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Title: Fabrication and mechanism of reversible wettability (hydrophilic-oleophilic) sponge

创新性申明

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Contents

Abstract

At present, it is difficult to process widespread thin oil films on the surface of water, and the Absorption Filtration Method is an ideal method for processing the oil films on the surface of water. In this method, the key is to choose the absorption and filtration material. Commonly used absorbent materials, such as oil- absorbing cloth and sponge, which canabsorb a large amount of water while absorbing oil, leading to low efficiency in absorption. So, a study on reversible wettability sponge that can flexibly switch between hydrophilic and oleophilic can effectively improve the oil- absorbing capacity, cleaning efficiency as well as the recovery efficiency of absorbed oil.

On the basis of existing research results, the fabrication method of reversible wettability sponge is based on porous material of polyurethane sponge, low surface-energy material of stearic acid and photosensitive material of titanium dioxide. The fabrication process of reversible wettability sponge has also been proposed. The reversible mechanism and the realization method of the reversible wettability sponge are studied. The wettability, oil absorbing capacity, acid and alkali resistance, self-cleaning property and the recycling rate of this sponge are studied, as well as the factors that affect its performance.

In the study, a simplified method for fabricating reversible wettability sponge modified by stearic acid and titanium dioxide with ultrasonic assisted immersion is proposed. A wettability reversing method of the modified sponge, which is processed by ultraviolet light and heat treatment, is formed— after 6 hours exposed to UV, the sponge switches from superhydrophobic and superoleophilic in water to superhydrophilic and superoleophobic in water. Then heated at 120°C for 20h, its wettability can return to be superhydrophobic and superoleophilic in water. The process above can be repeated multiple times, taking up less time and easy to complete. The main reason for the wettability conversion of modified sponge is the photosensitizing effect of TiO_2. The reversible wettability sponge fabricated in this way can absorb oil 20-60 times of its own weight, and it can also separate oil and water efficiently in strong acid, strong alkali and saturated salt solution, with a satisfactory self-cleaning property and recycling rate. This work provides a material for purifying water bodies contaminated by oil, and provides an approach to control oil pollution in environmental engineering.

Keywords: sponge, reversible wettability, superhydrophobic, superoleophilic, oil water separation

Fabrication and mechanism of reversible wettability (hydrophilic-oleophilic) sponge

Dinghan Liu

1 Introduction

A large amount of wastewater has been produced in the production and daily life, which causes serious pollution to the water body. At the same time, marine pollution due to oil spill events has occurred frequently, attracting worldwide attention[1,2]. How to deal with these oil-contaminated water bodies efficiently has become an urgent problem[3-6]. The processing approaches to oil-contaminated water bodies mainly include physical collection, chemical reaction, biological treatment, in-situ combustion and absorption filtration[3-6]. Physical collection and in-situ combustion, which can quickly deal with oil pollution which is of large thickness and wide range, are the widely adopted method used in the early stage of crude oil leakage, but it is difficult to cope with the dispersed oil film effectively[3-5]. Chemical and biological methods cause secondary pollution to water bodies[3-5], while absorption filtration method can efficiently collect dispersed oil films, which has a good prospect of application [5].

Commercial sponge such as polyurethane sponge and melamine sponge, with the characteristics of the stable structure, high porosity, low density, low price and materials easy to obtain, is an ideal absorbent material [7-14]. However, it also absorbs water while absorbing oil, which reduces the selectivity and separation efficiency of oil-water separation[4-6]. Thus, this kind of sponge needs to be modified to improve their selective absorbability[7-14]. The oil absorbability of sponge is related to its wettability, which depends on the roughness and the chemical composition of its surface. The main approach to improve the hydrophobic and oleophilic property of the material is to construct a multi-layer micro-rough structure and to reduce the surface energy[7]. At present, nanoparticles, such as zinc oxide (ZnO) [8-10], graphite[10], molybdenum disulfide[11], ferroferric oxide12], graphene[14], etc. have been used to increase the surface roughness of materials; polysiloxane[7,11-14], stearic acid (stearic acid)[8], palmitic acid (hexadecanoic acid)[9], lauric acid (dodecanoic acid)[10], etc. are used to reduce the surface energy of materials. The modified sponge with good oil-absorption effect has been fabricated through infiltration method[7-13], hydrothermal method[8-9] and microwave heating method[14]. These modified sponges have their own advantages, but also have different shortcomings, such as the fabrication process is complex, the chemical reagents used may do harm to the environment, the performance of the oil-water separation material is poor due to the low coverage rate of the super-hydrophobic coating, and the chemical stability is poor so it can not be used in both the acid and alkali environment. If the wettability conversion of sponge can be achieved, its applicability in different environments will be improved effectively.

Jianbao Huang[15] used the change of surface free energy of azobenzene due to the trans-cis photoisomerization caused by UV-visible irradiation to achieve the reversible wettability, but the contact angle was only changed by 30°. The wettability conversion effect is not obvious. Hui Li *et al.* converted the superhydrophobic ZnO nanorod array film to superhydrophilic by low-power UV irradiation, then it returned to be superhydrophobic after placed in a dark room for one month, which takes a long time. Chun Xiao *et al.* converted the superhydrophobic composite particles of tetramethylenetetranitramine and HMX/TiO_2 modified by cetyltrimethoxysilane to superhydrophilic by UV, the purpose of which is to adjust the hydrophilicity of underwater explosive. These wettability conversion studies provide the basis for subsequent researches, but it should also be noted that these wettability conversion methods have varied disadvantages such as the effect is not obvious, and a long time is needed. What's more, they have not been applied to modify sponges. Based on the existing study results, this work uses photosensitive TiO_2 and tearic acid with low surface energy to modify polyurethane sponge to fabricate a modified sponge that can be reversibly switched between oleophilic and hydrophilic. The switching method and the mechanism of reversible wettability of modified sponge based on UV and heat treatment are studied, as well as the wettability and oil-absorption capacity of the sponge. This study provides oil-water separation materials and methods for purifying water bodies contaminated by oil.

2 Fabrication of reversible wettability sponge

2.1 Ideas

Wettability, usually indicated by the contact angle of water, can be understood as the degree of hydrophilicity or hydrophobicity of the surface of the material. Generally, materials with the contact angle of a water droplet over 150° are called superhydrophobic materials. These kinds of materials are generally superhydrophobic and superoleophilic, and can separate the oil-water mixture quickly. So it is hoped that the fabricated modified sponge is superhydrophobic. In addition, in order to adapt to different conditions, the sponge should be able to switch between different wettability.

According to literature[7-14], the three-dimensional (3D) porous material is an ideal skeleton. Polyurethane sponge and foamed nickel are selected as candidate skeleton materials according to the price and the difficulty to obtain. Silicone and stearic acid have lower surface energy and are commonly used in the modification of porous materials to improve their hydrophobicity; thus they are selected as candidate modification materials. Surface roughness is an important factor affecting the hydrophobicity of materials. Graphite and ZnO are often used to modify materials to improve the surface roughness of the material, thereby improving the hydrophobicity of porous materials.

Considering that both ZnO and TiO_2 are photosensitive, which shows the possibility of wettability conversion, they are selected as candidate modified materials. Hydrothermal method and sol-gel method are commonly used materials fabrication methods. After many attempts, ultrasonic waves show better modification effects, so hydrothermal method and ultrasonic method are used as candidate methods for fabrication. Three superhydrophobic modified materials were successfully synthesized after a large number of attempts, including foamed nickel modified by Actyflon-G502 after heated, polyurethane sponge modified by ZnO and Actyflon-G502, and polyurethane sponge modified by stearic acid and TiO_2. The preliminary analysis results of the performance of the three modified materials are shown in Table 1.3. Their contact angles are similar, which are between 151-154°. The oil-absorption capacities of these three materials are quite different, and the foamed nickel show a poorer oil-absorption ability while the other two materials are much stronger and similar in this field. Considering that TiO_2 has the best reversibility of wettability and the toxicity of stearic acid is weaker than G502, stearic acid and TiO_2 modified polyurethane sponge is selected for further study.

Table 1 Test performance of three modified materials

Fabrication method	**Contact angle of water**	**oil-absorption ability**	**reversibility of wettability**
Foamed nickel modified by Actyflon-G502 after heated	154°	absorbing 3.1 times its own weight of triolein	-
polyurethane sponge modified by ZnO and Actyflon-G502	155°	absorbing 30 times its own weight of n-hexane	57° after UV irradiation 153° after heated
polyurethane sponge modified by stearic acid and TiO2	151°	absorbing 32 times its own weight of n-hexane	0° after UV irradiation 151° after heated

2.2 Fabrication procedure

Figure 1 shows the fabrication procedures of reversible wettability sponge modified by stearic acid and TiO_2, including preparation of polyurethane sponge, configuration of stearic acid and TiO_2 mixed suspension, and ultrasonic assisted coating treatment.

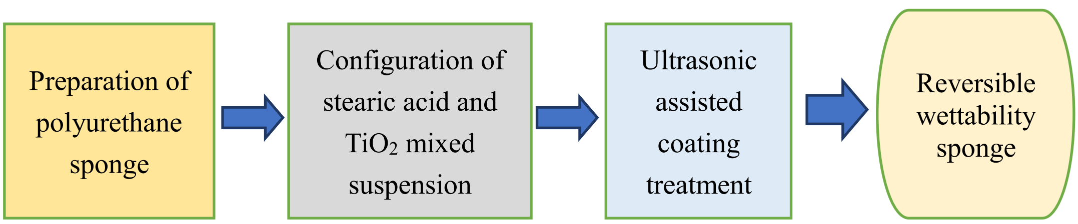


Figure 1 Fabrication procedures of reversible wettability sponge

(1) Preparation of sponge material

The polyurethane sponge was cut into 2cm×2cm×0.5cm cubes by a utility knife, and then ultrasonically cleaned in tertiary water and absolute ethanol for 30min respectively to remove impurities. Then the sponge was dried at 100°C for 1h before cooled naturally.

(2) Preparation of suspension

Five kinds of absolute ethanol, stearic acid and TiO_2 mixed suspensions were prepared, then the corresponding samples were prepared. The contact angles of the surface water of the test samples were shown in Table 2. It was found that with the content of stearic acid and TiO_2 increasing, the contact angle of the sample gradually increased and then kept constant. According to this, the ratio of the suspension was determined to be 400 mg TiO_2, 0.64 g stearic acid and 80 ml absolute ethanol.

Table 2 Contact angles of modified sponge fabricated from suspensions of different components

Group	TiO_2/mg	Stearic acid /g	Absolute ethanol /ml	contact angle /°
1	300	0.48	80.0	140
2	300	0.64	80.0	148
3	400	0.64	80.0	150
4	400	0.96	80.0	151
5	500	0.96	80.0	151

(3) Fabrication process

Efficient and reliable application of TiO_2 nanoparticles and stearic acid to polyurethane sponges was the key to the fabrication. The ultrasonic assisted coating method was determined to be used after tests and analysis, the ultrasonic effect of which made TiO_2 particles and stearic acid reliably fixed on the surface of the sponge. This fabrication process is simple, reliable and low-cost.

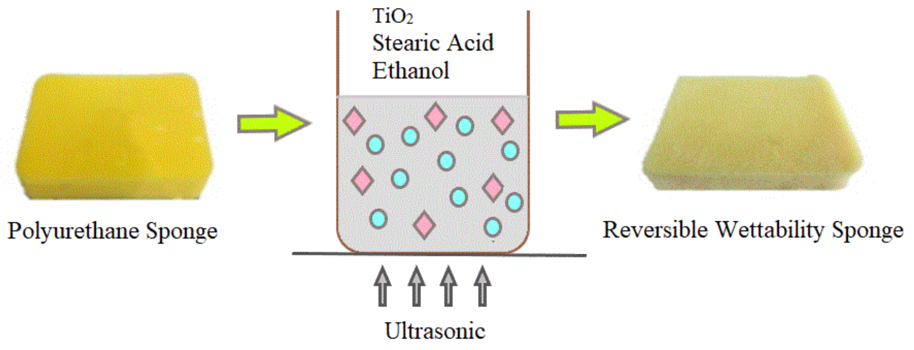


Figure 2 Fabrication process of reversible wettability sponge

The fabrication process of the reversible wettability sponge is shown in Fig. 2, that is, 0.64 g stearic acid was dissolved in 80 ml absolute ethanol, then 400 mg P25 TiO_2 was added, and a suspension was formed under ultrasonication. The pretreated polyurethane sponge was immersed in the above suspension under ultrasonic for 5 hours. Then the sponge was taken out, rinsed with tertiary water, and solidified at 120 °C for 2 hours to obtain a reversible wettability sponge.

2.3 Completion of reversible wettability

The pollution caused by the adhesion of oil will severely limit the repeated use and long-term use of oil-water separation materials. If the material is added with photosensitive P25 TiO_2 nanoparticles, the ability of the particles to degrade organic matter under UV will ensure the self-cleaning capacity, which contributes to the anti-pollution ability of materials. At the same time, the reversible wettability of sponge material will improve its flexibility in oil-water separation application. Based on the photosensitive property of TiO_2, the surface wettability in air of the modified sponge switched from superhydrophobic to superhydrophilic after UV irradiation. The irradiated sponge was found to recover to superhydrophobic after heated. According to the research, the wettability reversal process of the modified sponge was formed, and was shown in Fig. 3.

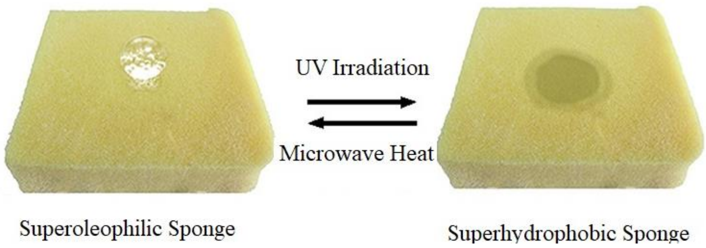


Figure 3 Wettability reversal process of the modified sponge

It was found that the contact angle of water on sponge surface decreased from the initial 151.1° to 0° after 6 hours of irradiation with a 10 W UV lamp. The surface wettability switched from superhydrophobic and superoleophilic in air to superhydrophilic in air, superoleophobic underwater. After the UV irradiated sponge was heated at 120 ° C for 20 hours, the surface of it would return to its original state, that is, superhydrophobic and superoleophilic. This wettability conversion is reciprocal and has good repeatability (Figure 4). The wettability reversal process proposed in this study only requires 6 hours of UV irradiation and 20 hours of heat treatment, which is easy to achieve. Compared with the conventional method of UV irradiation and shelved in dark[16-17], the efficiency and the cycle are obviously improved.

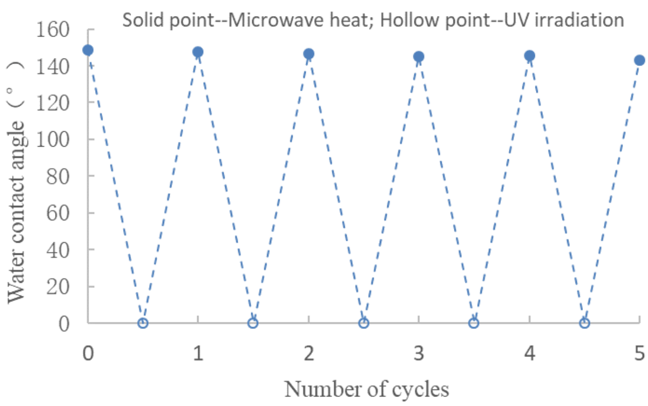
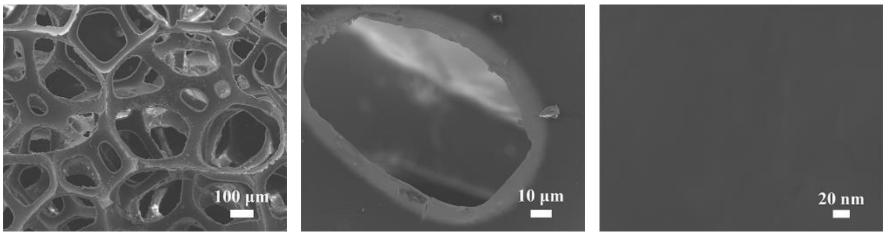


Figure 4 Changes in wettability of modified sponge in UV irradiation /heat cycle

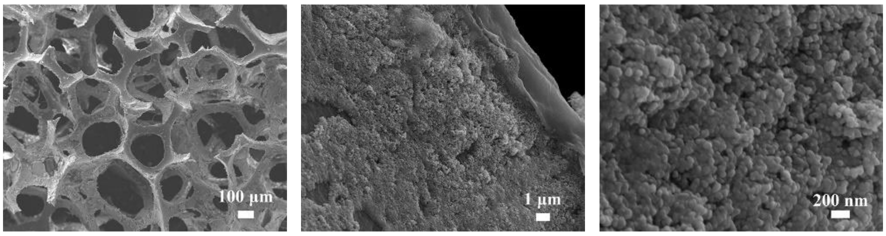
3 Discussion on the mechanism of reversible wettability

3.3.1 Morphology of materials

In order to study the mechanism of reversible wettability, the morphology of this sponge was studied first. The surface morphology of the sample was characterized by field emission scanning electron microscopy. The FE-SEM images of unmodified polyurethane sponge and modified polyurethane sponge are shown in Figure 5 respectively. Figure 5 (a) shows that the surface of the unmodified polyurethane sponge is a smooth skeleton, which is a three-dimensional hierarchical porous structure with the size of pores ranging from 65 to 300 μm. This porous structure has a large surface area, which is the basis of high absorption capacity. Figure 5 (b) shows that the modified sponge skeleton has a cauliflower-like bionic structure, forming a nano-scale rough surface. This bionic structure increases the surface roughness of the sponge and facilitates the formation of super wettability of the material.



(a) Unmodified polyurethane sponge



(b) Modified polyurethane sponge

Figure 5 FE-SEM images of unmodified polyurethane sponge and modified polyurethane sponge

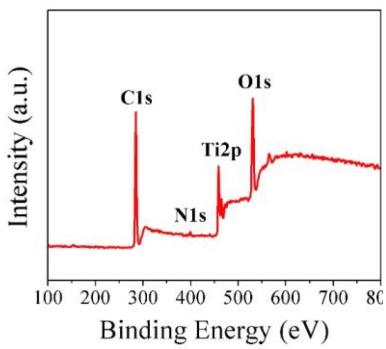


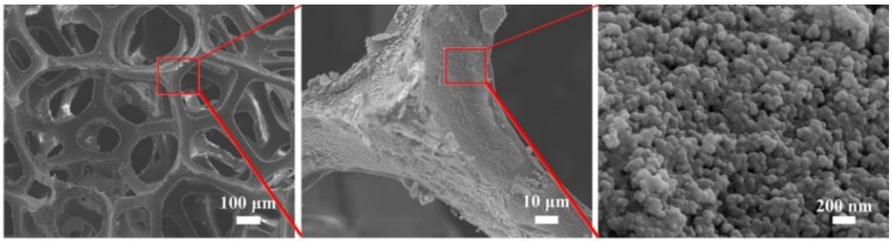
Figure 6 XPS full spectrum of modified sponge

The adhesion of the modification materials on the pored surface of the sponge can also be reflected by photoelectron spectroscopy, and the chemical composition attached to the surface of the sponge pore plays an important role in its hydrophobicity and oleophilicity. The X-ray photoelectron spectroscopy (XPS) of the surface of modified sponge sample is shown in Figure 6. It can be seen from the figure that the main elements attached to the surface of modified sponge are C, Ti and O, indicating that TiO_2 particles and stearic acid have successfully modified the surface of the sponge, which created conditions for superhydrophobicity superoleophilicity.

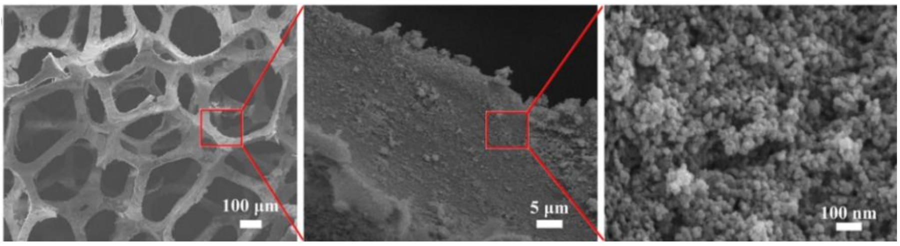
3.2 Mechanism of reversibility

In order to understand the wettability conversion mechanism of the modified sponge after UV irradiation and heat treatment, the morphology and surface chemical composition of the sponge were analyzed. Figure 7 and 8 are the FE-SEM images and XPS spectrums of the treated sponge. It can be observed from the figure that after the reversible cycle of the modified sponge, the surface morphology did not change significantly, but the chemical composition changed, indicating that the main factor causing the reversal of wettability is the change of exterior chemical composition.

Further analysis of chemical composition of modified sponge surface is based on XPS map. Figure 9(a) is a high-resolution plot of the O 1s peak on the surface of the modified sponge. This peak can be fitted to four peaks of 529.9, 530.9, 531.7 and 532.4 eV, corresponding to O–Ti in TiO_2, O=C–O and O–C=O in stearic acid, and NCOO in polyurethane. The high-resolution image of the O 1s peak after UV irradiation is shown in Figure 9(b). The peak can be fitted to five peaks of 529.9, 530.9, 531.7, 532.4 and 532.7 eV. The additional peak at 532.7 eV corresponds to C-O-H, which is the result of the absorption of water molecules (hydroxyl groups) on the surface. These absorbed hydroxyl groups increase the hydrophilicity of the surface. The image of the O 1s peak after UV irradiation and heated at 120 °C for 20 h is shown in Figure 9 (c). This peak can be fitted to four peaks of 529.9, 530.9, 531.7 and 532.4 eV, and the peak at 532.7 eV disappears, indicating that the absorbed hydroxyl group is eliminated, and the surface hydrophobicity is enhanced. The photoactive effect of TiO_2[18] is the main reason for the wettability conversion of modified sponge.



(a) After UV irradiation



(b) After UV irradiation and heated at 120 °C

Figure 7 FE-SEM images of the modified sponge surface after UV irradiation /heated

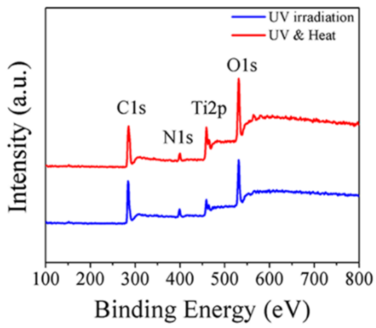
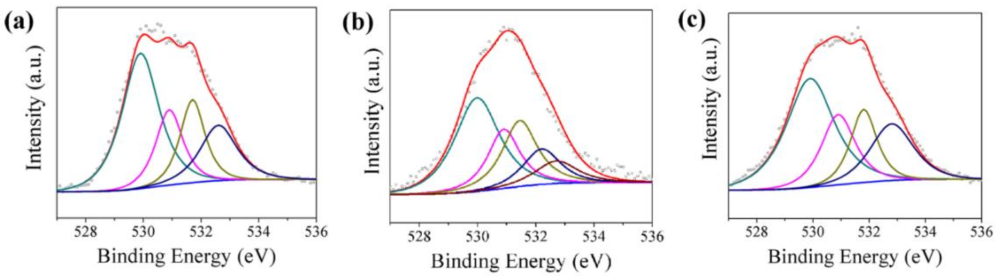


Figure 8 XPS full spectrum of modified sponge surface after UV irradiation/heated



(a) Modified sponge (b) After UV irradiation for 6 h (c) After UV irradiation for 6 h and heated at 120 °C for 20 h

Fig. 9 High-resolution images of O 1s peak on the sponge surface after UV irradiation/heated

TiO_2 is photosensitive, and when the smart sponge with special wettability is irradiated by UV, the photogenerated holes can react with the lattice oxygen in TiO_2 nanoparticles to form Ti^{3+} and surface oxygen vacancies[18]. As shown in Fig. 10, there are seven electrons on the outer orbit of the Ti atom, which is electron deficient. Therefore, in order to achieve a stable state, Ti atoms easily form hydrogen bonds with water molecules at the interface, resulting in a hydrophilic hydration structure. After the surface of the sponge was irradiated by UV and heated at 120 °C for 20 h, the absorbed water molecules were removed, and the hydrophilic surface returned to a hydrophobic state.

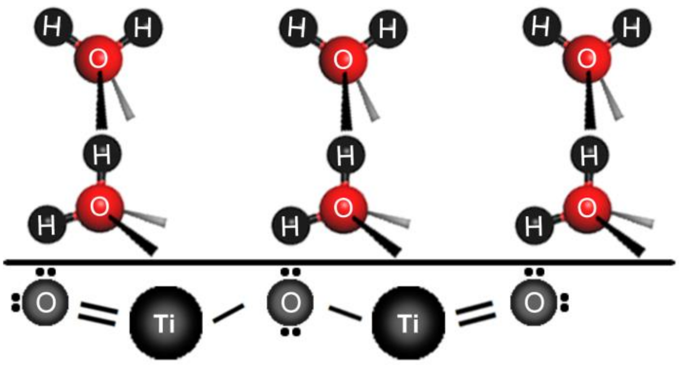


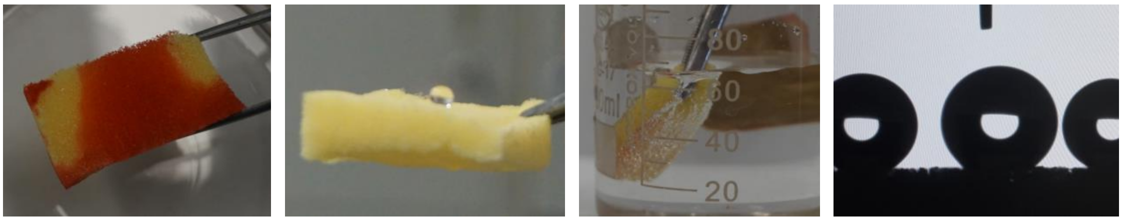
Figure 10 Orientation of water molecules on the surface of modified sponge after UV irradiation

4 Analysis of properties and influence factors

4.1 Properties

4.1.1 Wettability

The wettability of the material was analyzed based on the water contact angle, the state on and under the water and the state of oil and water on the surface. The n-hexane (dyed red with Silver III) and water were dropped on the surface of modified sponge respectively, as shown in Figures 11(a) and 11(b). The water droplet remained spherical on the surface and was easy to fall off, indicating that the modified sponge was superhydrophobic, while the n-hexane droplet was immediately absorbed by the sponge upon touched the surface, indicating that the modified sponge is superoleophilic. As shown in Fig. 11(c), when the modified sponge was completely immersed in water under external forces, the surface of it would be like a silver mirror because a continuous air layer was formed between the superhydrophobic surface and the water. The contact angle of the modified sponge measured by the contact angle measuring instrument was 151.1° (Fig. 11(d)), indicating that it was a superhydrophobic material. Therefore, the modified sponge is superhydrophobic and superoleophilic.



(a) the state of oil (b) the state of water (c) the state of the sponge underwater (d) the contact angle

Figure 11 Wettability of modified sponge

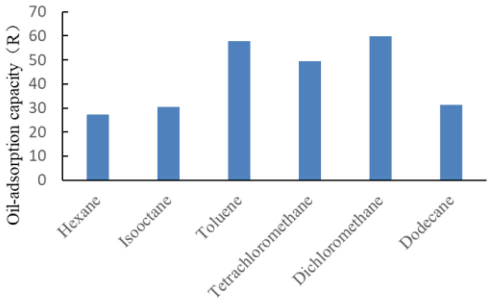
4.1.2 Oil-absorption capacity

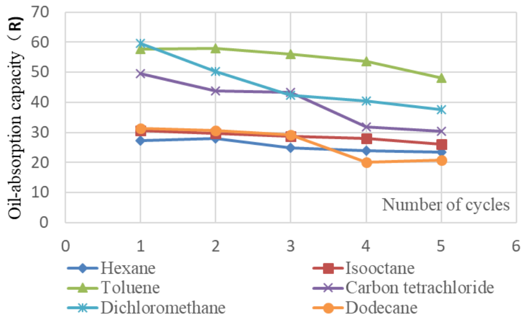
The oil-absorption capacity is the basis of the application of modified sponge. The calculation formula of the oil-absorption capacity is:

$$R = (W_a - W_i) / W_i \qquad (1)$$

Where, W_i and W_a are the weights of the sponge before and after the absorption respectively.

Six kinds of oils and organic solvents were used to test the oil-absorption capacity of the sponge, including n-hexane, toluene, dichloromethane, carbon tetrachloride, isooctane and dodecane. The modified sponge was cut into cubes of 1cm×1cm×0.5cm in size and immersed in the above six kinds of oils and organic solvents respectively until saturated. Then the cubes were taken out quickly and weighed. The oil-absorption capacity was calculated according to Formula (1). The oil-absorption capacities of the modified sponge for 6 six kinds of oils and organic solvents are 27-60 (Fig. 12(a)), which is higher than other reported sponge materials [7-14].





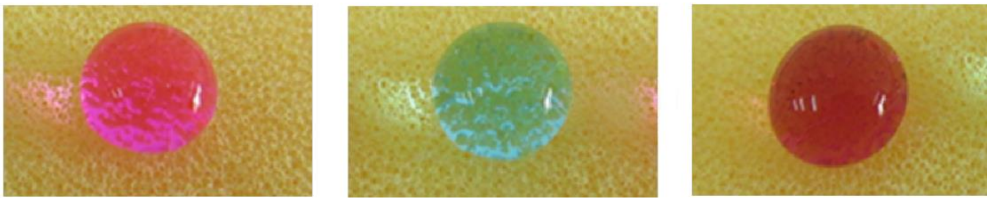
(a) oil-absorption capacity (b) oil-absorption capacity after multiple cycles

Figure 12 Oil-absorption capacity of the modified sponge

Oil absorbed by sponge can be recycled by a simple extrusion process, and then the sponge can be used to absorb the oil again. The absorption capacity for above 6 kinds of oils and organic solvents was still more than 20 times of its own weight (Fig. 12(b)). Outstanding absorption capacity and excellent recyclability make the sponge suitable for oil-water separation.

4.1.3 Resistance to acid and alkali

Chemical stability of modified sponge in acid and alkali environment plays an important role in practical applications. N-hexane-NaOH mixture (NaOH dyed rose red with rhodamine B), n-hexane-NaCl mixture (NaCl dyed blue with methylene blue) and n-hexane-H_2SO_4 mixture (H_2SO_4 dyed purple with catechol violet) were prepared to study the states of droplets with different pH on the surface of sponge. As is shown in Fig. 13, the droplets with different pH can maintain a spherical state, which shows that the sponge was superhydrophobic. This indicates that modified sponge shows strong repellency to strong alkali, saturated salt solution and strong acid, so it has good chemical stability. The oil-water separation experiment of modified sponge in strong acid, strong alkali and saturated salt solution was carried out, and it was found that the modified sponge can effectively separate oil and water in these mixtures. It shows that the fabricated modified sponge is resistant to strong acid, strong alkali and saturated salt solution, making it able to be applied to oil-water separation in harsh environments.



(a) n-hexane-NaOH mixture (b) n-hexane-NaCl mixture (c) n-hexane-H_2SO_4 mixture

Figure 13 States of droplets with different pH on the surface of modified sponge

4.1.4 Self-cleaning property

With reversible wettability and the degradation of organic matter in P25 TiO_2 nanoparticles under UV, the modified sponge has a good self-cleaning property. The self-cleaning process based on the reversible wettability is shown in Figure 14. Firstly, the surface of the sponge, which had been irradiated by UV for 6 hours was contaminated with low-volatility dodecane, and the surface water contact angle was increased from 0° to 109.8°, indicating that the hydrophilic ability of the material decreased after being contaminated. Then the contaminated sponge was irradiated by UV for 6 h again, and the surface water contact angle was decreased from 109.8° to 0°. The wettability was restored to superhydrophilicity. The sponge was further heated at 120 °C for 20 hours, and the surface water contact angle was raised from 0° to 150.4°. The wettability was restored from hydrophilic to superhydrophobic, and the oleophilicity was restored. This process makes the decontamination of modified sponge possible, and can be repeated many times (Fig. 15), which improves the anti-pollution ability of the modified sponge and realizes the reuse of the oil-water separation material.

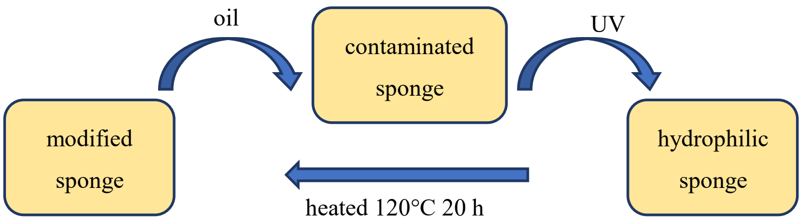


Figure 14 Improving the recycling effect of materials based on the reversible wettability

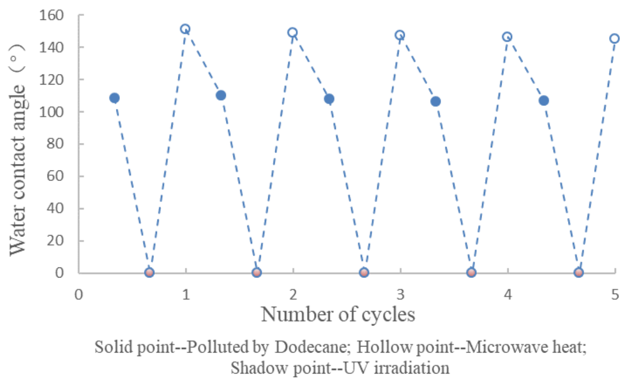


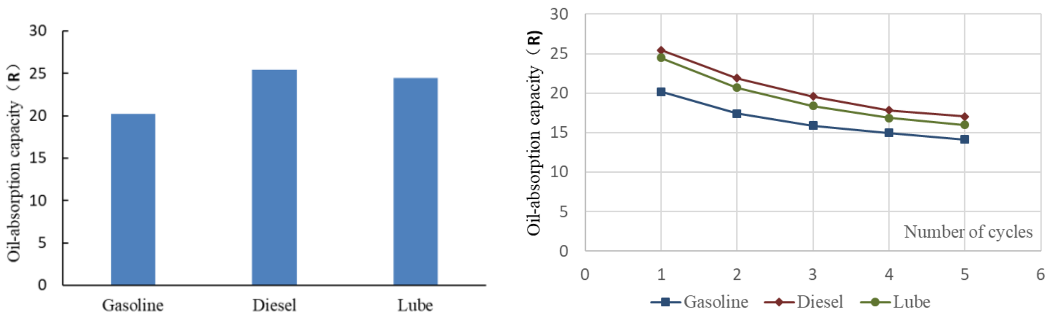
Figure 15 Multiple anti-pollution ability of modified sponge

4.2 Influencing factors

Considering that the actual conditions are usually harsher than in the laboratory, this section analyzes the absorption effect on petroleum contamination, the effect of sponge's thickness on modification process, the effect of sponge's thickness on the reversible wettability and the recycling capacity of reversible wettability sponge.

4.2.1 Absorption effect on petroleum contamination

In the previous study, it was found that the reversible wettability sponge has a good absorption ability for oils and organic solvents such as n-hexane, toluene, dichloromethane, carbon tetrachloride, isooctane and dodecane. However, the actual oil pollution is mainly caused by petroleum, and the absorption effect of the modified sponge on such oil remains to be studied. The petroleum products of gasoline, diesel oil and lubricating oil were selected, and the tested oil-absorption capacities for them were 20-25 times respectively, which were lower than that of the organic solutions (27-60 times), but the sponge still showed strong oil-absorption capacity (Fig. 16a). After 5 cycles, the absorbency for gasoline, diesel oil and lubricating oil remained above 14 times of its own weight (Fig. 16 (b)). Recycling ability of modified sponge in petroleum is lower than in organic solution, but it still shows a good recycling ability. Due to the relatively high viscosity of gasoline, diesel oil and lubricating oil, the modified sponge has lower oil-absorption and recycling capacity, but the modified sponge still has good applicability to petroleum contamination.



(a) oil-absorption capacity for petroleum (b) recycling capacity for petroleum

Figure 16 Absorption properties of modified sponge for petroleum

4.2.2 Influence of sponge's thickness on modification

The sponge cubes used in the preparation of the reversible wettability sponge are 2cm×2cm×0.5cm, and the size is a little small. Sponge with a larger size may be used in practical applications, but the modification effect needs to be studied. The sponge cubes of 4cm×4cm×4cm ware selected and modified by the above process. Then, the cubes were cut into 0.5cm in thickness, and the water contact angles on the surface were tested as shown in Fig. 17. The thickness of the sponge was only about 4 cm, so there was only about 2 cm between the center and the surface. The test showed that the entire sponge, including the interior of it, was superhydrophobic, indicating that the fabrication process was still effective for the modified sponge with 4cm in thickness. Since the 4cm-thick sponge can meet the needs of applications in environmental engineering, the fabrication process can be used to produce modified sponges for actual environments.

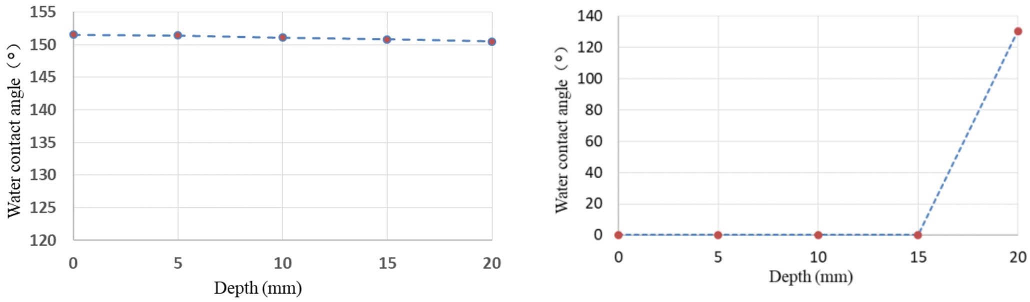


Figure 17 Modification effect inside the sponge Figure 18 Depth of reversible wettability affected by UV

4.2.3 Influence of sponge's thickness on reversible wettability

Because the depth that UV can reach is limited, the thickness of the sponge will influence the result of reversible wettability. The modified sponge cube of 4cm×4cm×4cm was treated with the UV irradiation with above intensity and duration, then it was cut into a 0.5cm-thick cube. The water contact angle on the surface was tested as shown in Fig. 18. It can be seen from the figure that after UV irradiation, the contact angle at 15 mm from the surface of the sponge was zero, and the wettability of the sponge in this range was switched from superhydrophobicity to superhydrophilicity. However, the water contact angle at the depth of 20 mm was still about 135°, and its wettability did not change significantly. Therefore, the effective depth of the reversible wettability under the UV irradiation with above intensity and duration is about 15 mm, and if two-sided irradiation is used, the depth can reach 30 mm. Therefore, the thickness of the sponge should not exceed 30 mm in practical application. If a thicker sponge is needed, it can be used in multiple layers.

4.2.4 Influence of the number of cycles

In the previous study, the number of cycles was only 5. In actual engineering application, the number of cycles is much more than that, and oil-absorption capability in more cycles is still to be studied. The recycling capability of the modified sponge was reflected by the contact angle tested after every 10 cycles of absorption-extrusion and high-temperature treatment. Due to the high boiling point of gasoline, diesel oil and lubricating oil, they may not be able to withstand a high temperature, therefore the test was carried out with toluene, carbon tetrachloride and dichloromethane, the results of which are shown in Table 3. The result shows that the water contact angle of the sponge surface does not change significantly with the increase of the number of cycles. After 80 cycles, the contact angle remained to exceed 150°. After 90 cycles, although the contact angle was smaller than 150°, the sponge remained extremely hydrophobic and oelophilic. This indicates that the modified sponge has good recycling capability and can be applied to the actual environment.

Table 3 Water contact angles of modified sponge after multiple absorption-extrusion-high temperature evaporation treatments

The number of cycles	Toluene	Carbon tetrachloride	Dichloromethane
0	151.5	151.6	151.5
10	151.3	151.5	151.3
20	151.1	151.0	151.2
30	150.9	150.7	150.9
40	150.7	150.6	150.6
50	150.6	150.4	150.6
60	150.4	150.3	150.5
70	150.2	150.1	150.2
80	150.0	150.0	150.1
90	149.7	149.8	149.8

5 Conclusion

A reversible wettability sponge which can flexibly switch between hydrophilicity and oleophilicity is studied. The main conclusions are as follows:

(1) A simple fabrication method for reversible wettability sponge with simultaneous modification of stearic acid and TiO_2 and ultrasonic assisted immersion is proposed.

(2) This sponge is superhydrophobic and superoleophilic in e air. After 6 hours of UV irradiation, the wettability is converted into superhydrophilic in air and superoleophobic under water. Then heated at 120 °C for 20 h, it returns to the initial wettability in air. The above process can be repeated many times, and this method takes shorter time and is easier to complete than traditional methods. The photosensitive effect of TiO_2 is the main reason for the reversible wettability of the modified sponge.

(3) This reversible wettability sponge has good stability in acid and alkali, self-cleaning property and a high recycling rate, and its oil absorption can reach 20-60 times its own weight.

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