable to industrial levels.

Experimental Section

Preparation of GO: GO was prepared by oxidizing expandable graphite (EG) powders based on the modified Hummers method.^[33,34] 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 added to the mixture very slowly, to avoid the temperature exceeding 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, bringing about 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 GO product. 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 could 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.

Fabrication of SG: A colloidal dispersion of GO (thus, containing individual layers of graphite oxide (graphene oxide, G-O) was subjected to hydrothermal treatment with distilled water. 57 mg of GO was dispersed in 35 mL of a distilled water/ammonia mixture, followed by sonication for 15 min. The dark brown colloidal dispersion was transferred to a sealed reactor with the required shape and heated at 180 °C for 24 h. The reactor was cooled down naturally in RT. Then the as-prepared graphene gel was taken out from reactor and subsequently freeze-dried for 48 h to obtain SG blocks.

Dynamic Photographing of Oil Absorption: A series of photographs of oil floating on the surface of pure water and artificial seawater was taken and analyzed to characterize the dynamic process of oil absorption. Every milliliter of dodecane was stained with 1 mg of Sudan red 5B to facilitate evaluation by the naked eye. Photos were taken every 20 s. The following were added to 1 kg of water (artificial seawater, reduced version)^{[35]:}

sodium chloride, 23.926 g; sodium sulfate, 4.008 g; potassium chloride, 0.667 g; sodium bicarbonate, 0.196 g; potassium bromide, 0.098 g; boric acid, 0.026 g; and sodium fluoride, 0.003 g.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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