

Fabrication of a Superhydrophobic, Fire-Resistant, and Mechanical Robust Sponge upon Polyphenol Chemistry for Efficiently Absorbing Oils/Organic Solvents

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Supporting Information

ABSTRACT: In this study, a superhydrophobic, fire-resistant, and mechanical robust sponge was fabricated through a two-step polyphenol chemistry strategy for efficiently absorbing oils/organic solvents (*rapidity in absorption rate and large quantity in absorption capacity*). Specifically, the Fe^(III)–polyphenol complex is formed upon the metal–organic coordination between tannic acid (TA, a typical polyphenol) and Fe^(III) ions, which is spontaneously coated on the surface of the pristine melamine sponge. Then, free catechol groups in the polyphenol are applied for grafting 1-dodecanethiol, thus generating the superhydrophobic sponge. Several characterizations have confirmed the chemical/topological structures, superhydrophobicity, fire-resistant merits, and mechanical robust property of the sponge. As a result, this sponge exhibits excellent absorption capacities of oils/organic solvents up to 69–176 times its own weight, indicating promising sorbents for removing oily pollutants from water. Meanwhile, owing to the facile fabrication process and inexpensive/easy available raw materials, the large-scale production of this sponge will be convenient and cost-effective.

■ INTRODUCTION

Nowadays, or in the long-term future, petroleum is becoming one of the three major energy resources (i.e., coal, petroleum, and natural gas) all over the world. As a result, frequent oil spillages during the exploitation/transportation of petroleum as well as the industrial discharge of organic solvents during the refining/processing of petroleum have brought about severe environmental damage or even crisis.^{1–3} Particularly, from the years of 1970 to 2010, hundreds of oil spillage accidents from well blowouts, pipeline spills, and tanker spills with the highest spilled oil of over 400,000 tons in the Oil Spillage from the Gulf of Mexico (*Deepwater Horizon*) have caused the death of thousands of animals and seriously damaged the ocean/coast near the oilfield.² Therefore, rapid and efficient recovery of oils/organic solvents from water will be urgently required for achieving the sustainable development of energy and environment.⁴

Absorption and removal of oils/organic solvents by using hydrophobic porous materials, which possess superhydrophobic property and highly porous structure, have been proven a feasible and promising way for solving the issue as mentioned above.^{5–25} Generally, an ideal hydrophobic porous material for absorbing oils/organic solvents should simultaneously meet the following requirements: easy fabrication procedure, low cost, high absorption capacity with rapid absorption rate, fire resistance, and mechanical robustness with easy reusability/recyclability. Up to date, several kinds of hydrophobic porous materials, including 1) carbon-based porous materials (including graphene sponge/aerogel,^{8,24} carbon nanofiber aerogel,^{10,12,13} graphene/carbon nanotube hybrid foam,²² carbon nanotube sponge,²³ etc.), 2) organosilicon-based porous materials,^{14,17} and 3) porous materials coated with an

organosilane layer or a lotus leaf-mimic layer,^{5,6,15,19–21,25} have been successfully applied for the removal of oils/organic solvents and showed good performance in this process. Particularly, one of them can even maintain a high oil uptake capability under extreme temperature (−196 °C to 400 °C), making it a promising candidate for oil cleanup under harsh conditions.²³ Unfortunately, most of the hydrophobic porous materials face problems, e.g., complicated/harsh fabrication processes (*mainly refers to carbon-based materials*), high cost of reagents/equipment (*mainly refers to organosilicon-based porous materials*), or easy inflammability (*mainly refers to porous materials coated with an organosilane layer or a lotus leaf-mimic layer*), thus preventing the use of these materials in the practical applications. Fortunately, very recently, Lu and co-workers²¹ fabricated a superhydrophobic sponge through functionalizing the surface of a fire-resistant melamine sponge with a polydopamine layer, followed by grafting with a hydrophobic molecule (*1H,1H,2H,2H-perfluorodecanethiol*) under ambient conditions. This as-acquired sponge exhibits a facile fabrication process and an excellent absorption performance and inherits the intrinsic fire-resistant nature of the pristine melamine sponge.²⁶ Nevertheless, the surface functionalization process seems to be time-consuming (>10 h), as well, both dopamine and the hydrophobic molecule would raise the cost of the final absorbent product. Therefore, a much lower-cost and time-saving method to fabricate “an ideal hydrophobic porous material” is still highly required and confronts huge challenges.

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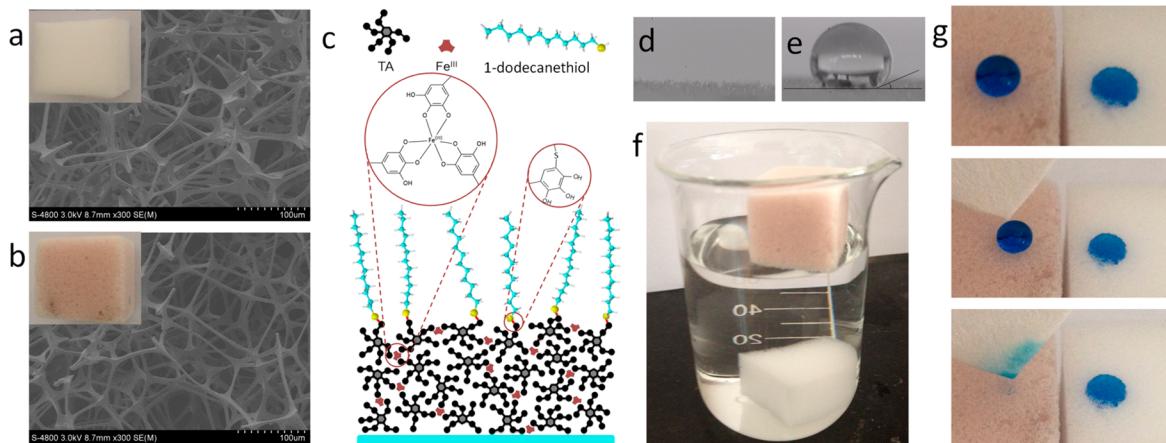


Figure 1. a) SEM image and photograph (inset) of the pristine melamine sponge; b) SEM image and photograph (inset) of the functionalized sponge; c) schematic illustration of the surface structure of the functionalized sponge;²⁹ d) the water contact angle of the pristine melamine sponge; e) the water contact angle of the functionalized sponge ($157.0 \pm 0.3^\circ$); f) photograph of the pristine melamine sponge and the functionalized sponge after contacting with the water surface; g) the residue of the water (stained with methylene blue) on the surface of the pristine melamine sponge and the quasi spherical water droplet on the surface of the functionalized sponge, which can be completely absorbed by a piece of filter paper.

The recent great discovery of synthesizing materials from polyphenol chemistry gives us great inspiration.^{27–33} In general, polyphenols with catechol or pyrogallol groups can either coordinate with metal/metal ions through a coordination reaction or react with amine- or thiol-containing molecules through a Michael addition reaction (or a Schiff base reaction). Typically, Caruso and co-workers found that tannic acid (TA, a typical polyphenol) could coordinate with $\text{Fe}^{(\text{III})}$ ions to form a TA– $\text{Fe}^{(\text{III})}$ complex on a surface of nearly all kinds of substrates. The whole process is completed within only 1 min, and the raw materials (tannic and FeCl_3) are rather low-cost. Besides, the free catechol groups in TA are considered to be able to react with amine- or thiol-containing molecules.^{6,32,33} Upon the polyphenol chemistry and Caruso's finding, herein, we develop a two-step polyphenol chemistry strategy to fabricate a superhydrophobic sponge with fire-resistant and mechanical robust properties under ambient conditions. First, the pristine melamine sponge (a fire-resistant sponge) is simply immersed into an aqueous mixing solution of TA and FeCl_3 , which would lead to the spontaneous deposition of a thin TA– $\text{Fe}^{(\text{III})}$ complex layer over the entire sponge surface (within 1 min). Second, a monolayer of 1-dodecanethiol is covalently grafted on the sponge through simple immersing of the TA– $\text{Fe}^{(\text{III})}$ complex-coated sponge into a 1-dodecanethiol ethanolic solution. The as-obtained superhydrophobic sponge exhibits excellent absorption performance in the removal of oily pollutants from water mainly due to the combination of its high porosity, superhydrophobicity, and mechanical robust property. Moreover, as a result of the fire-resistant property of a melamine sponge, the superhydrophobic sponge also shows a similar property, thus reducing the risk of fire once applied as an absorbent for oils/organic solvents. Furthermore, just owing to the facile fabrication process and the inexpensive/easy available raw materials, the large scale production of this sponge will be cost-effective and convenient.

EXPERIMENTAL SECTION

Materials. Melamine sponge was obtained from Hongchang Plastic Industrial Co., Ltd. (Sichuan, China). Tannic acid (TA), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), anhydrous ethanol, 1-dodecanethiol, sodium hydroxide (NaOH), and

hydrochloric acid (HCl) were obtained from Guangfu Chemical Company (Tianjin, China). All other reagents (analytical grade) were used without further purification. Deionized water was used throughout all the experiments.

Fabrication of the Superhydrophobic Sponge. Typically, several pieces of melamine sponge (2 cm × 2 cm × 2 cm) were soaked in water in a 500 mL baker. Solutions of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and TA were added to this aqueous solution to acquire the following concentrations ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$: 0.1 mg mL^{-1} , TA: 0.4 mg mL^{-1} in 400 mL of water). The solution was mixed by vigorously stirring for 20 s immediately after the individual additions of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and TA. The pH of this solution was subsequently adjusted to ca. pH 8 through adding 1 M NaOH solution. Then, the as-obtained sponge was washed with ethanol several times to remove the water. After having been dried, the TA– $\text{Fe}^{(\text{III})}$ complex-coated sponge was put into an ethanolic solution of 1-dodecanethiol (2.0 mg mL^{-1} , pH 8.5, the amount of 1-dodecanethiol was excess) followed by stirring for 24 h. Next, the sponge was taken out and washed with ethanol several times. The superhydrophobic sponge was acquired after thoroughly drying in air. All the reactions were performed at room temperature (25 °C). For comparison, another kind of superhydrophobic sponge comprising another hydrophobic molecule (1H,1H,2H,2H-perfluorodecanethiol) instead of 1-dodecanethiol was also fabricated through the above method. The related comparison test can be found in Figures 2 and S4 of the Supporting Information.

Characterizations. Raman spectrum was recorded by using a DXR Smart Raman Spectrometer of Thermo Fisher Scientific with Nd:YAG laser (633 nm) as excitation source. Scanning electron microscopy (SEM) images were acquired on a field-emission SEM (FESEM, Nanosem 430) operated at an accelerating voltage of 3.0 kV. The elemental analysis was determined by energy-dispersive X-ray spectroscopy (EDS) attached to the SEM. The water contact angle measurements were performed on a contact angle goniometer (JC2000C, Shanghai, China) at room temperature. The volume of water droplet was ca. 4 μL . The compression test was performed on an electronic universal testing machine (wdw-02, Yangzhou, China) with the compressive rate of 50 mm min^{-1} . Fourier transform infrared spectroscopy (FTIR) spectra were obtained

on a Nicolet-6700 spectrometer. Thirty-two scans were accumulated with a resolution of 4 cm^{-1} for each spectrum.

Absorption Tests of Oils/organic Solvents. In a typical absorption process, different types of oils and organic solvents (including methanol, ethanol, isopropyl alcohol, acetone, toluene, chloroform, dichloromethane, soybean oil, pump oil, used pump oil, crude oil, DMF, DMSO, *n*-hexane, cyclohexane, *n*-heptane, *n*-hexadecane) were adopted. Typically, the absorbent (the Superhydrophobic Sponge) was dropped into the organic liquid until the absorbent was completely filled with the liquid. Subsequently, the obtained sponge was taken out and quickly weighed to avoid evaporation of the absorbate.

The absorption capacity was defined as $(M_a - M_0)/M_0$, which was mainly applied for calculating the absorption abilities of the superhydrophobic sponge. M_0 was the weight of the pristine dry absorbent for absorbing organic liquid; M_a was the total weight after saturation with liquids.

The net absorption capacity was defined as $(M_n - M_{n, desorption})/M_0$, which was mainly applied for calculating the recycling abilities of the superhydrophobic sponge. M_0 was the weight of the pristine dry absorbent for absorbing organic liquid; M_n was the total weight after saturation with liquids at the n^{th} -time recycling; and $M_{n, desorption}$ was the total weight after desorption of liquids at the n^{th} -time recycling.

RESULTS AND DISCUSSION

Obviously as shown in Figure 1a and 1b, after the functionalization process, the resultant product retains its original morphological structures with a color changing from white to light orange. Both of the sponges possess an interconnected three-dimensional (3D) network and a highly porous structure, which should be beneficial for the rapid uptake of oils/organic solvents. The chemical structure of the functionalized layer on the sponge is characterized by several techniques, including Raman spectrometer, Fourier transform infrared spectroscopy (FTIR), and energy dispersive X-ray spectrometer (EDS). Clearly, as shown in Figure S1 (Raman spectra, Supporting Information), the newly appeared peaks at ca. 591 cm^{-1} and $1350/1485\text{ cm}^{-1}$ of the functionalized sponge compared to the pristine sponge are, respectively, assigned to the TA–Fe^(III) interactions and TA (or polyphenol) ring vibrations,³⁴ indicating the existence of the TA–Fe^(III) complex on the surface of the functionalized sponge. Besides, as illustrated in the FTIR spectra (Figure S2 in the Supporting Information), the increase in the intensity of the –CH₂– groups at 2920 cm^{-1} confirms the successful grafting of 1-dodecanethiol through the Michael addition reaction between the thiol groups of 1-dodecanethiol and the catechol groups of TA,^{32,33,35} which is also verified by the EDS result (Figure S3 in the Supporting Information, the observation of the S element in the functionalized sponge). Then, the surface wetting property of the functionalized sponge is examined by means of water contact angle measurements. As shown in Figure 1d, a water droplet is immediately absorbed by the pristine sponge once contacting with the surface, suggesting the superhydrophilicity of the pristine sponge. By contrast, the functionalized sponge shows a water contact angle of $157.0 \pm 0.3^\circ$ (Figure 1e), thus confirming its superhydrophobicity. After being placed on the surface of water, the pristine sponge quickly sinks to the bottom owing to the superhydrophilicity and highly interconnected three-dimensional (3D) porous structure (Figure 1f). However, the functionalized sponge could completely float on the water surface primarily due to the superhydrophobicity, lightweight,

and water-repellent property. Moreover, the water-repellent property of the functionalized sponge is further verified by the photographs in Figure 1g.

Besides, the superoleophilicity of the functionalized sponge in air and under water is also confirmed by the oil contracting experiments (Figure 2). Specifically, once an oil droplet (*n*-

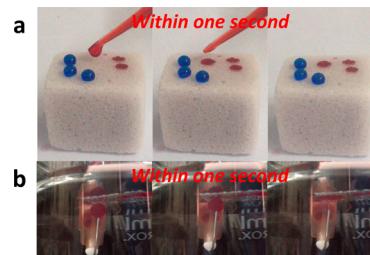


Figure 2. Contacting experiments of an oil droplet (stained with oil red O) on the superhydrophobic sponge surface a) in air and b) underwater.

hexadecane stained with oil red O) is dropped on the surface of the functionalized sponge in air, the oil droplet was immediately spread (within one second), where the contact angle is 0° (Figure 2a). To further characterize the underwater contact angle of an oil droplet, the functionalized sponge is put on the surface of water. Then, an oil droplet (*n*-hexadecane stained with oil red O) is pushed out of the syringe needle to contact with the surface of the functionalized sponge underwater. As illustrated in Figure 2b, the oil droplet is immediately spread (within one second) on the surface of the functionalized sponge, where the contact angle is also 0° . All evidence as illustrated above confirms the superhydrophobicity and superoleophilylicity (either in air or underwater) of the functionalized sponge.

In the past five years, several oil spillages occurred such as the Gulf of Mexico oil spill (2010), the Gulf of Bohai oil spill (2011), and the Gulf of Thailand Rayong Sea oil spill (2013), which were highly flammable and rather dangerous for marine organisms and human beings. As is well-known, the pristine melamine sponge has a fire-resistant property. Therefore, the as-obtained superhydrophobic sponge might inherit its fire-resistant nature, which could reduce the risk of fire of oil spills or organic pollutants. To verify this assumption, the heating and combustion tests are conducted. More specifically, the superhydrophobic sponge is placed on the asbestos net heated by an alcohol lamp. With the heating time being prolonged to longer than 300 s, a minor difference in the morphology of the superhydrophobic sponge could be observed (Figure 3c). Besides, once directly contacted with the fire, the flame on the superhydrophobic sponge is rather weak and continued for more than five seconds, resulting in a black residue (ca. 20% of its original weight, Figure 3f). A further attempt as shown in Figure 3b and 3e has confirmed that the heat- and fire-resistant property of the superhydrophobic sponge is mainly inherited from the heat- and fire-resistant nature of the pristine melamine sponge. By contrast, a polyurethane sponge is also subjected to the same test. For the heating test, the polyurethane sponge is completely converted into combustion ash with some other carbon-based residue within 40 s (Figure 3a). Additionally, after being ignited, a bright and vigorous flame is observed on this polyurethane sponge, which continues to burn completely (Figure 3c). Collectively, the heating and combustion tests

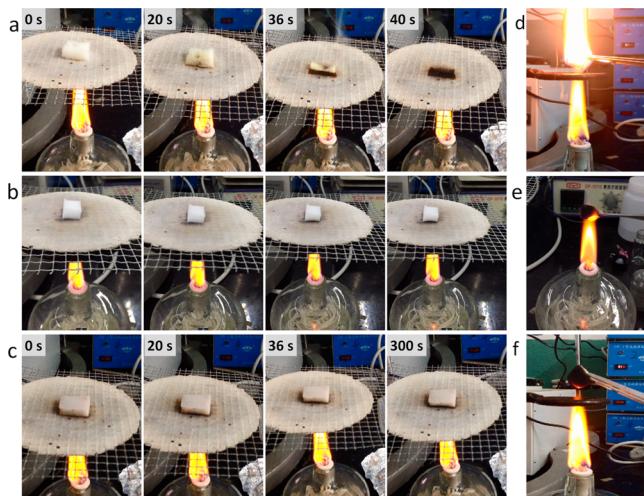


Figure 3. a–c) heating and d–f) combustion process of the a, d) polyurethane sponge, b, e) pristine melamine sponge, and c, f) superhydrophobic sponge.

confirm the good fire-resistant property of the superhydrophobic sponge, thus making the superhydrophobic sponge an ideal candidate to reduce the risk of fire once applied in the removal of oils/organic solvents.

In practical applications, the robust mechanical stability, especially the property against the repeated compression/release, is highly required for the absorbent. Herein, mainly as a result of the high mechanical stability of the pristine melamine sponge, the superhydrophobic sponge might show a similar robustness in mechanical stability. In detail, the superhydrophobic sponge in cube shape ($2.0\text{ cm} \times 2.0\text{ cm} \times 2.0\text{ cm}$) can bear a manual compression stain high up to 70%, exhibit excellent flexibility, and nearly fully recover its original shape after the release of the compression (Figure 4a).

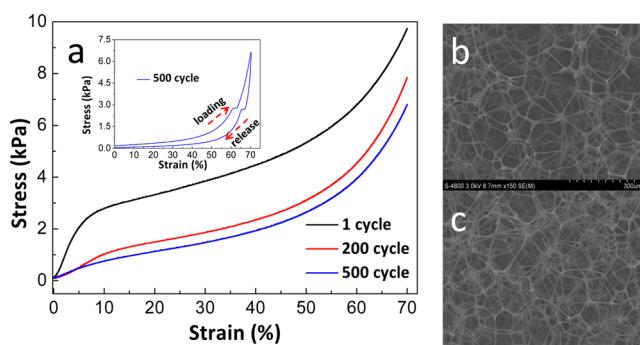


Figure 4. a) The compressive stress–strain curves of the superhydrophobic sponge over 1, 200, and 500 compression/release cycles (inset of part a: the stress–strain curves of the superhydrophobic sponge over 500 compression/release cycles, including both compression and release process); SEM images of the superhydrophobic sponge b) before and c) after 500 compression/release cycles.

Particularly, the 3D interconnected porous structure of the superhydrophobic sponge is maintained without apparent structural damage even after 500 cycles at a 70% compression stain (Figure 4b and 4c). The robust mechanical property would then endow the superhydrophobic sponge excellent reusability and recyclability, leading to great promise for practical applications.

Collectively, the superhydrophobic sponge exhibits several advantages, including superhydrophobicity/superoleophilicity, high porosity, fire resistance, and mechanical robustness, which promotes this material as a promising candidate for efficient removal of oils/organic solvents. The absorption process as well as the calculated absorption capacities of oils/organic solvents by using this superhydrophobic sponge can be found in Figure 5a–5c. Two kinds of oils/organic solvents, heptane ($\rho_{\text{heptane}}/\rho_{\text{water}} = 0.68$) and chloroform ($\rho_{\text{chloroform}}/\rho_{\text{water}} = 1.50$), are chosen as the examples to illustrate the absorption process. Specifically, once contacted with a heptane layer (stained with oil red O) on a water surface, the superhydrophobic sponge can fully absorb the heptane rather rapidly (within one second) (Figure 5a and Movie S1 in the Supporting Information). Besides, the superhydrophobic sponge can float on the water surface after the absorption of the heptane, which was mainly due to the much lower density of heptane ($\rho_{\text{heptane}}/\rho_{\text{water}} = 0.68$) and the superhydrophobicity of the sponge, thus suggesting an ease of recycling of this absorbents. Subsequently, the absorption experiment of chloroform (stained with oil red O) at the bottom of the water is also implemented. The high absorption rate (fully absorbed within two seconds) and excellent absorption behavior as shown in Figure 5b and Movie S2 (Supporting Information) further makes this superhydrophobic sponge a desirable candidate for removal of oils/organic solvents. To further testify the oils/organic solvents removal ability of this superhydrophobic sponge, absorption experiments of 16 kinds of oils/organic solvents that are common pollutants in daily life/industry are implemented, including petroleum products (e.g., crude oil, pump oil, used pump oil), fats (e.g., soybean oil), alcohols (e.g., methanol, ethanol, isopropyl alcohol), ketones (e.g., acetone), hydrocarbons (e.g., hexane, cyclohexane, heptane, n-hexadecane), aromatic compounds (e.g., toluene), and other organic solvents (e.g., chloroform, dichloromethane, dimethylformamide (DMF), dimethyl sulfoxide (DMSO)). After calculation, this superhydrophobic sponge shows excellent absorption capacities up to 69–176 times its own weight, which is primarily dependent on the density of the absorbed liquid. To our surprise, the acquired absorption capacities are much higher than that of marshmallow-like organosilicon-based gel (6–15 times),¹⁴ organosilicon-based nanowire membranes (4–20 times),¹⁷ and even comparable to that of some typical carbon-based absorbents, such as carbonaceous nanofiber aerogels (40–115 times),¹⁰ graphene/carbon nanotube foams (80–140 times),²² and twisted carbon fibers (TCF) aerogels (50–192 times).¹² (More related information can be found in Table S1.) Combined with the facile/mild preparation process and low cost of raw materials, this superhydrophobic sponge developed in our work is a environmentally-friendly, cost-effective, and promising sorbent for the removal of oil spills and organic pollutants.

The reusability of the absorbent as well as the recyclability of the absorbed liquid is also a key criteria for the cleanup of oil spills/organic pollutants in practical applications. Typically, three approaches, i.e., combustion, squeezing, and distillation, can be utilized for testing to the properties of the absorbents, which primarily depend on the species of the pollutants.^{12,36} More specifically, combustion is suitable for recovering the flammable/useless pollutants; squeezing is applicable for recovering precious/nonflammable pollutants having high boiling points; and distillation is an effective method for removing precious pollutants having low boiling points.

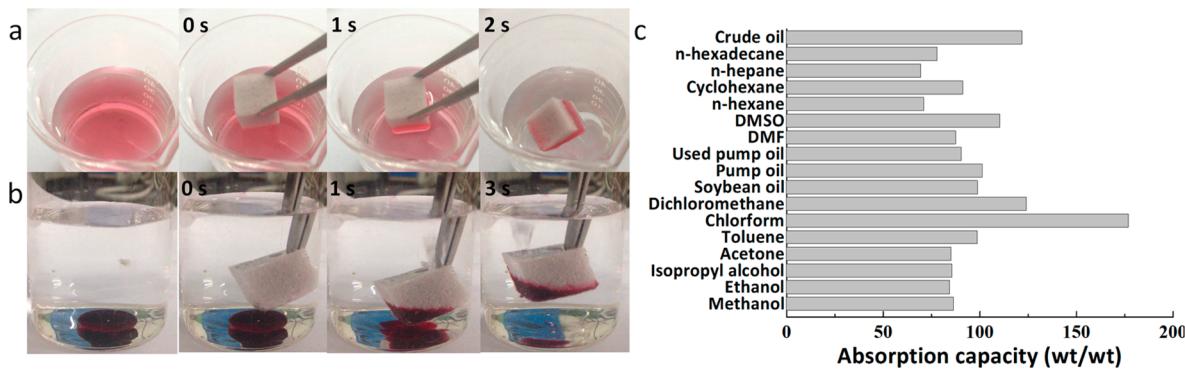


Figure 5. Snapshots of the removal process of a) heptane (stained with oil red O) from the water surface and b) chloroform from the bottom of water using the superhydrophobic sponge; c) summary of the absorption capacities of the oils/organic solvents for the superhydrophobic sponge.

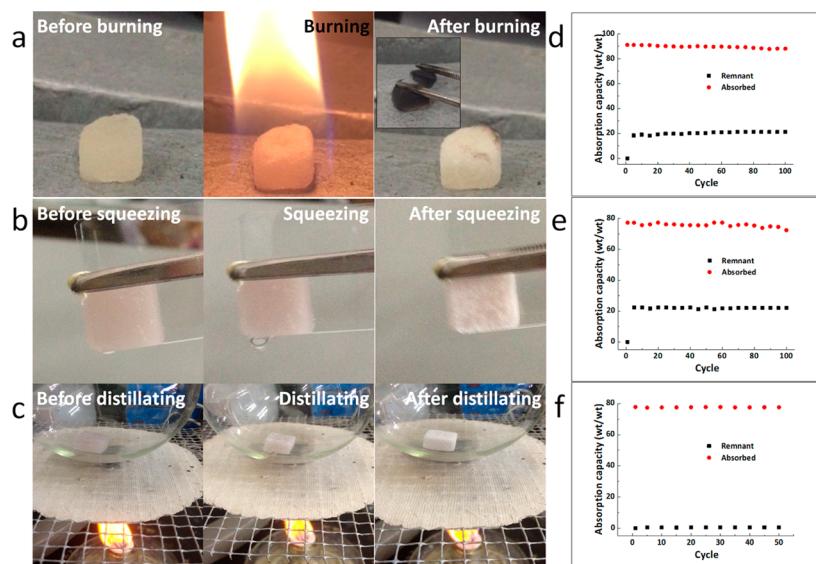


Figure 6. a–c) Photographs showing the process of recycling the superhydrophobic sponge via a) combustion of cyclohexane, b) squeezing of *n*-hexadecane, and c) distillation of heptane; d–f) recyclability tests of the superhydrophobic sponge: d) combustion is used to recycle the superhydrophobic sponge absorbed with cyclohexane, e) squeezing is applied to recycle the superhydrophobic sponge absorbed with *n*-hexadecane, and f) distillation is adopted to recycle the superhydrophobic sponge absorbed with heptane.

Measurements of three typical examples are conducted to illustrate the recycling process (Figure 6). For example, cyclohexane absorbed by the superhydrophobic sponge can be removed by combustion. After the combustion, no change in the shape and morphology of the superhydrophobic sponge can be found. Notably, for this approach, the combustion process should be ended before the color of the superhydrophobic sponge changes to black (inset of Figure 6a). After calculation, 66.05% of the net absorption capacity (72.4% of its initial absorption capacity, Figure 6d) could be achieved for cyclohexane after the 100-cycled absorption/combustion process. The decrease in absorption capacity should be owing to the residual cyclohexane in the superhydrophobic sponge after combustion. Alternatively, *n*-hexadecane, a high boiling point of 286.8 °C, can be recovered through a squeezing approach (Figure 6b). After 100 absorption/squeezing cycles, the net absorption capacity of the superhydrophobic sponge is lowered to 65.09% of its initial absorption capacity (50.33% of the net absorption capacity, Figure 6e). Finally, distillation is adopted to recycle heptane with a relatively low boiling point of 98.5 °C (Figure 6c). After absorption, the heptane-absorbed superhydrophobic sponge is heated to make the evaporation of

the absorbed liquid, which is simultaneously gathered by condensing equipment. As shown in Figure 6f, no obvious changes in net absorption capacity could be observed after a 50-cycled absorption/distillation process. Nevertheless, in comparison to other two approaches, this distillation approach would consume a relatively longer time to fully gather the absorbed liquid. In a short summary, as proved by the three recycling approaches, the fire-resistant and mechanical robust properties confer the superhydrophobic sponge highly efficient recyclability, which promotes the great potential of this superhydrophobic sponge in treating oil pollutions or organic pollutions.

CONCLUSIONS

In summary, a superhydrophobic, fire-resistant, and mechanical robust sponge with excellent absorption performance of oils/organic solvents (*including high capacity with good selectivity, extraordinary recyclability, and simple/versatile recycling routes*) is prepared through a two-step polyphenol chemistry strategy. In the first step, catechol groups in the polyphenol are in charge of coordinating with Fe^(III) to form the polyphenol–Fe^(III) complex coating on the surface of the sponge. In the second

step, free catechol groups in the polyphenol are responsible for chemically conjugating 1-dodecanethiol. Since none use this complicated process, expensive raw materials, and sophisticated equipment, the fabrication of this sponge is easy and cost-effective to scale up. Therefore, this sponge as-fabricated in our work could offer great potential in addressing the energy and environmental issues (*water pollutions, marine oil spillages, etc.*) resulting from the oil spills/organic pollutants.

■ ASSOCIATED CONTENT

Supporting Information

Raman spectra and FTIR spectra of the pristine melamine sponge and superhydrophobic sponge; EDS curve of the superhydrophobic sponge; Photographs of water droplets on the surface of the superhydrophobic sponge after low-/high-temperature exposure; Photographs of water droplets and oil droplets on a superhydrophobic sponge comprising another hydrophobic molecule ($1H,1H,2H,2H$ -perfluorodecanethiol) instead of 1-dodecanethiol; Photographs of acid, alkaline, and salty water droplets on the surface of the superhydrophobic sponge; Snapshots of the absorption process of crude oil by using the superhydrophobic sponge; the weight of the superhydrophobic sponge before absorption and after absorption; Comparison of various sorbent materials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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