

Mussel-Inspired One-Step Copolymerization to Engineer Hierarchically Structured Surface with Superhydrophobic Properties for Removing Oil from Water

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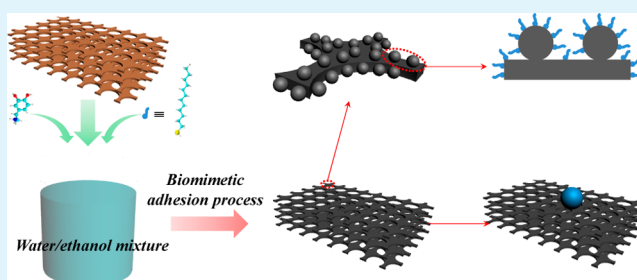
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S Supporting Information

ABSTRACT: In the present study, a superhydrophobic polyurethane (PU) sponge with hierarchically structured surface, which exhibits excellent performance in absorbing oils/organic solvents, was fabricated for the first time through mussel-inspired one-step copolymerization approach. Specifically, dopamine (a small molecular bioadhesive) and *n*-dodecylthiol were copolymerized in an alkaline aqueous solution to generate polydopamine (PDA) nanoaggregates with *n*-dodecylthiol motifs on the surface of the PU sponge skeletons. Then, the superhydrophobic sponge that comprised a hierarchical structured surface similar to the chemical/topological structures of lotus leaf was fabricated. The topological structures, surface wettability, and mechanical property of the sponge were characterized by scanning electron microscopy, contact angle experiments, and compression test. Just as a result of the highly porous structure, superhydrophobic property and strong mechanical stability, this sponge exhibited desirable absorption capability of oils/organic solvents (weight gains ranging from 2494% to 8670%), suggesting a promising sorbents for the removal of oily pollutants from water. Furthermore, thanks to the nonutilization of the complicated processes or sophisticated equipment, the fabrication of the superhydrophobic sponge seemed to be quite easy to scale up. All these merits make the sponge a competitive candidate when compared to the conventional absorbents, for example, nonwoven polypropylene fabric.

KEYWORDS: mussel-inspired chemistry, hierarchically structured surface, superhydrophobicity, oil/water separation, polydopamine



INTRODUCTION

Nowadays, the frequent oil spillages, as well as the industrial discharge of oils/organic solvents, have caused energy, environmental, and ecological problems or even crisis, all around the world.^{1–3} For instance, the Gulf of Mexico oil spill in 2010, the Gulf of Bohai oil spill in 2011, and the Gulf of Thailand Rayong sea oil spill in 2013 all greatly harmed the coastline and near-shore waters, leading to a disaster for marine organisms. Therefore, it is urgent to develop high-performance absorbent materials for the efficient removal of oils/organic solvents.

Hydrophobic porous materials have gained tremendous interests because of their capability of selective absorption of oils/organic solvents while completely repelling water.^{4–28} To date, numerous hydrophobic porous materials, as well as their synthesis methods (including carbon-based porous materials derived from pyrolysis of polymers^{5,12,13,17,18} or self-assembly of carbon-based building blocks,^{14–16} organosilicon-based porous materials derived from copolymerization of functionalized alkoxysilane precursors,^{11,19} organosilanes-coated porous materials derived from surface grafting/coating methods,^{4,8,9,20} porous materials comprising a lotus leaf-mimic surface derived from varies

nanoparticle decorating methods^{4,21,22,25–28}), have been developed for removing oils/organic solvents from water. Unfortunately, most of the methods as mentioned above have problems such as complicated/lengthy processes and high costs for reagents/equipment, which prevent the use of these materials in practical applications. Therefore, developing a facile, mild and inexpensive method to synthesize hydrophobic porous materials is urgently required, but still faces a great challenge.

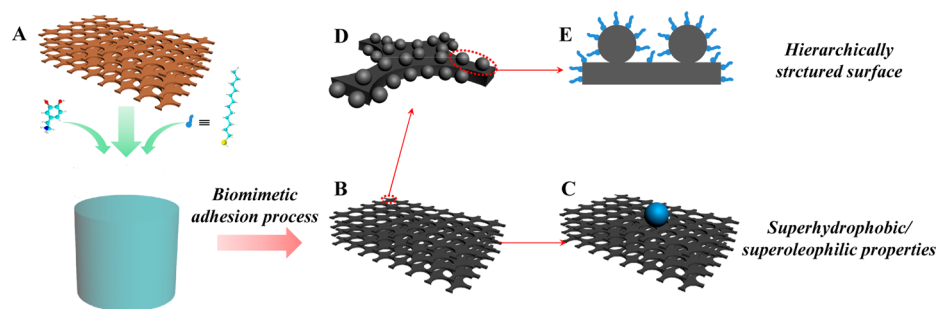
Recently, the bioadhesion phenomenon of marine organisms, such as mussels, has also drawn great attentions. Inspired by bioadhesion, Messersmith and co-workers first demonstrated dopamine could polymerize and deposit on all kinds of organic and inorganic surfaces under quite facile and mild conditions.²⁵ Besides, the resultant polydopamine (PDA) can be used as a platform for diverse secondary reactions, including reducing noble metal ions into metals, grafting amino-/thiol-containing molecules, etc.²⁹ Upon the mussel-inspired chemistry, Xu and co-workers synthesized core/shell/satellite composite particles

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Scheme 1. Illustration for the Synthesis Process of the Superhydrophobic PU Sponge: (A) the Pristine PU Sponge, (B) the Superhydrophobic (or the modified) PU Sponge, (C) Water Droplet on the Superhydrophobic PU Sponge, (D) Enlarged Region of the Superhydrophobic PU Sponge, (E) the Hierarchically Structured Surface of the Superhydrophobic PU Sponge



with a hierarchical structure similar to the chemical/topological structures of lotus leaf.³⁰ Briefly, silver nanoparticles were formed by reduction and located on the external surface of PDA-coated core particles. Both PDA and silver nanoparticles were then exploited to react with alkanethiol, thus resulting in superhydrophobic silica/PDA/silver/alkanethiol core-shell particles. Just owing to the hierarchical structured surface (both chemical and topological structures), the resultant core-shell particles showed potential use in oil/water separation and transportation. Upon the same method, superhydrophobic polyurethane (PU) sponges with PDA/silver/alkanethiol layers on the surface of the sponge skeletons were also synthesized for efficient adsorbing organic pollutants from water by Zhang and co-workers.³¹ Collectively, the mussel-inspired chemistry provides us a rather mild and effective method to synthesize superhydrophobic materials. Nevertheless, during the generation of a surface with a hierarchical structure similar to the chemical/topological structures of lotus leaf, the whole process also seems to require multiple steps, which might lower the efficiency of this method. Therefore, simplifying the process of this mussel-inspired chemistry method to synthesize superhydrophobic porous materials is highly desired.

Fortunately, in the previous study,³² we found that, under high dopamine concentration ($>8 \text{ mg mL}^{-1}$) with polymerization of longer than 6 h, the acquired PDA layer derived from the self-polymerization of dopamine on the surface of substrates were mainly composed of numerous nanoaggregates, which were similar to the as-formed silver nanoparticles synthesized from the reduction of silver ions by a polydopamine layer with smooth surface. Therefore, it can be conjectured that the silver nanoparticles could be discarded in the process of generating a lotus leaf-mimic surface, and a much simpler process upon the mussel-inspired method could be developed.

Herein, a superhydrophobic PU sponge with hierarchically structured surface is fabricated through a mussel-inspired one-step copolymerization method. As is well-known, the pristine PU sponge is considered as a highly porous, lightweight, and strong mechanical stable candidate, which can be exploited for the synthesis of high-performance absorbent. Using pristine PU sponges as the raw substrate, a facile and mild one-step copolymerization approach is developed to prepare the superhydrophobic PU sponges. Specifically, the simple immersion of the original hydrophilic PU sponge in an ethanol-water (1:1) solution of the mixture of dopamine and *n*-dodecylthiol would lead to the spontaneous deposition of numerous PDA nanoaggregates with *n*-dodecylthiol motifs over the entire surface on the sponge skeletons (Scheme 1). Just as a

result of the combination of their superhydrophobicity, high porosity, and strong mechanical stability, the obtained sponges exhibit good absorption performance, including a high absorption capacity, excellent selectivity, and superior recyclability. Moreover, this approach is rather facile, economical, and environmental-benign than conventional processes for surface functionalization, including chemical vapor deposition, dip coating with a polymer and electrostatic deposition. Multistep procedures, sophisticated equipment, harsh conditions, or an aggressive etching solution could be avoided, thus making the superhydrophobic PU sponges possible to synthesize on a large scale.

EXPERIMENTAL SECTION

Materials. Dopamine was obtained from Yuancheng Technology Development Co. Ltd. (Wuhan, China). Polyurethane (PU) sponge was purchased by the local market (Tianjin, China). 2-Amino-2-(hydroxymethyl)-1,3-propanediol (tris), sodium hydroxide (NaOH), hydrochloric acid (HCl), anhydrous ethanol, and *n*-dodecylthiol were obtained from Guangfu Chemical Company (Tianjin, China). All other reagents were of analytical grade, which were used without further purification. Deionized water was used throughout all the experiments.

Fabrication of the Superhydrophobic PU Sponges. Dopamine hydrochloride (160 mg) and *n*-dodecylthiol (40 μL) were dissolved in a H_2O /ethanol solution (20 mL, 1:1 v/v) at pH 8.5 under ultrasonication. Afterward, a piece of PU sponge (1.5 cm \times 1.5 cm \times 1.5 cm) was immersed in the resultant solution followed by stirring for 10 h. After it was rinsed with water and dried at 80 $^\circ\text{C}$, the superhydrophobic PU sponge was acquired.

Characterizations. Scanning electron microscopy (SEM) images were obtained through a field-emission SEM (FESEM, Nanosem 430). The elemental analysis was determined by energy-dispersive X-ray spectroscopy (EDS) attached to the SEM. The surface wettability of the sponge was measured by conducting the static contact angle measurement through a contact angle goniometer (JC2000C, Shanghai, China). More than five contact angles at different locations on one surface were averaged to obtain a reliable value. The compression test was performed on an electronic universal testing machine (wdw-02, Yangzhou, China) with the compressive rate of 20 mm min^{-1} . The dynamic light scattering measurements were implemented by using Brookhaven Instruments (BI200SM). An argon-ion vertically polarized laser (532 nm) was adopted as the light source.

Absorption of Oils/Organic Solvents by Using the Superhydrophobic PU Sponge. Typically, a piece of superhydrophobic PU sponge was immersed to a kind of oils/organic solvents until it was completely filled with the oils/organic solvents. Subsequently, the superhydrophobic PU sponge loaded with the oil/organic solvent was taken out for weight measurement. The weight of the super-

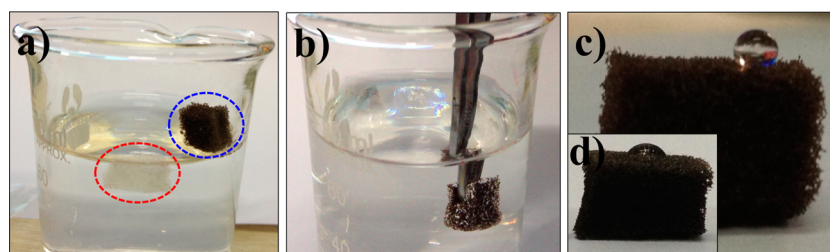


Figure 1. (a) Photograph of the pristine (white) and superhydrophobic PU (black) sponge after being placed on water, (b) photograph of the superhydrophobic PU sponge completely immersed in water by a force, and (c, d) water droplets on the surface of the (c) superhydrophobic PU sponge and (d) PDA-coated PU sponge.



Figure 2. Contacting experiments of an oil droplet on the superhydrophobic sponge surface (a) in air and (b) under water.

hydrophobic PU sponge (*one piece*) before and after adsorption was recorded for calculating the weight gain, as illustrated as eq 1).

$$\text{weight gain (\%)} = (M_{\text{after}} - M_{\text{before}}) / M_{\text{before}} \times 100\% \quad (1)$$

where M_{before} was the weight of the superhydrophobic PU sponge before adsorption (mg) and M_{after} was the weight of the superhydrophobic PU sponge after adsorption (mg).

RESULTS AND DISCUSSION

The surface wettability of the pristine and superhydrophobic sponge is demonstrated by using the water contact angle measurement. Figure 1a shows that a pristine sponge (white) can be fully immersed in the beaker without external force. However, the superhydrophobic sponge (black) could completely float on the water surface. When the superhydrophobic sponge is immersed in water by an external force, it would instantaneously float on the water surface after the force is released, and little water uptake could be found (weight gain lower than 10%). Besides, the presence of silver mirror-like reflection for the immersed superhydrophobic sponge (Figure 1b) should be ascribed to the existence of air layer trapped between the superhydrophobic sponge surfaces and water.¹⁷ Subsequently, as shown in Figure 1c and 1d, the water droplet is supported by the superhydrophobic sponge, which displays a water contact angle of ca. $157.3(\pm 2.5)^\circ$, thus confirming the superhydrophobicity of the sponge (*Herein, the error should be caused by the unclear baseline and the basic surface property of the sponge.*). After dropping water droplet on the sponge functionalized with only PDA nanoaggregates, the water contact angle is only $\sim 40^\circ$, suggesting the crucial role of the *n*-dodecylthiol motifs. Besides, according to previous literature,³³ a secondary verification of the surface hydrophobicity is made

upon water bouncing measurements. As shown in Figure S1 of the Supporting Information, once the water droplet is dropped on the surface of the superhydrophobic sponge, no bouncing phenomenon could be observed. Since the static contact angle of the sponge synthesized in our study is higher than 150° , this observation (no bouncing phenomenon) seems to be different from that found in previous literature.³³ Such difference could be ascribed to the highly porosity of the superhydrophobic sponges, which interferes the bouncing experiment result. Specifically, in previous literature,³³ the substrate is composed of dense and flat materials, which are then functionalized with the superhydrophobic layer. The water droplets can only be compressed or spread when they are dropped from a height of 2 cm. By contrast, in our study, once a droplet is dropped onto the surface of the superhydrophobic sponge from a height of 2 cm, the highly porous structure of the sponge might make the falling water droplet partially entrap into the macropores of the sponge, thus resulting in no bouncing phenomenon.

Moreover, the oleophilic property of the superhydrophobic sponge is also evaluated either in air or under water. More specifically, once an oil droplet (*n*-hexadecane stained with oil red O) is dropped on the surface of the superhydrophobic sponge in air, the oil can be immediately spread (*within one second*), where the contact angle is 0° (Figure 2). Then, to characterize the contact angle of an oil droplet on the surface of the superhydrophobic sponge under water, the 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 sponge under water. As shown in Figure 2, the oil droplet can be immediately (*within one second*) spread on the surface of the sponges, where the contact angle is also

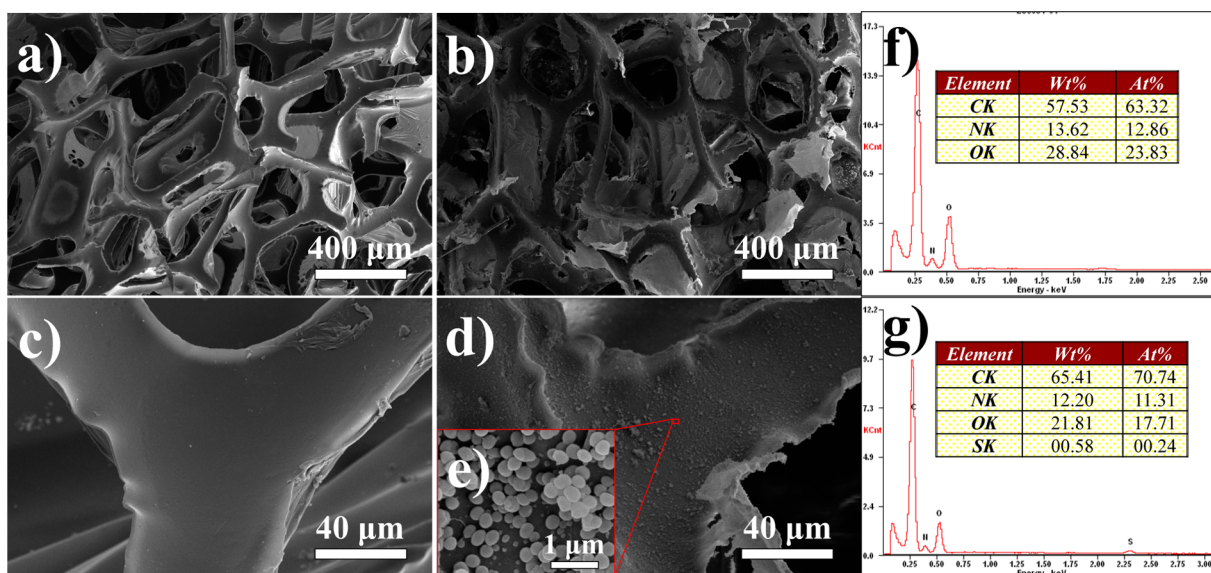


Figure 3. Typical (a, b) SEM images, (c, d, e) higher magnification SEM images, and (f, g) EDS curves of the (a, c, f) pristine PU sponge and (b, d, e, h) superhydrophobic PU sponge.

0° . Both experiments offer strong evidence of the superoleophilicity of the sponges either in air or under water.

The surface superhydrophobicity as demonstrated above may be as a result of the combination of the macroporous structure of the sponge, the micro/nanotextured structure of PDA nanoaggregates, and the hydrophobic chemical property of the *n*-dodecylthiol motifs on the sponge skeletons. Then, SEM is used for clarifying the morphological evolution of the sponge before and after functionalization with the PDA nanoaggregates and *n*-dodecylthiol motifs. As illustrated in Figure 3a, the sponge exhibited a three-dimensional hierarchical porous structure with pore size ranging from 200 to 350 μm . After coated with the PDA nanoaggregates with the *n*-dodecylthiol motifs, the interconnected porous structure of the resultant sponges is maintained (Figure 3b), indicating the simple functionalization process cannot influence the original structure of the pristine sponge. Furthermore, the micro/nanotextured structure of the coated PDA nanoaggregates on the sponge skeletons could be found under higher magnification by using SEM. Clearly, the surface of the skeletons for the pristine sponge is quite smooth (Figure 3c), which becomes rather rougher as a result of the existence of numerous nanoaggregates on the skeletons after the coating process (Figure 3d and 3e).³⁴ To further understand the chemical compositions of the pristine/superhydrophobic sponge as well as the formation process of the numerous nanoaggregates on the surface of the sponge, two characterizations of the energy-dispersive X-ray spectroscopy (EDS) and dynamic light scattering measurement (DLS) are conducted. In the EDS experiment (Figure 3f), C, N and O elements could be found in the pristine sponge, which are basic elements of PU materials. By contrast, the superhydrophobic sponge comprises not only C, N and O elements, but also S element. This newly presented element should be ascribed to the *n*-dodecylthiol, confirming the immobilization of *n*-dodecylthiol. Besides, after calculation, the N/O atom ratio for the pristine and superhydrophobic sponge is, respectively, 0.54 and 0.64 (Figure 3g). Since no N and O elements are existed in *n*-dodecylthiol, the change in N/O atom ratio proves the functionalization of PDA on the surface of pristine sponge. In the DLS experiment, we find that no

particles can be detected in the fresh mixture of *n*-dodecylthiol and dopamine in water/ethanol solution. After continuous stirring for 10 h (Supporting Information Figure S2), particles with an average size of 400–3150 nm could be detected in the dark brown (or nearly black) colored solution. However, as shown in Figure 2e, the size of particles on the surface of the superhydrophobic sponge was mainly located at ~ 200 –300 nm. The wide distribution of particle size herein (Supporting Information Figure S2) could be owing to the occurrence of particles aggregation. Collectively, the micro/nanoscale protrusion of the PDA nanoaggregates, hydrophobicity of the *n*-dodecylthiol molecular motifs in combination with porous structure of the sponge create a dually roughened surface, which is close to the surface structure of a lotus leaf, therefore showing superhydrophobic property.

Owing to the strong mechanical stability of the substrate (*the PU sponge*), the superhydrophobic sponge may exhibit desirable robustness against various harsh conditions, especially repeated compression tests. More specifically, the cubic shaped superhydrophobic sponge ($1.5 \times 1.5 \times 1.5 \text{ cm}$) can bear a manual compression to higher than 80% volume reduction and completely recover their original volume after releasing the compression. Meanwhile, as shown in Figure 4, when the superhydrophobic sponge is undergone 1000 compression/release cycles, they can maintain the original morphologies and microstructures (Figure S3 in the Supporting Information). The robust stability endows the sponge with excellent recyclability, which is of great significance for practical applications.

The high porosity, superhydrophobicity, and strong mechanical stability make the superhydrophobic sponge a promising candidate for the efficient removal of various oils/organic solvents. More specifically, organic/water separation and absorption capacities of the superhydrophobic sponge are measured to investigate the efficiency of the absorbents. In Figure 5a, when a piece of superhydrophobic sponge is forced to contact with a layer of the hexane (stained with oil red O) on the water surface, it would fully absorbed the oil within 24 s, resulting in the transparent region (clean water). Meanwhile, other organic solvent such as *n*-hexadecane stained with oil red

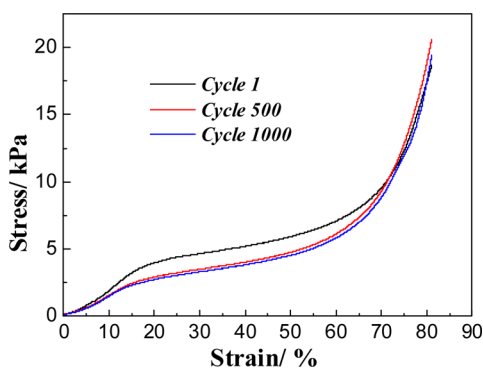


Figure 4. Compressive stress–strain curves of the cubic shaped superhydrophobic PU sponge over 1000 cycles (size of the sponge length = 1.5 cm, width = 1.5 cm, height = 1.5 cm).

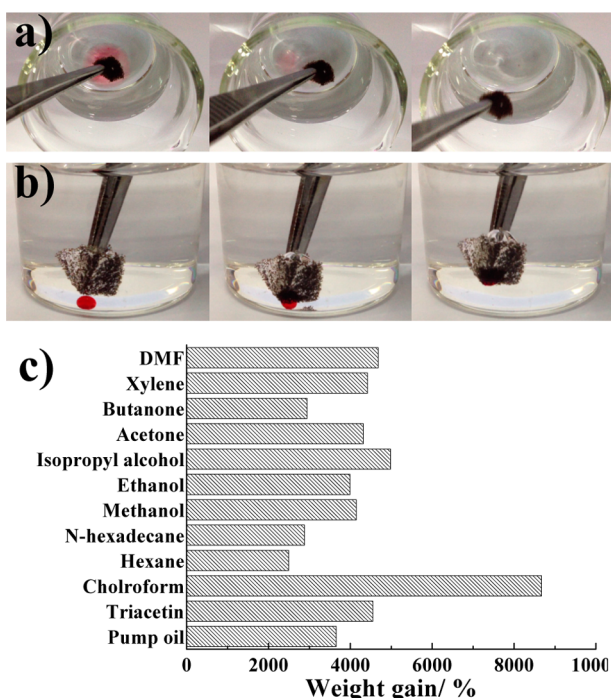


Figure 5. Absorption of oils/organic solvents by the superhydrophobic PU sponge: (a) photographs of the absorption process of hexane by using the superhydrophobic PU sponges taken at intervals of 8 s (*a hexane film stained with oil red O floating on water*); (b) photographs of the absorption process of chloroform by using the superhydrophobic PU sponge taken at intervals of ~ 2 s (*a droplet of chloroform stained with oil red O settled at the bottom of water*); (c) absorption efficiency of the superhydrophobic PU sponge for various organic liquids.

O can also be quickly adsorbed by this superhydrophobic sponge (Figure S4 in the Supporting Information). Similarly, when the superhydrophobic sponge is held to contact with chloroform under water, the chloroform droplet can be rapidly sucked up by the sponge (Figure 5b). Herein, the detail explanation for the “weight gain” can be found in the Experimental Section. In typical absorption measurements, the superhydrophobic sponge is placed on the surface of various oils (*pump oil, triacetin, etc.*) and organic solvents (*methanol, ethanol, isopropyl alcohol, n-hexadecane, butanone, acetone, xylene, hexane, chloroform and N,N-dimethylformamide (DMF)*), then left briefly for saturated absorption, and finally weighed instantaneously to avoid evaporation of oils/organic

solvents. As shown in Figure 5c, the superhydrophobic sponge exhibits the weight gains ranging from 2494% to 8670% for the 12 kinds of oils/organic solvents. The changes in absorption capacity could be as a result of the difference in density of the oils/organic solvents. As an example, the superhydrophobic sponge shows absorption capacities of 1.53 ton m^{-3} for pump oil and 3.64 ton m^{-3} for chloroform, respectively. The absorption capacities are much higher than those of nonwoven polypropylene (PP) fabric (5–12 times),³⁵ marshmallow-like organosilicon-based porous gel (6–15 times),¹⁹ nanowire membranes (~ 20 times),²⁴ microporous polymers (~ 33 times),²³ and seems to be comparable to (*or slightly lower than*) some carbon-based sponges.^{14,15} Fortunately, the fabrication process of our superhydrophobic sponge in our study is much more facile and easier to scale up.

To the best of our knowledge, the recyclability of a sorbent is also proven to be an important role in oils/organic solvents cleanup applications. In this study, to testify this property of the superhydrophobic sponge, two approaches, that is, squeezing and distillation, are adopted, which mainly depend on the species of pollutants. Specifically, squeezing, as an efficient approach, is usually utilized to recover nonflammable/precious pollutants possessing high boiling points. In comparison, distillation is much more suitable for the removal of valuable pollutants comprising low boiling points. Herein, two typical experiential examples are conducted to demonstrate the recycling process (Figure 6). Specifically, distillation is employed to recycle hexane (Figure 6a). After the absorption process, the as-obtained sample is heated to release the absorbed liquid (*the heating temperature should be higher than the boiling point (68.7 °C) of hexane*), which is gathered by using condensing equipment. As is illustrated in Figure 6a, little changes in absorption capability of the superhydrophobic sponges could be observed after five absorption/distillation cycles. Compared with hexane, *n*-hexadecane possessing a much higher boiling point (286.8 °C) is recovered by squeezing process (Figure 6b). After five absorption/squeezing cycles, the absorption capability of the superhydrophobic sponges is lowered to 69.3% of its initial absorption capacity. This phenomenon could be owing to the following aspects: during the first absorption/squeezing cycle, $\sim 33.2\%$ amount of *n*-hexadecane is left, which is mainly as a result of the incomplete compression of the superhydrophobic sponge. Collectively, as verified by the two commonly used approaches (i.e., squeezing and distillation), the excellent mechanical stabilities could confer the superhydrophobic sponge highly efficient recyclability, thus promoting a great potential of this material in removing oils/organic solvents.

CONCLUSIONS

In summary, taking the inspiration from the superhydrophobicity of lotus leaf and the adhesive ability of mussel adhesive protein, we developed a facile, mild and inexpensive method to fabricate a superhydrophobic sponge for the use of separation and absorption of oils/organic solvents from water. This innovate sponge exhibits unique properties, including excellent absorption capacities up to 87 times its own weight, high selectivity, desirable recyclability and inertness to corrosive environments. Hopefully, this kind of sponge is a promising candidate for large-scale removal of organic contaminants from water.

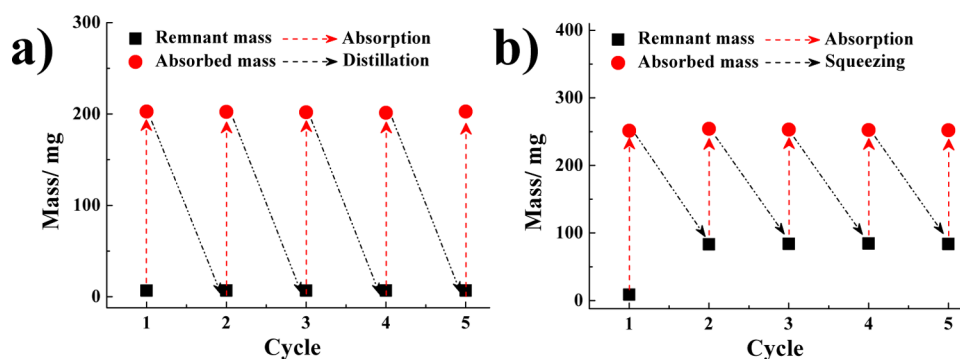


Figure 6. Recyclability investigation of the superhydrophobic PU sponge after squeezing or distillation. Specifically, (a) distillation is applied for recycling the superhydrophobic PU sponge for the absorption of hexane, and (b) squeezing is utilized for recycling the superhydrophobic sponge for the absorption of *n*-hexadecane.

■ ASSOCIATED CONTENT

Supporting Information

Series of photographs of an 8 μL water droplet dropped from a height of ~ 2 cm as a function of time; the particle size frequency of the mixture of dopamine and *n*-dodecylthiol in water/ethanol solution after 10 h-continuous stirring; the SEM images of the superhydrophobic PU sponge after 1000 compression-release cycles; and the photographs of the absorption process of *n*-hexadecane stained with oil red O by using the superhydrophobic sponge. 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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