

Oil-absorbent polyurethane sponge coated with KH-570-modified graphene

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ABSTRACT: Polyurethane (PU) sponge has become a preferred oil adsorbent in recent oil-spill accidents. To make the sponge superhydrophobic and superoleophilic, this study used graphene (GN), which was modified with γ -methacryloxypropyl trimethoxy silane (KH-570), to coat the PU sponge (called the KH-GN sponge). This study showed the best loading capacity (11.96%) of the KH-570-modified GN on the sponge. The contact angles of the KH-GN PU sponge were 161° for water and 0° for soybean, diesel, and pumping oil. It had good selectivity for oil over water, and the KH-GN sponge achieved adsorption equilibrium within a few seconds. The absorption capability of the KH-GN sponge was up to 39 times greater. Additionally, the KH-GN PU sponge could be reused for oil-water separation for more than 120 cycles without losing its superhydrophobic and superoleophilic properties. Therefore, the sponge prepared in this study could be a desirable material for the cleanup of oil spills. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 41821.

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INTRODUCTION

Because of the alarming attention toward severe environmental issues arising from oil spills, there is a growing demand for the preparation of oil-adsorbing materials.^{1,2} To date, a number of oil absorbents, including clay,³ activated carbon,^{4,5} zeolites,⁶ carbon nanotubes,^{7,8} polymers,^{9,10} rubber materials,¹¹ wool fibers,¹² and straw,^{13,14} have been developed. However, these materials have respective drawbacks, such as a high cost, low absorption capacity, and poor reusability. So, new materials with low prices, excellent absorption capacities, and outstanding reusability should be further exploited. In recent years, three-dimensional (3D) porous materials have been considered as promising high-capacity absorbents because of their large surface area and surface roughness.^{15,16} However, these materials absorb water and oil simultaneously. Therefore, carbon materials with hydrophobic and oleophilic properties have been used as coatings.^{17,18} Nevertheless, the complicated synthetic procedures of superhydrophobic 3D porous materials and expensive carbon materials have limited their practical applications.

Polyurethane (PU) sponges, having a very rough surface, are a type of commercially available 3D porous materials.^{15,18} As an

absorbent substrate, recently, they have been used to fabricate superhydrophobic absorbents for oil-water separation.^{15,16,18–20} PU is composed of carboxyl and amino groups,^{21,22} so its hydrophilicity is a major problem in the fabrication of superhydrophobic absorbents.

Graphene oxide (GO) is an oxygen-abundant material, which has aroused great interests because of its chemical stability and facile preparation method. Its epoxy, carboxyl, and hydroxyl groups can interact with other materials.¹⁸ The reduction of GO can remove most of the hydroxyl and carboxyl groups (hydrophilic) and produces graphene (GN). GN,^{18,23–25} a novel two-dimensional carbon nanomaterial, has hydrophobic and oleophilic properties. Therefore, it has recently attracted tremendous attention in the oil-absorption field.

Some studies have been done with carbon materials to modify sponge, for example, Gui *et al.*⁸ prepared carbon nanotube sponges, Zhu *et al.*¹⁵ produced methyltrichlorosilane modified sponges, Nguyen *et al.*¹⁷ fabricated GN-based melamine sponges, and Singh *et al.*²⁶ fabricated superhydrophobic GN foams. All of the materials showed hydrophobic and oleophilic properties. However, when the PU sponge was coated by GN, it

remained a challenge to make GN superhydrophobic and superoleophilic. According to our understanding, GN, when modified with a hydrolysis product of γ -methacryloxypropyl trimethoxy silane (KH-570), could become more superhydrophobic and superoleophilic. Nevertheless, few of the previous studies reported the preparation process of KH-570-modified GN and the coating process of it onto PU sponges.

In this study, we examined a facile strategy, the dip-coating method, to coat KH-570-modified GN onto PU sponge. With the coating process, the as-fabricated KH-GN sponge showed a high selectivity, superhydrophobicity [contact angle (CA) = 161°], and excellent recyclability. The KH-GN sponge could absorb up to 39 times more when it was used as an absorbent for collecting oil. It could be reused more than 120 times without losing its absorption capacities. Consequently, the findings of this study might offer a simple method for the cleanup of oil spillage.

EXPERIMENTAL

Materials

PU sponge was supplied by Yiqing Polyurethane Sponge Co., Ltd. (Shanghai, China). Sulfuric acid (H_2SO_4), sodium nitrate (NaNO_3), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2 ; 30%), hydrochloric acid (HCl; 5%), ethyl alcohol (95%), and acetic acid (CH_3COOH) were all analytically pure and were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). KH-570 was purchased from Desong Co., Ltd. (Guangzhou, China). Graphite (187.5 μm) was purchased from Tianshengda Graphite Co., Ltd. (Qingdao, China). Diesel (density at 20°C = 0.8170 g/cm^3 , viscosity = 6.51 mm^2/s) was obtained from Minghe Petrol Station of Sinopec in Baoshan district (Shanghai, China). Pumping oil (density at 20°C = 0.7881 g/cm^3 , viscosity = 47–57 mm^2/s) was obtained from Shanghai Hasitai Lubricating Oil Co., Ltd. (Shanghai, China). Soybean oil (density at 20°C = 0.9275 g/cm^3 , viscosity = 8.5 mm^2/s) was purchased from Wal-Mart supermarket (Shanghai, China).

Synthesis of GO

The GO was prepared with a modified Hummers method.^{20,26} First, graphite (2 g) was added to a beaker (500 mL) with H_2SO_4 (98%, 46 mL) and NaNO_3 (1 g) mixed into the beaker at 4°C . With the reaction temperature kept below 20°C , KMnO_4 (6 g) was slowly added with magnetic stirring. The suspension was stirred continuously for 1.5 h with the temperature increasing up to 35°C . Deionized water (92 mL) was mixed slowly with the temperature rising to 98°C . The reaction was kept for 15 min to increase the oxidation degree of GO. Then, deionized water (280 mL) was added again to dilute the suspension. H_2O_2 (30%) was slowly mixed into the suspension until a golden solution appeared. After that, the mixture was centrifuged at 4000 rpm for 10 min and washed with HCl (5%) to remove SO_4^{2-} until the SO_4^{2-} disappeared; this was checked with a BaCl_2 solution. To remove the residual acid, the mixture was finally washed with deionized water several times. The GO sheet was obtained by drying at 60°C in an oven.

Preparation of the KH-570-Modified GN

GO (100 mg) was dispersed in ethyl alcohol (100 mL) with ultrasonic processing for 2 h. KH-570, deionized water, and

ethyl alcohol were added at a ratio of 1:1:18.²⁷ After it was stirred for a while, CH_3COOH (36%) was mixed until the pH of the solution turned to 4.0–4.5. The solution was then added to the GO suspension with ultrasonic treatment for another 30 min. The system was heated at 80°C in an oil bath and condensed for 4 h. Then, the suspension was centrifuged and washed twice with deionized water (100 mL) and three times with ethyl alcohol (100 mL). The KH-570-modified GO sheet was obtained after it was fully dried in an oven and dispersed in ethyl alcohol at a concentration of 2 mg/mL.

Fabrication of the KH-GN Sponge

The commercial PU sponge was cut into a square shape (1 g in weight, 3–4 cm in width, and 3 cm in height) and cleaned with ethanol and distilled water for 30 min successively with an ultrasonic cleaner. Then, the sponges were dried in an oven at 60°C for several hours to remove the moisture completely. The ammonia solution was mixed to increase the pH of the GO dispersion to 9. The sponges were dipped into the dispersion for 1 h and then oscillated for an hour again. A solution of hydrazine hydrate was added to the suspension and sealed to react at 95°C for 1.5 h to reduce the GO to GN. The sponges were taken out and washed by deionized water. We dried the sponges at 30°C in a vacuum oven for 24 h, and the KH-GN sponges were finally obtained. To study the best loading capacity of KH-570-modified GN, the PU sponges were dipped into the solution of modified GN for different times (1–5 loading times). The resulting sponges were named as first, second, third, fourth, and fifth loading sponges, respectively. The loading capacity was defined as the weight ratio $W_{\text{KH-GN}}/W_{\text{sponge}} \times 100\%$,¹⁷ which we measured by weighing the original and KH-GN sponges immediately after taking them out of the oven to prevent moisture absorption. For further comparison, the KH-570-modified sponge (KH sponge) and GN-modified sponge (GN sponge) were prepared. The KH sponge was fabricated by the immersion of the sponge into the solution of hydrolysis of KH-570, whereas the GN sponge was fabricated by the dipping of sponge into the ethanol solution of GN.

Method for the Oil and Water Absorption Tests

The as-prepared KH-GN sponges were immersed in an oil sample at room temperature. The KH-GN sponges were weighed first. Then, they were immersed into the oil sample to adsorb it for a certain time. After they were removed from the oil sample, the sponges were put on testing meshes for 1 min to make the extra oil drain out. The sponge and the testing mesh were then weighed together. The oil-absorption capacity (Q) was calculated by measurement of the weight of the samples before and after absorption (1×10^{-4} g accuracy)¹¹ and calculated according to the following equation:

$$Q = \frac{M_1 - M_2 - M_3}{M_3} \quad (1)$$

where M_1 is the total weight of the wet sample with oil (g), M_2 is the mass of a testing mesh (g) that was immersed in oil and then allowed to remove excess oil from its surface for 1 min, and M_3 is the initial weight of the sponge (g). The desorption test was performed by simple squeezing of the sponges with a large syringe, and the oil was obtained by ultrasonic extraction

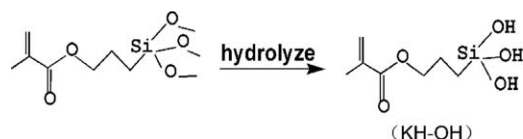
with *n*-hexane. Meanwhile, they were weighed at various time intervals until all of the liquid evaporated from the samples.

RESULTS AND DISCUSSION

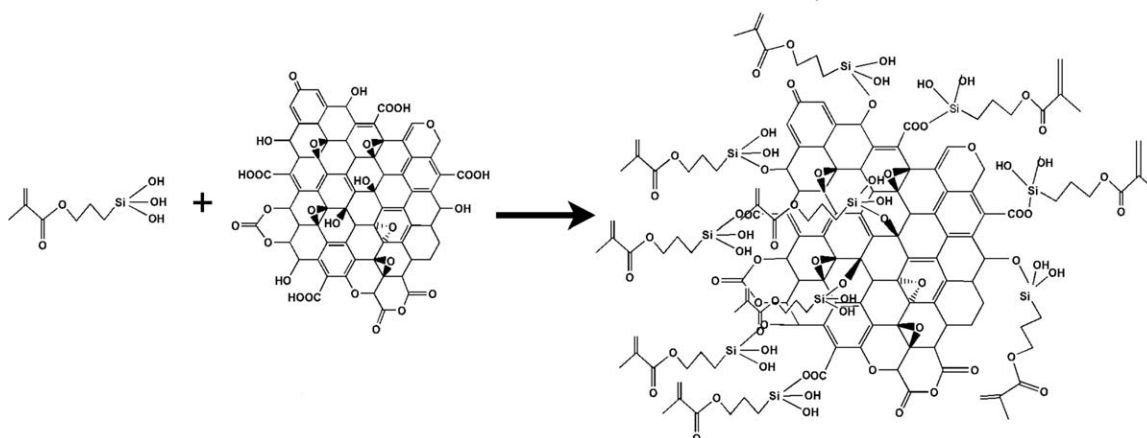
Fabrication of the KH–GN Sponge

The preparation process of the KH–GN sponge is demonstrated in Figure 1. Figure 1(a) shows a photograph of the original sponge used in this study. With the dip-coating treatment of KH–OH (the hydrolysis product of KH-570) and GO, the sponge became black in color, as shown in Figure 1(b). After it was reduced by the vapor of hydrazine hydrate [Figure 1(c)] in a sealed sample bottle, the KH–GN sponge was finally obtained

[Figure (d)]. The hydrolysis of KH-570 played an important role in the fabrication process. The methoxy of KH-570 was hydrolyzed into hydroxyl,^{28,29} which is shown in eq. (1):



The combination process of KH–OH and GO is shown in eq. (2):



The hydroxyl groups of KH–OH were combined with the carboxylic and hydroxyl groups of GO.

Absorption Capacities of the KH–GN Sponge

Different loading capacities of the KH-570-modified GN were tested. As the loading process started, the capacity increased gradually from the first to the third loading. After dipping the sponge into the solution, there was no increment in the loading. Thereafter, the best loading time was the third loading, with the loading capacity up to 11.96%. The absorption capacities of the KH–GN sponges for different oils under different loading capacities are illustrated in Figure 2(a–c). The KH–GN sponge with the third loading had the highest absorption capacity of the three kinds of oil. The capacities were up to 35 g/g for soybean oil, 38 g/g for diesel oil, and 39 g/g for pumping oil. The capacities of the KH–GN sponge were higher than the capacities of the methyltrichlorosilane-treated sponge (25 g/g)¹⁵ and the polypyrrole-1H,1H,2H,2H-Perfluorooctyltriethoxysilane (PPy-PTES) sponge (20 g/g).¹⁶ Hence, the KH–GN sponges with the third loading were taken for subsequent experiments.

The absorption capacities of differently treated sponges were also compared, as shown in Figure 2(d). For the three kinds of oil, the KH–GN sponge had the maximum absorption capacity compared to the other treated sponges. The capacity of the GN sponge had a slight increase compared to the original and KH sponges because GN increased the roughness of the sponge.^{18,24}

However, the absorption capacity of the KH sponge showed little change compared to the original sponge, for KH–OH was not combined with the sponge directly. The adsorption capacity of diesel was high for the original, KH, and GN sponges compared to the adsorption capacities of the soybean and pumping oils because of the low viscosity and light weight of the diesel oil.¹¹

Characterization of the KH–GN Sponge

To confirm the existence of the coating on the sponge surface, the attenuated total reflectance (ATR) and X-ray photoelectron spectroscopy (XPS) were conducted to explore the chemical composition of the KH–GN sponge. Figure 3 shows that the changes of the functional groups on the sponge surface were not obvious between the original and KH–GN sponges. This demonstrated that the changes in the surface chemical bonds were not obvious. Therefore, the XPS test was carried out for further observation. The carbon, oxygen, nitrogen, and silicon elements were detected. The XPS survey spectra proved that the element Si was successfully attached to the sponge surface during the dip-coating treatment [Figure 4(a)]. In the hydrolytic process of KH-570, hydroxyl groups were produced. These groups were combined with GO through a condensation reaction.^{28,29} Then, the final products were attached to the sponge through physical adsorption and hydrogen-bonding interactions. Meanwhile, the peaks of Si 2p at 101.1 and 103.2 eV were split;^{30,31} these were observed from Figure 4(b). The generation of Si–O–C was due to the combination of the hydrolytic

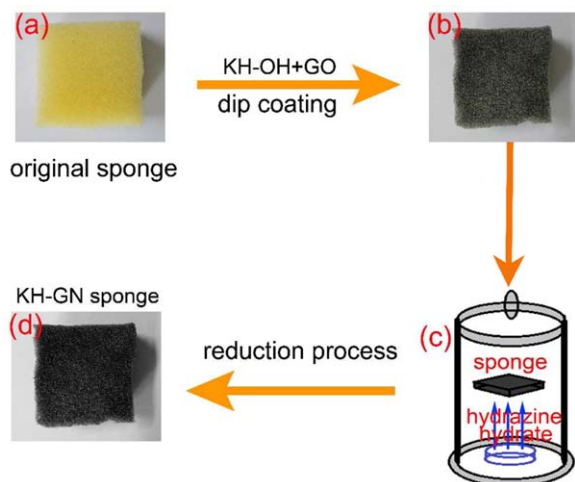


Figure 1. Photographic and schematic illustrations of the KH-GN sponge fabrication process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

products (KH-OH) of KH-570 and GN, whereas the Si-O-Si was generated by the self-condensation reaction of KH-OH.^{32,33} All of the chemical bonds enhanced the attachment of the KH-570-modified GN on the sponge surface, which, as a result improved the superhydrophobicity and reusability of KH-GN sponge.

The optical and morphological images of the original and KH-GN sponge are shown in Figure 5. The morphologies were char-

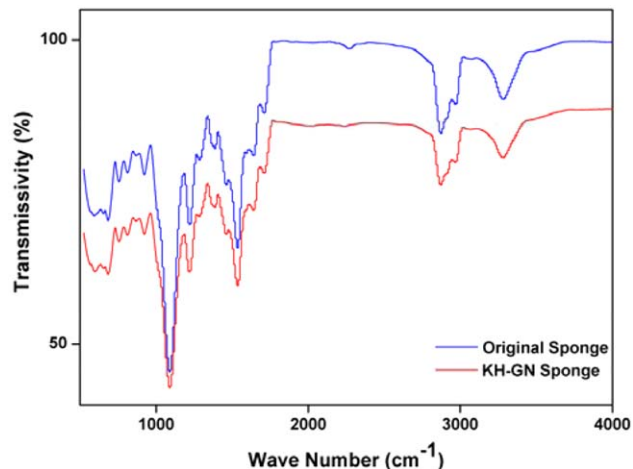


Figure 3. ATR spectra of the original and KH-GN sponges. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

acterized with scanning electron microscopy. The original sponge, which had been cleaned, was yellow in color [Figure 5(a)], and it became black [Figure 5(b)] after modification with KH-570-modified GN. This change also proved the existence of the coating. The morphologies of original sponge with smooth surfaces under low and high magnifications are shown in Figure 5(c,d), respectively. For contrast, the coating covered the interconnected skeleton of the KH-GN sponge, which was also

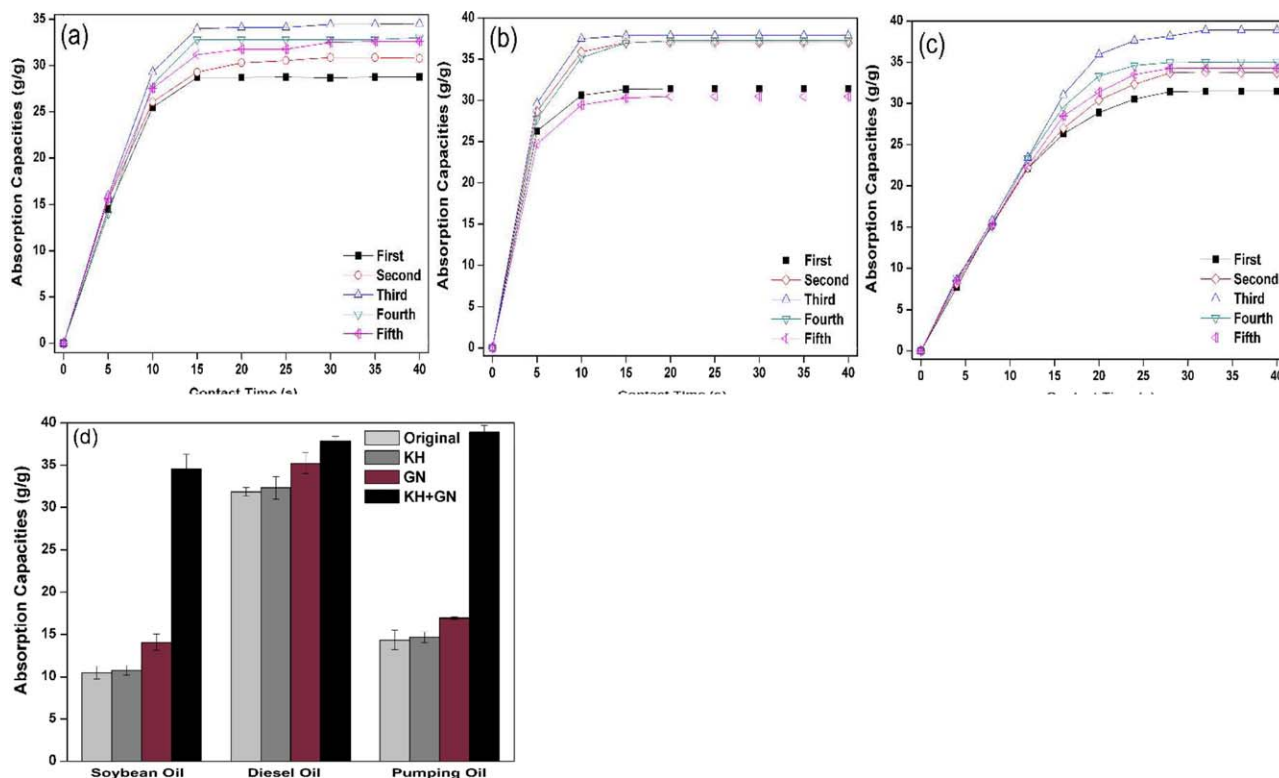


Figure 2. Absorption capacities of different oils under different loading capacities: (a) soybean, (b) diesel, and (c) pumping oils. (d) Absorption capacities of different oils with different treatments: original, KH, GN, and KH-GN sponges. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

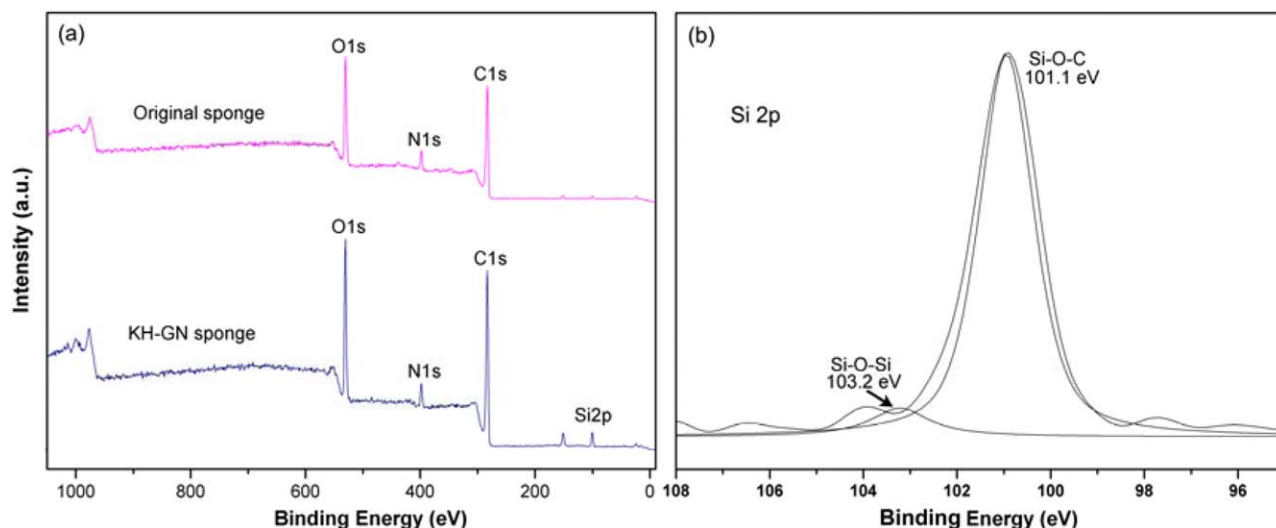


Figure 4. XPS survey spectra of the (a) original and KH-GN sponges and (b) peak split of the Si 2p scan. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

characterized under low [Figure 5(e)] and high magnification [Figure 5(f)]. The rough surface showed the high oil-absorption capacity of the KH-GN sponge. Also, pores with diameters ranging from a few hundred nanometers to dozens of micrometers composed the hierarchical roughness required for a superhydrophobic surface.^{15,34}

The hydrophobicity of the sponges was measured by a CA apparatus with a droplet (8 μL) of distilled water as an indicator. We observed that the original sponge had a similar CA with the KH sponge [Figure 6(a,b)]; this also indicated KH-OH was not coated on the sponge surface directly. The CA of the GN sponge increased to 129.3° [Figure 6(c)]; this revealed that GN improved the hydrophobicity of the PU sponge. However, it was not superhydrophobic for the GN sponge compared to the KH-GN sponge with a CA of 161° [Figure 6(d)]. The KH-GN

sponge had a large water CA; this was higher than that of the polydimethylsiloxan (PDMS)-coated PU sponge (140°),¹⁹ PU foam (152.2°),³⁵ and conjugated microporous polymers (150°).³⁶ Intuitively, the water droplets were almost adsorbed by the original sponge, whereas they remained stable on the surface of the KH-GN sponge [Figure 6(e)]. A drop of diesel oil, which was dyed with Sudan I for obvious comparison, was completely adsorbed into the pores of the KH-GN sponge in 1 s, and no CA could be measured [Figure 6(f)]. Figure 6(g) shows that an impacting water column bounced off the KH-GN sponge's surface; this further showed the superhydrophobicity of the KH-GN sponge. Generally, superhydrophobic surfaces are fabricated by a combination of appropriate surface roughness with hydrophobic materials.³⁷ Therefore, two factors contributed to the superhydrophobicity, roughness and low surface energy.³⁸ In the present case, GN was coated onto the sponge; this increased its

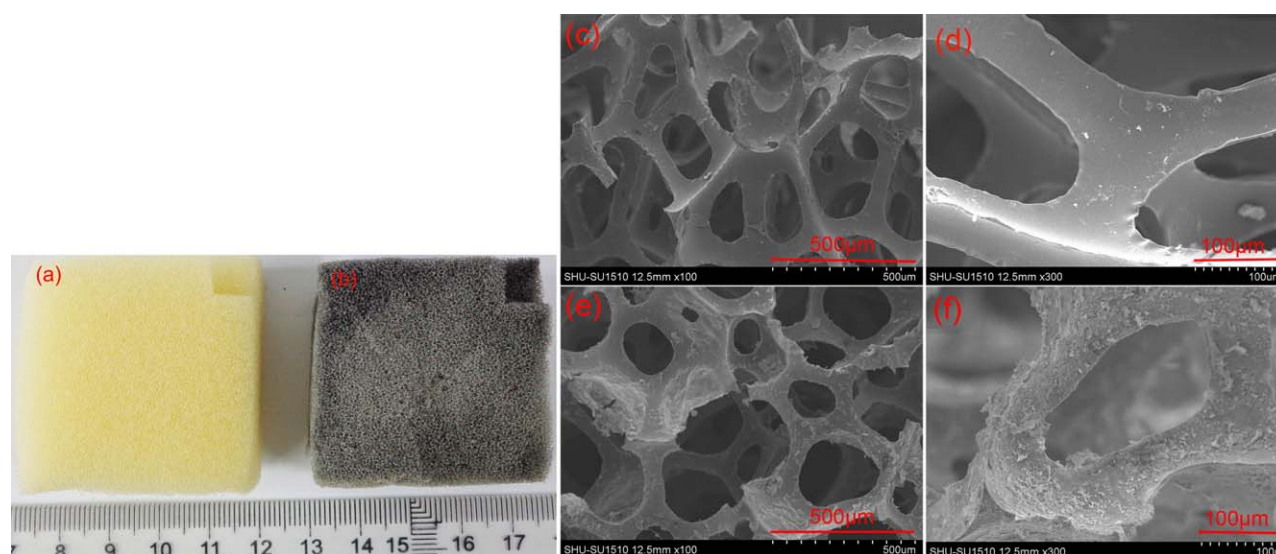


Figure 5. Photographic images of the (a) original and (b) KH-GN sponges. Morphological images of the (c,d) original and (e,f) KH-GN sponge. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

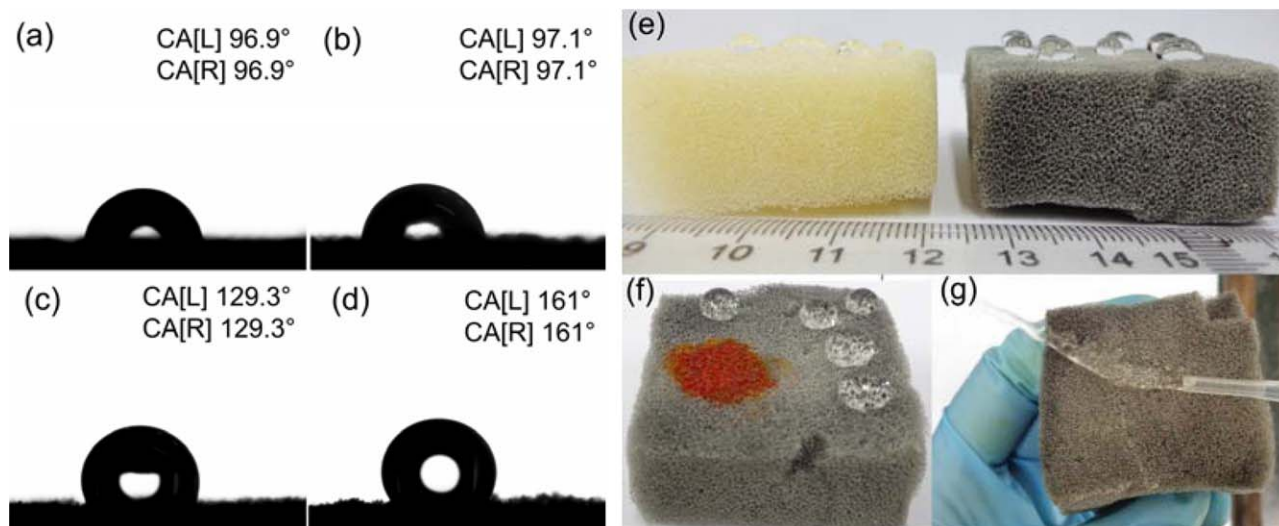


Figure 6. CAs of the (a) original, (b) KH, (c) GN, and (d) KH-GN sponges. (e) Photographic images of water droplets on the original and KH-GN sponges. (f) Photographic image of water droplets and a diesel oil droplet on the KH-GN sponge. (g) Photographic image of a water column squirted onto the KH-GN sponge (L-left, R-right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

roughness. After it was modified with KH-570, the surface energy of both the GN and the sponge became lower. Thereafter, the fabricated KH-GN sponge became superhydrophobic. On the other hand, it became more superoleophilic than the original sponge.

Reusability of the KH-GN Sponge

Additionally, the reusability of the KH-GN sponge is presented in Figure 7. The maximum absorption capacity of the KH-GN sponge for different oils did not decrease when the KH-GN sponge was recycled more than 120 times. The reusability of the KH-GN sponge was much better than that of other oil absorbents, including the GN-based sponge (five cycles)¹⁷ and the reduced GO-coated PU sponge (50 cycles).¹⁸ Their low reusabilities might have been due to the weak adhesion between the sponge skeletons and the GN sheets or reduced GO sheets. On the other hand, because of the good adhesion of the KH-570 to the sponge surface and the excellent elasticity and durability of the PU sponge itself, the KH-GN sponge had high adsorption

capacities with the integrated structure and no KH-GN falling off. Therefore, the oil-absorbent capacities of the KH-GN sponge hardly decreased after 120 cycles of reuse. Furthermore, the weight of the sponge after 5–120 cycles of desorption showed little change, although it actually had a slight increase within five cycles. After five cycles for the three kinds of oil, the weight of the KH-GN sponges increased by 1.6–1.9 g. The relative quantity of the adsorption capacity might have shown a slight reduction. However, it had little effect on the maximum adsorption capacity for oil.

These results show that the KH-GN sponge with superhydrophobicity not only had a high absorption capacity for different oils but also had excellent reusability.

CONCLUSIONS

In summary, this study showed a facile and inexpensive approach for fabricating superhydrophobic and superoleophilic PU sponges by their immersion in a KH-570-modified GN dispersion solution. This novel sponge exhibited the characteristics of superhydrophobic properties ($CA = 161^\circ$) and a unique absorption capacity. The maximum absorption of the prepared KH-GN sponge for oil was up to 39 times. Furthermore, the coated sponge was reused more than 120 times without losing its maximum absorption capacities. Because of the good commercial availability of raw materials, simple fabrication process, and superior properties of the sponge, the KH-GN PU sponge could be a promising product for the removal of oil spillage in the ocean on a large scale.

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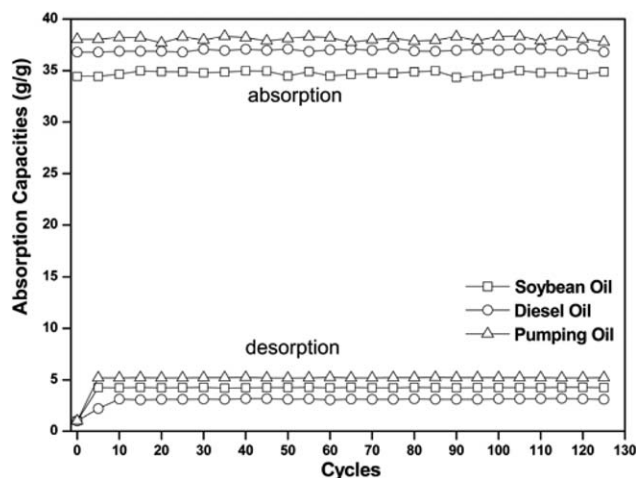


Figure 7. Reusability of the KH-GN sponge.

electron microscopy and XPS experiments were conducted under the approval of the Test Center of Analytical Instruments at Shanghai University.

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