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Self-assembly modification of polyurethane sponge for application in oil/water separation†

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A polyurethane (PU) sponge with excellent oil/water separation property has been successfully prepared by modifying with octadecyltrichlorosilane (OTS) self-assemblies. The chemical structure, surface topography, and surface wettability of the sponge were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy, and contact angle experiments, respectively. The prepared sponge could completely absorb oil within a few seconds. In addition, it also possessed excellent selectivity for oil, high absorption capacity (25 times the self-weight), high oil retention (92.6%), and good recyclability. The sponge was synthesized by a facile, mild and inexpensive method, and has excellent potential for use in practical applications because of its desirable property of oil/water separation.

1. Introduction

In recent decades, there has been an increase in the number of oil spillages as well as the industrial discharge of oils/organic solvents, which pose a significant threat to marine ecosystems.^{1–9} Therefore, there is a growing demand for the preparation of oil-absorbing materials.

Recently, a number of traditional materials, including activated carbon,^{10,11} carbon nanotubes,^{12,13} zeolites,^{14,15} fibers,¹⁶ and straw¹⁷ have been used to remove and collect spilled oil. However, these materials have a number of drawbacks, such as low absorption capacity, none or poor selectivity, and poor reusability. Therefore, it is urgent to develop absorbent materials with better performance for the efficient removal of oils/organic solvents.

Hydrophobicity is desirable and crucial for an oil absorbent, since it will absorb oils selectively while repelling water.¹⁸ To date, many studies have focused on developing materials with both hydrophobicity and lipophilicity. These include mesh/membranes,¹⁹ carbon nanotubes,^{20,21} polymer gels, and nanoporous polymers.^{22,23} Various materials with three-dimensional (3D) structure have been reported with high porosity, low density, and recyclability and showed great advantages in the absorption of oils and organic solvents; these include CNT- and graphene-based absorbent materials and bacterial cellulose.²⁴ Unfortunately, complicated processes and high costs prevent the use of these materials in practical applications.

PU sponge is an inexpensive, highly porous, good elasticity, 3D material with a large internal surface area, and has been modified for oil/water separation applications.^{25–28} At present, the preparation of hydrophobic sponges has attracted considerable attention. For example, Zhu *et al.*²⁹ prepared a superhydrophobic PU sponge through a solution immersion method. The as-prepared sponges absorbed various kinds of oils up to above 13 times the sponges' weight. Nguyen *et al.*³⁰ modified sponges with graphene by a dip-coating method, and they showed superhydrophobicity and excellent absorption performance for a broad range of oils. However, the oil absorption capacity drastically dropped after the first absorption-squeezing cycle. Zhu *et al.*³¹ coated polysiloxane onto a PU sponge, which improved the durability in a corrosive environment. Although these sponge absorbent materials exhibited great absorption capacity for oils/organic solvents, they were still limited in application because of some limits, such as expensive materials and complicated procedures. Therefore, it is necessary to establish a facile and mild method for preparing hydrophobic porous materials. The modification of a sponge from superhydrophilic to superhydrophobic while maintaining its capability of absorbing oils/organic solvents, thus realizing its application for removal of oils or organic solvents from water is desirable.³² The hydrophilicity of a PU sponge is a major problem in the modification process, because it is composed of carbonyl and amino groups.³³

In this study, a PU sponge with a great absorption capacity was prepared using OTS self-assemblies. The schematic illustrations of the preparation method and oil/water separation process are presented in Fig. 1. The as-prepared sponge has an excellent potential to be used in practical applications because of its desirable property of oil/water separation. More interestingly, the as-prepared sponge could completely absorb oil within a few seconds. In addition, it also possessed excellent

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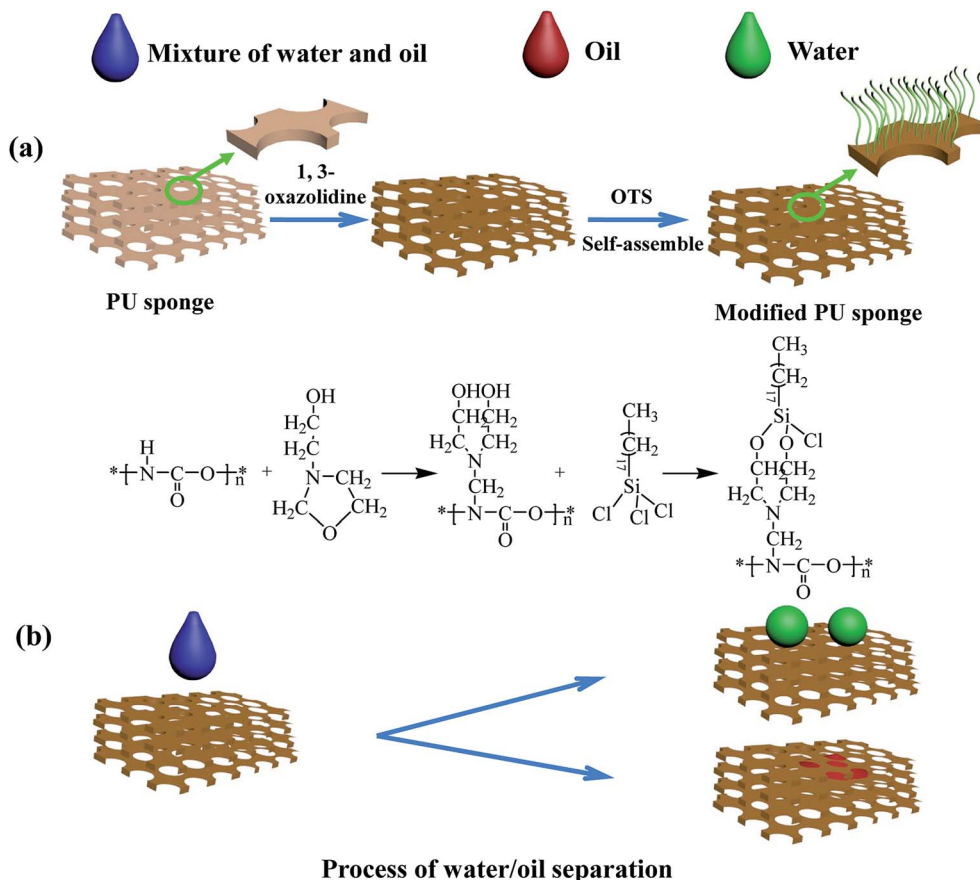


Fig. 1 (a) Schematic of the PU sponge modifying process; (b) the process of oil/water separation.

selectivity for oil, high absorption capacity (25 times the self-weight), and high oil retention (92.6%). This study provides a simple and inexpensive method for fabricating a hydrophobic and lipophilic sponge that might be applied to oil/water separation.

2. Experimental

2.1. Materials

1,3-oxazolidine was synthesized according to the previous literature.³⁴ Analytical reagent grade OTS was purchased from Aladdin Industrial Inc., Shanghai, China. Diethanolamine, formaldehyde, anhydrous ethanol, toluene, and hexane were obtained from Sinopharm Chemical Reagent Co., Ltd, China and used as received without further purification. The sponge used in this study was commercially available polyurethane sponge. Deionized water was used in all preparations.

2.2. Preparation of the hydrophobicity and lipophilic PU sponges

First, the PU sponge was cut into a square shapes ($2 \times 2 \times 2$ cm), and they were ultrasonically cleaned with ethanol and deionized water, respectively, for 30 min to remove surface stains and oils. Then, the sponges were placed in an oven at 60°C for 24 h to dry completely.

The dried sponge was immersed in 200 mL of water solution, which contained 10% of 1,3-oxazolidine at 120°C for 1 h. Finally, the sponge was washed with ethanol and distilled water repeatedly to remove the unreacted 1,3-oxazolidine solution, and then dried at 60°C for 24 h.

The dried sponges modified with 1,3-oxazolidine were immersed in an anhydrous hexane solution of 3 mM OTS for 24 h at ambient temperature. Then, the sponges were washed with anhydrous hexane to remove the residuals, and then dried at 60°C for 24 h. Finally, the long-chain OTS with $-\text{CH}_3$ terminal groups self-assembled on the hydroxyl. The schematic of the fabrication process for the assembly of OTS SAMs on the sponges are presented in detail in Fig. 1.

2.3. Test of oil/water separation property

The modified sponge was immersed into an oil/water mixture (oil was dyed red for clear observation) until it was completely filled with oil. Then, the sponge was removed from the water surface to test the weight. Oil absorption capacities were calculated by testing the weight of the modified sponge before and after absorption, according to eqn (1):

$$R(\%) = [(m - m_0)/m_0] \times 100\% \quad (1)$$



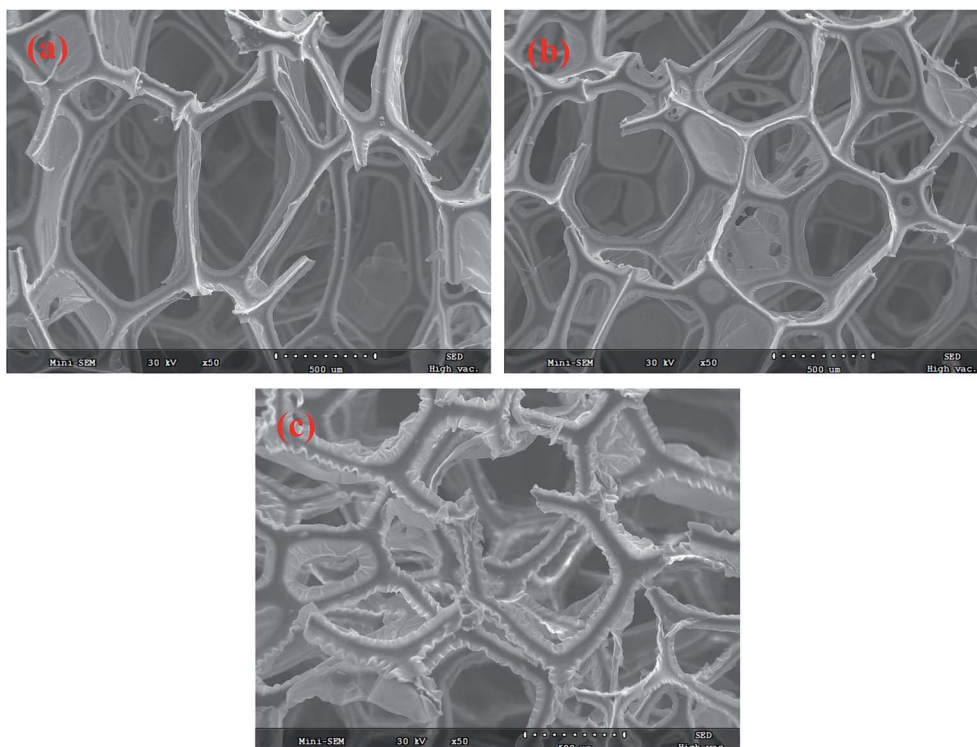


Fig. 2 SEM images of the PU sponge: (a) pristine sponge; (b) after ring-opening reaction of 1,3-oxazolidine with PU sponge; (c) the PU sponge after modifying with OTS self-assemblies.

where R (%) is the oil absorption capacity, m and m_0 are the weight of sponge after absorption with oil and the weight of the control sponge, respectively.

The separation efficiency of the as-prepared sponge for different oil/water mixtures was calculated by testing the weight of oil before and after absorption, according to eqn (2):

$$Q(\%) = [(n_0 - n)/n_0] \times 100\% \quad (2)$$

where Q (%) is the separation efficiency, n and n_0 are the weight of the absorbed oil and the weight of the oil before being absorbed, respectively.

2.4. Oil retention rate test

A sponge was immersed into an oil/water mixture and placed until it achieved complete absorption saturation with oil. Then, the saturated sponge was wiped with a filter paper to remove the excessive oil. The oil retention rate R of the sponge was calculated by testing the weight of the saturated sponge before and after centrifugation at 3000 rpm for 1 min, according to eqn (3):

$$T(\%) = [(m_a - m_0)/(m_b - m_0)] \times 100\% \quad (3)$$

where T (%) is the oil retention capacity, m_a , m_0 , and m_b are the weight of sponge after centrifugation, the weight of the control sponge, and the weight of the saturated sponge with oil (g), respectively.

2.5. Characterizations

The chemical structures were investigated using an FTIR instrument (Nicolet 170SX). SEM images were obtained by a scanning electron microscope (SEM, Korea EM-30). Contact angles were measured using an OCA50 machine (Data-Physics, Germany) under ambient temperature. The continuous oil/water separation process was investigated using a peristaltic

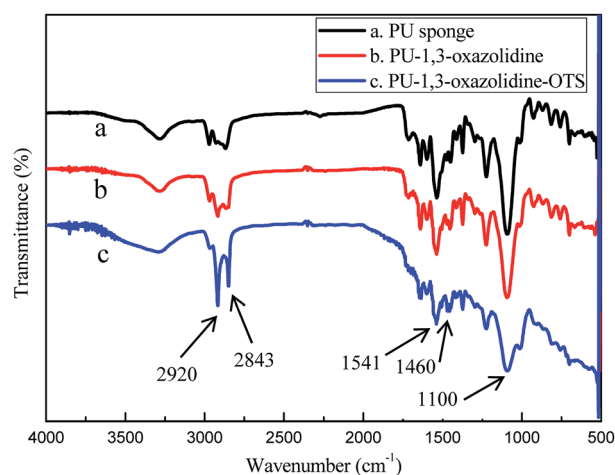


Fig. 3 FTIR spectra of PU sponge: (a) pristine sponge; (b) after ring-opening reaction of 1,3-oxazolidine with PU sponge; (c) after modifying with OTS self-assemblies.



pump (BT300-01, Longer Precision Pump Co., Ltd). The water-in-toluene emulsion particle size value was determined by dynamic light scattering (DLS) using a Zetasizer-HS (Malvern Instruments, UK). All the photos in this study were taken by a Canon camera.

3. Results and discussion

3.1. Analysis of SEM morphology

The morphologies of the PU sponge before and after copolymerization were examined by SEM. As shown in Fig. 2a, the results clearly showed that the sponge had a 3D porous structure. The pore size was about 500 μm and the skeleton had a diameter of about 50 μm . The 3D network structure is gainful for the absorption of a liquid. Meanwhile, the modified sponge had the same porous structure after the polymer modification, which confirms that the modification process couldn't destroy the porous structure of the sponge (Fig. 2c). However, compared to the pristine sponge, it is clearly observed that the 3D skeleton became rough after modification because of the presence for polymers, and the interconnected porous structure could be maintained. Surface roughness is very important for successfully preparing a hydrophobic and lipophilic surface. The results indicated that the simple functionalization process couldn't change the original structure of the pristine sponge.

3.2. FTIR spectroscopy analysis

In this study, two hydroxyl groups were introduced on one secondary amine N-H bond of the PU surface by a grafting

reaction, which could significantly improve the surface reactivity of the PU sponge. Then, the long-chain OTS self-assembled on the hydroxyl group, which was obtained from a ring-opening reaction of 1,3-oxazolidine and the secondary amine N-H bonds of the PU sponge. Finally, the OTS SAMs with $-\text{CH}_3$ terminal groups were prepared on the substrates of the sponges, which could remarkably increase the hydrophobicity and lipophilicity.

The chemical structures were further characterized by FTIR. Fig. 3 shows the FTIR spectra of the pristine sponge and polymer-modified sponge. As shown in Fig. 3, the vibration peaks appear at about 1100, 1460, and 1541 cm^{-1} , which are assigned to C-O stretching vibrations, C-H bending vibrations, C-N stretching vibrations, respectively.³⁵ The peaks appearing at about 2843 and 2920 cm^{-1} are attributed to the C-H stretching vibrations of methyl and methylene groups, respectively. The results confirmed that copolymerization took place as expected and the sponge was covered with OTS SAMs on the surface.

3.3. Properties of hydrophobicity and lipophilic

Oil/water separation typically concerns the interface, and the effective strategy is to design novel materials with special wettability.³⁶ To further estimate the surface wettability of the sponges, contact angle measurements were performed by placing droplets of oil and water on the surface of sponges. As shown in Fig. 4, the unmodified sponge had a good hydrophilic property based on the shape of a water droplet (Fig. 4a). However, the water droplet remained stable on the surface of

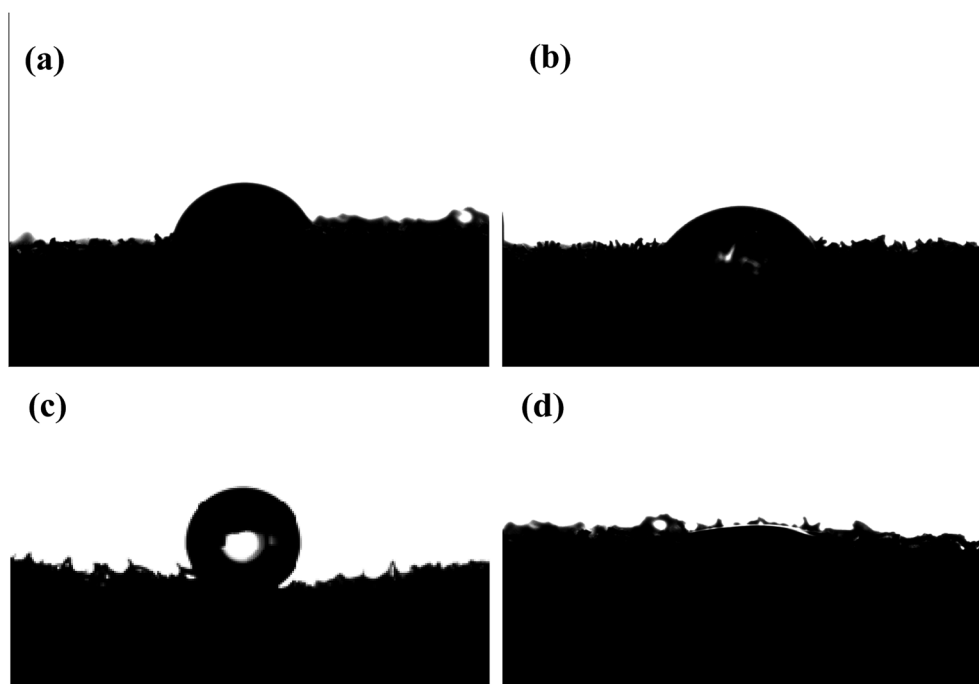


Fig. 4 The water contact angle (CA) tests of PU sponges: (a) the image of a water droplet (2 μL) on the pristine sponge with a contact angle of about 63°; (b) the image of a bean oil droplet (2 μL) on the pristine sponge with a contact angle of about 46°; (c) the image of a water droplet (2 μL) on the modified sponge with a contact angle of 156°; (d) bean oil droplet (2 μL) spread and permeated quickly on the modified sponge.

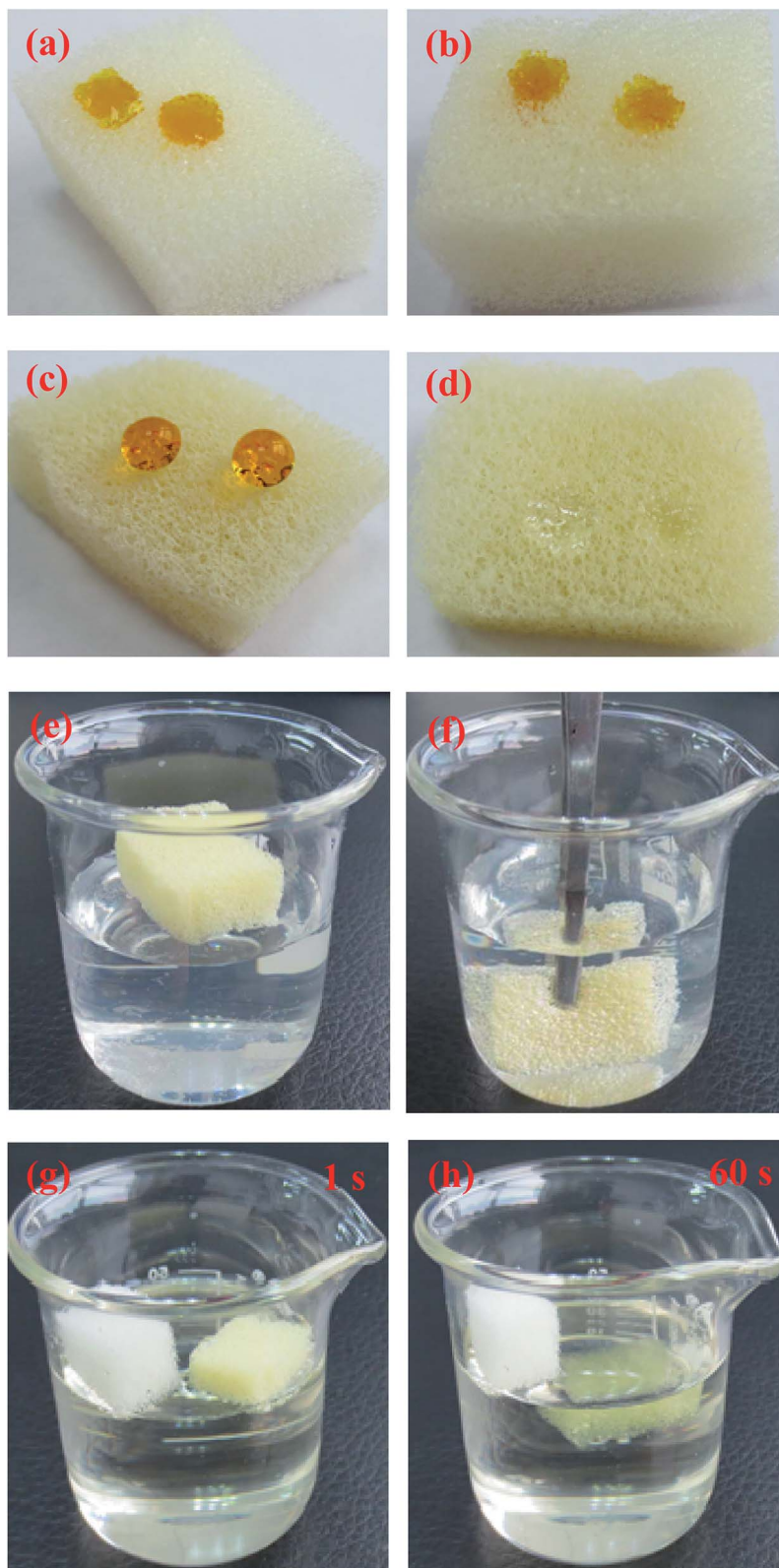


Fig. 5 The hydrophobicity and lipophilic photographs of the modified sponges: (a) the image of a water droplet (10 μL) on the pristine sponge; (b) the image of a water droplet (10 μL) on the sponge after modifying with 1,3-oxazolidine; (c) the image of a water droplet (10 μL) on the sponge after modifying with OTS self-assemblies; (d) the image of a bean oil droplet (10 μL) on the sponge after modifying with OTS self-assemblies; (e) optical image of the grafted PU sponge with OTS self-assemblies floating on water due to its hydrophobicity and light weight; (f) optical image of the grafted sponge immersed in water by an external force, exhibiting a silver mirror-like surface due to the surrounding air bubbles; (g and h) optical image of the immersion process of the pristine (left) and modified sponges (right) in the bean oil. The pristine sponge floated on the surface of the oil with poor wettability, while the modified sponge was completely immersed in oil with excellent wettability after 60 s.



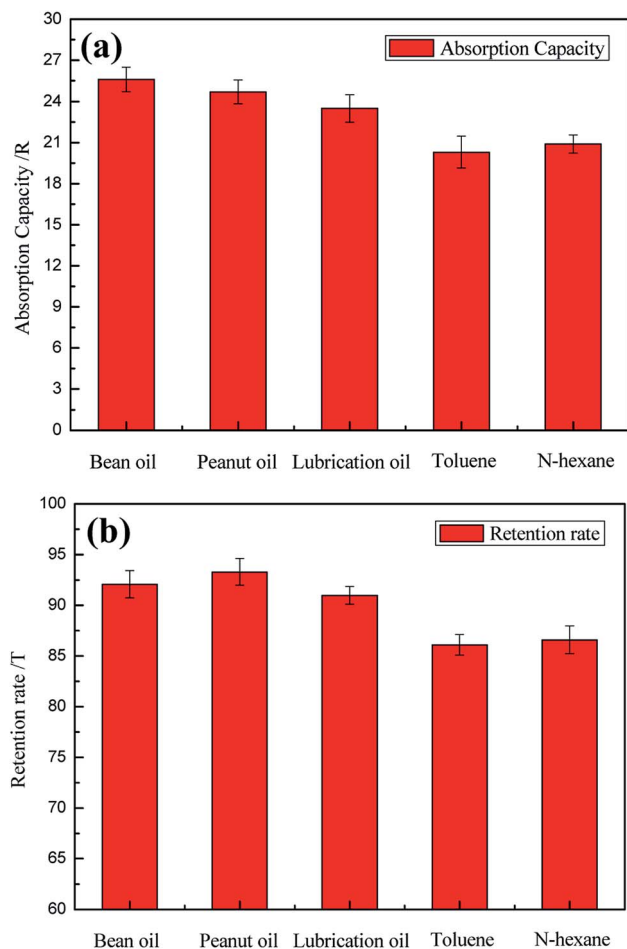


Fig. 6 (a) The absorption capacities of the modified sponge for different kinds of oils; (b) the oil retention rates of the modified sponge.

the modified sponge, indicating that it displayed hydrophobicity because of the alkyl chain of OTS SAMs with the low surface tension, and the water contact angle was about 156° (Fig. 4c). However, the bean oil droplet was almost absorbed into the pores of the modified sponge, and the bean oil contact angle was about 0° (Fig. 4d). The bean oil could spread on the surface and permeate into the inner part of the modified sponge. This phenomenon was due to the strong lipophilicity of the functional alkyl chain attached to the sponge and the capillary force of the pores, resulting in great oil absorption performance.

The photographs of the modified sponge with hydrophobicity and lipophilic wettability were also obtained. As shown in Fig. 5, the modified sponge had special surface wettability. The water droplets (dyeing using a disperse dye for obvious comparison) stood on the modified sponge surface like balls, and it could very easily roll off the surface (Fig. 5c). Nevertheless, the water droplets were absorbed by the pristine sponge as soon as they were placed on the surface (Fig. 5a). In contrast, when the bean oil droplet was dropped on the surface of the sponge modified with OTS SAMs, it was immediately absorbed by the sponge very quickly, as indicated in Fig. 5d, demonstrating the superoleophilic property.

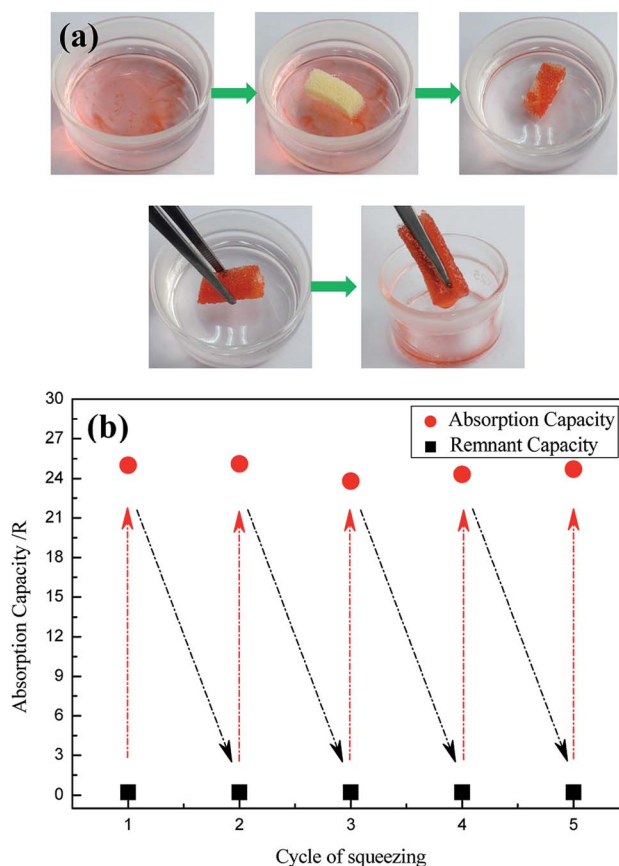


Fig. 7 (a) The process of oil/water separation for the modified sponge, and the collection of bean oil (dyed by oil red) from the water surface; (b) the changes in the adsorption capacity of bean oil for the modified sponge after 5 squeezing cycles.

When the modified sponge was placed on water, it could float on the water surface due to hydrophobicity and its light weight (Fig. 5e). In addition, when the sponge was immersed in water, it could exhibit a typical silver mirror-like surface as

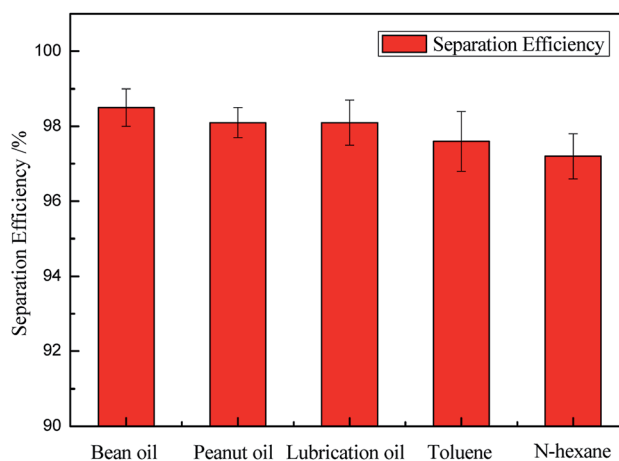


Fig. 8 The separation efficiency of the as-prepared sponge for different oil/water mixtures.

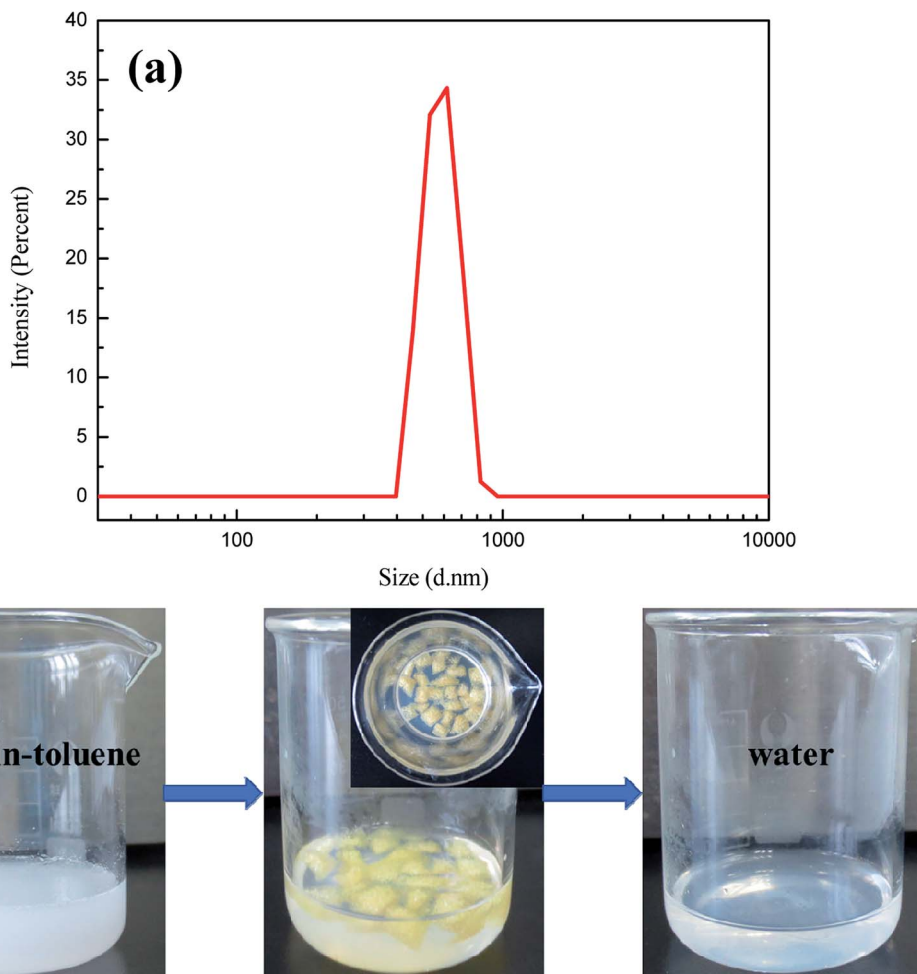


Fig. 9 (a) Droplet size distribution of surfactant-stabilized water-in-toluene emulsion; (b) photo of a surfactant-stabilized water-in-toluene emulsion before and after separation.

a result of a uniform air layer trapped between the hydrophobic surface and water. After releasing the external force, it would instantaneously float on the surface of water again without any water being absorbed into the sponge (Fig. 5f). This phenomenon was referred to the non-wetting Cassie–Baxter model.^{37,38} Moreover, the lipophilic property of the sponges was investigated. When both the sponges were put on a bean oil surface simultaneously, the pristine sponge floated on the surface of oil due to its low oil wettability. In contrast, the modified sponge

was completely immersed into oil because of its excellent wettability after 60 s (Fig. 5g and h). Based on the above discussions, we conclude that the modified sponge has excellent potential to be used in oil/water separation.

3.4. Absorption capacity and oil retention rate of the modified sponge

The absorption capacity of the modified sponge for oil was investigated. The amount of absorbed oil was determined using



Fig. 10 A peristaltic pump-assisted continuous oil/water separation of the modified sponge. Toluene was dyed with oil red for clear observation. (a) Before separation; (b) during separation; (c) after separation.



the mass method, as shown in eqn (1). The results are shown in Fig. 6a. The modified sponge could exhibit good absorption for kinds of oils and organic solvents, such as lubrication oil, bean oil, acetone, peanut oil, and *n*-hexane. It was revealed that the modified sponge exhibited excellent absorption capacity in the range 20–25 times the amount of its own weight at a saturated state. The 3D hierarchical porous structure and lipophilic property ensure excellent absorption capacity. Furthermore, the as-prepared sponge modified with OTS SAMs exhibited higher absorption capacity than previously reported absorbent materials, such as PDMS foam (4–11 times)³⁹ and superhydrophobic sponges (13–18 times).³⁶ Therefore, the sponge had greater potential for oil absorption applications.

As we know, in the process of oil clean up, the saturated sponge needs to be recycled. This requires the modified sponge to have a good oil retention property to prevent the desorption of oil caused by some external force. The oil retention rates for several oils and organic solvents were tested. As shown in Fig. 6b, the modified sponge exhibited nearly perfect oil retention (92.6% for bean oil as an example).

3.5. Separation of oil/water

Oil/water separation and the recyclability of the modified sponge are important in oils/organic solvents cleanup applications. Oil/water separation of the modified sponge was investigated. As shown in Fig. 7a, when a piece of modified sponge was placed on the surface of oil/water mixtures, bean oil (dyed by oil red) could be absorbed within a few seconds, resulting in the transparent region (clean water) that was originally contaminated by the oil. The modified sponge floated on the water surface during the whole absorption process because of its low density and superhydrophobicity. Subsequently, the oil was separated entirely from the water simply by taking the sponge out, and the absorbed oil could be collected from the sponge through a simple mechanical squeezing process. The as-prepared sponge also effectively absorbed some oils and organic solvents, such as peanut oil, lubrication oil, toluene, and *n*-hexane.

For practical applications, oil absorption capacity and recyclability of the modified sponge are important factors. The reusability of the modified sponge was investigated by repeated absorption-desorption process. The changes in the absorption capacity of bean oil for the modified sponge with squeezing cycles are presented in Fig. 7b. Because of its excellent elasticity and durability, it was very interesting to note that the modified sponge still maintained high absorption capacity after being squeezed for 5 cycles. The excellent properties implied that the as-prepared sponge has excellent potential for use in practical applications.

The separation efficiency of the as-prepared sponge for different oil/water mixtures was calculated, as shown in eqn (2). The mixtures of bean oil/water, peanut oil/water, lubrication oil/water, toluene/water, and *n*-hexane/water were successfully separated with high efficiency. Almost no visible oil existed in the water after separation. The separation efficiency of the as-prepared sponge for different oil/water mixtures is presented in Fig. 8. It can be seen that the separation efficiency is high

regardless of the mixture of oil and water. The excellent performances imply that the as-prepared sponge is a prospective candidate for oil/water separation.

Industrial waste often contains some surfactants. In order to further investigate the separation performance for surfactant-stabilized emulsions, a surfactant-stabilized water-in-toluene emulsion was prepared. The size of the particles in the water-in-toluene emulsion was investigated by DLS. As shown in Fig. 9a, the average size of the emulsion particles was about 710 nm. After separation of the emulsion through modified sponge absorption, the separated emulsion became much transparent compared to the original milky white emulsion by the removal of oil, as shown in Fig. 9b. The significant difference in phase composition before and after separation illustrates that the emulsion could be separated effectively.

3.6. Continuous oil/water separation

The continuous oil/water separation was investigated using a peristaltic pump. Large amounts of oil (the toluene was dyed with oil red for clear observation) were continuously collected from oil/water mixtures, as illustrated in Fig. 10. When the tube tied with the modified sponge was placed at the oil/water interface, it quickly absorbed oil and repelled water completely due to its hydrophobicity and lipophilic wettability. Furthermore, when the peristaltic pump was turned on, a stream of oil (toluene) was formed in the tube, because toluene was continuously absorbed through the modified sponge, and the thickness of the oil layer gradually decreased. Finally, the oil could be successfully collected by a small piece of modified sponge under the peristaltic pump, and no water could be found in the collected oil (Fig. 10 and Video S1 in ESI†). The good selectivity of the modified sponge for oil/water mixtures was probably owing to its high capillary action as well as its hydrophobicity and lipophilic wettability. These results indicated that the modified sponge has potential in application for oil/water separation.

4. Conclusions

A sponge with excellent oil/water separation property has been successfully prepared by modifying with OTS self-assemblies. The sponge exhibiting hydrophobicity and lipophilicity was synthesized by a facile, mild and inexpensive method, and has excellent potential for use in the separation of oils or organic solvents from water. The oil absorption process of the sponge was completed within a few seconds and no water was detected in the sponge. In addition, it also possessed excellent selectivity for oil, high absorption capacity (25 times the self-weight), high oil retention (92.6%), and good recyclability. The sponge developed in this study will be a promising material for large-scale removal of oils and organic contaminants from water.

Conflicts of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.



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