Superhydrophobic treatment of polyurethane sponge and its application in oil-water separation

Abstract

The superhydrophobicity of the polyurethane sponge was realized by attaching the complex of copper and mercaptan on the outer surface of the polyurethane sponge. As a special case，the complex of 1-dodecanthiol and copper chloride was intensively studied in this thesis, with emphasis on the influences of concentration, temperature and residence time on the reaction. SEM and EDS were used to analyze the surface structure and elemental composition of the sponge. The reasons for the superhydrophobicity of the sponge are analyzed, the surface of the sponge is roughened by treatment while a large number of long carbon chains appear on the surface, which reduces the surface energy. The wettability of the surface was measured by contact angle meter. The results show that the material has great oil-water separation effect, and the sponge keeps its superhydrophobicity during the process of the separation of oil and water before first 39 times.

Keywords**:** *Superhydrophobicity; Polyurethane sponge; Oil/water separation; Wettability*

1. Introduction

With the continuous development of industry and agriculture, the consumption of petroleum and other energy products is increasing[1]*, and the environmental pollution caused by the leakage of oil products is becoming increasingly serious. The oil spill reported in recent years has resulted in a spate of water pollution .There are physical, chemical and biological* [234]*methods for the treatment of contaminated water. Physical method is simple but has low efficiency, and both chemical and biological methods require a certain proportion of chemical reagents in polluted water sources, it may cause a certain degree of secondary pollution if the addition is unreasonable. With the emergence and development of new materials, researchers hope to produce efficient oil-water separation materials*[5] *for the treatment of contaminated water, this method has the advantages of high efficiency and no pollution.*

The understanding of the superhydrophobic surface originates from some plants and animals in nature[6]*.They are waterproof, anti-fouling, reducing resistance and so on*[7]*. There are differences in the way superhydrophobic surfaces are constructed, but there are two main steps :(1) Construct a rough surface (2) Modified with low surface energy substances.*

Polyurethane sponge, as the basis of materials, has great advantages in *practical application since it has the characteristics of porosity, low cost and stability*[891011].

In this experiment, the compounds of mercaptan and bivalent copper were prepared and then covered in the surface of PU sponge, so that the sponge had the superhydrophobicity. It is also found that superhydrophobic sponge has excellent performance in oil and water separation[12].

2. Experimental

Reagents

High-density sponge,200-400 μm; Medium-density sponge,330-480 μm; Low-density sponge,700-850 μm, all sponges were bought from Nanjing Yongsheng sponge factory; Sodium hydroxide, AR; Copper chloride, AR; Decyl mercaptan, AR; 1-Dodecanethiol;AR; 1-Octadecanethiol,AR; Sudan Red, AR; Dimethylbenzene, AR; Ethanol, AR;All reagents were bought from Shanghai Taitan Technology.

2.2 Preparation of superhydrophobic sponge

First, the sponge(2cm×2cm×1cm)was washed with sodium hydroxide solution for 15 min to remove the grease from the sponge, and then deionized water was used for ultrasonic washing for 15 min, drying and waiting. In the ratio of 4:1, the temperature is 30℃, the time is 8 min, and the pH is 8, and the reaction of 1-dodecanthiol and copper chloride is precipitated. By dispersing dry solid ultrasound into ethanol, the dispersion of 8 mg mL^{-1} *was obtained. The clean PU sponge was added to the dispersion solution, and the ultrasound was used for 15 min, drying and obtaining the product.*

2.3 Characterization

The surface morphology and structure of the samples were analyzed by scanning electron microscopy (S-3400 N, Hitachi, Japan). The composition of the sample was quantified using an energy spectrometer (ESCALAB 250 xi, Thermo Fisher Scientific, USA). The wettability of the sample was analyzed by static contact angle meter (YIKE-360 A, Chengde Yike, China). The droplets were distilled water, and the water volume was 3 μL, the droplets were discontinuous. In order to ensure the reliability of the experiment, five different areas were selected for the surface of the sample.

3. Results and discussion

3.1 The influence of the ratio of mercaptan to copper chloride

The weight of copper chloride was controlled at 1g,and the complexes were prepared, the ratio of 1-dodecanthiol to copper chloride was 1:2、1:1、2:1、3:1、4:1、5:1. Fig.1 shows the variation of weight with proportion. When the ratio of mercaptan *to copper chloride was 4:1, the weight of the product was the largest. It was observed that the color of final solution was blue when the ratio was less than 4:1 and the solution is colorless at 4:1.The experiment found that when the ratio was greater than 4:1, a large amount of mercaptan was wrapped by the product, which resulted in a decrease in weight. After the complexes were attached to the sponge, the contact angle of the sponge was determined.Fig.2 shows the relationship between contact angle and ratio. The results show that the contact angle has weak relation with the ratio. EDS analysis showed that the ratio of mercaptan to copper in the complexes was n:1, and the proportion of each product was distributed.*

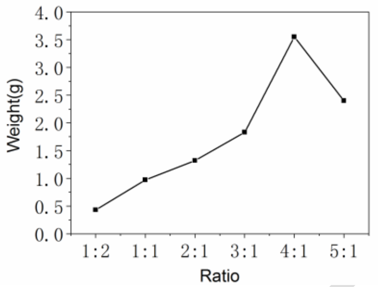

Fig.1 The influence of the ratio on the weight

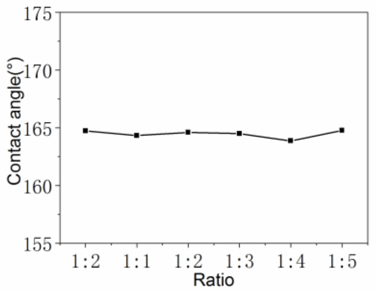

Fig.2 The influence of the ratio on contact angle

3.2 The influence of temperature on the weight

In order to determine the optimal reaction temperature, the temperature of the reaction was changed to obtain the relation of the product weight. Fig.3 shows the relationship between product weight and time. The weight of complex increased slowly with the increase of temperature when the temperature was lower than 30℃, and the weight tends to be stable when the temperature is higher than 30℃,so the most suitable reaction temperature is 30℃.

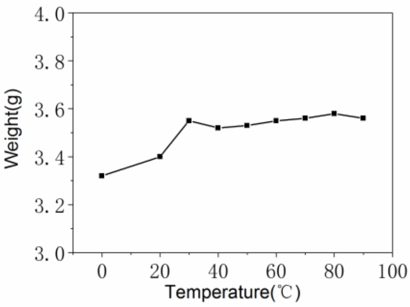

Fig.3 The influence of temperature on the weight of products.

3.3 The influence of reaction time on the weight

In order to explore the influence of reaction time on the product weight, the weight of the product at different times was measured to determine the optimal time. To accelerate the reaction rate, the reaction of complex was carried out under the Ultrasonic of 50 kHz. According to the Fig.4, the weight of the product increased with the time of reaction when the time was less than 7 min, and the weight was almost the same when the time was higher than 8 min, so the optimal reaction time was 8 min.

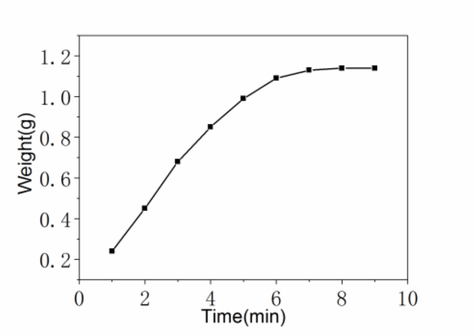

Fig.4 The influence of reaction time on the weight of the product.

3.4 The influence of pH on the weight

The influence of pH on the weight of products was explored.Fig.5 shows the relationship between the pH and the weight of product . The weight of the product was almost the same as the pH were 2 and 4, then the weight increased sharply with the growing of pH and reached the highest as the pH of 8.When the pH was greater than 8, the weight decreased rapidly, because of a large amount of copper precipitating in the form of copper hydroxide as the pH is larger than 8.

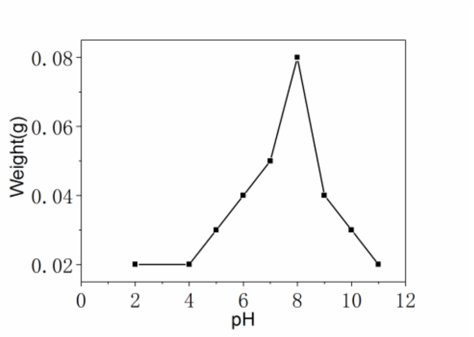

Fig.5 The influence of the pH on the weight.

3.5 The influence of concentration of complex in suspension liquid on wettability

The pristine sponge is not hydrophobic with the contact angle of 93° ,the hydrophobicity of sponge could be developed when the complex prepared in 3.1-3.4 was attached to the surface of sponge, the method of attaching was described in 2.2. Here, the influence of the concentration of complex in suspension on the wettability was explored. The results are shown in Fig.6, the contact angle of sponge rises slowly from 152°to 166° with the increase of concentration of complex in suspension liquid from 2 mg mL^{-1} to 12 mg mL^{-1}.Fig.6 also shows that the contact angle is 147° with the concentration of 0.2 mg mL^{-1}.The investigation found it was easy for the complex to fall out from the sponge when the concentration was higher than 8 mg mL^{-1}.The reason may be the sponge is overloaded for the complex. So the optimal concentration of complex was set at 8 mg mL^{-1}.

In order to explore the effect of the pore size of sponge on the wettability, three sponges with different pore sizes were used for the investigation. The complex was distributed to those sponges as mentioned in 2.2, and the contact angle of those sponges attached to complex was measured, the results are also contained in Fig.6,the contact angles differ a little for the medium density sponge and low density sponge, the reason is considered that the size of pore for the medium density sponge and low density sponge is larger than the size of water drop, and the high density sponges with smallest size of pore show the biggest contact angle at different concentration.

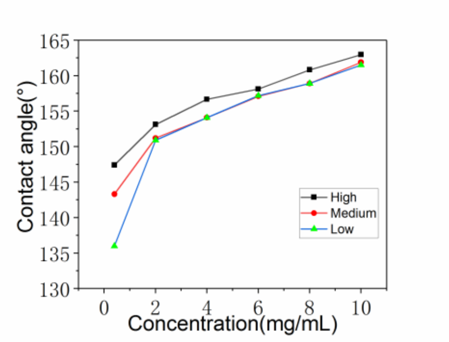

Fig.6 The influence of concentration on wettability.(High---high density sponge;Medium---medium density sponge;Low---low density sponge)

3.6 The influence of the mercaptans on wettability

The different lengths of the carbon chains for mercaptans can affect the wettability of the sponge. In this investigation, three mercaptans, decyl mercaptan, 1-dodecanethiol and 1-octadecanethiol were used because they are available in the market. The complexes of those mercaptans with copper chloride were prepared and distributed to the sponges respectively. Their contact angle were measured and the result is shown in Fig.7.According to the Fig.7,with the increase of carbon chain for mercaptans, the contact angle of the sponge rises within for concentration of 2、4、6、8 mg mL^{-1}.Since 1-octadecanethiol is more expensive than 1-dodecanethiol and the contact angle of the sponge with 1-dodecanethiol also larger than 150° at the concentrations showing Fig.7.So the 1-dodecanethiol was selected.

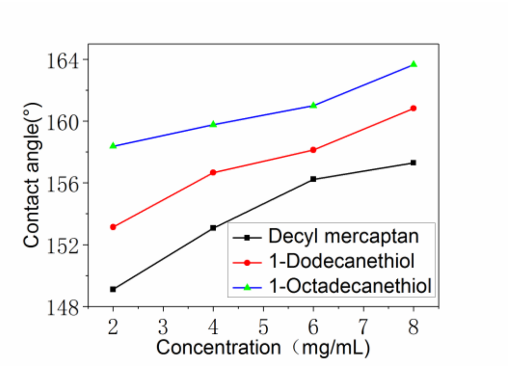

Fig.7 The effect of the type of mercaptan on the wettability of materials.(Decyl mercaptan---Sponge attached by complex of decyl mercaptan with copper chloride;1-Dodecanethiol---Sponge attached by complex of 1-dodecanethiol with copper chloride;1-Octadecanethiol---Sponge attached by complex of 1-octadecanethiol with copper chloride)

3.7 Surface structure of the sponge

Fig.8 shows the surface structure for the pristine and superhydrophobic sponge with SEM images. From Fig. 8, the pristine sponge has a smooth surface(Fig.8.A-B), and the surface of superhydrophobic sponge is rough(Fig.8.C-D).The solid particles produced by copper chloride and dodecyl mercaptan are attached to the surfaces of sponges resulting in the sponge's rough surface. It is believed that the roughness of surface is one of key factors for the superhydrophobicity.

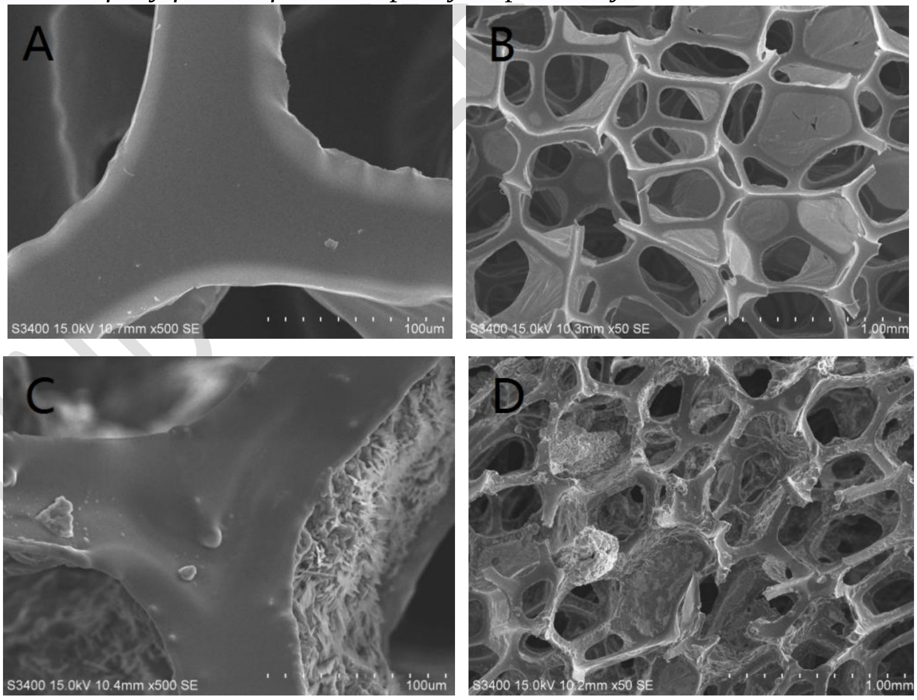

Fig.8 SEM analysis of sponge surface.(A and B are SEM images of the pristine sponge;C and D are SEM images of superhydrophobic sponge)

3.8 EDS for the surface of sponge

To verify the complex of mercaptan and copper chloride were attached to the surface of the superhydrophobic sponge, EDS was used to identify the presence of sulfur and copper on the sponge. The result was shown in Table.1.From the Table.1, sulfur and copper are found in the superhydrophobic sponge and their content in weight reach 8.16％and 8.24％.It demonstrates that the complex was attached to the surface of the sponge.

Table.1 EDS for the surface of pristine sponge and superhydrophobic sponge

Elements	Pristine sponge(Wt％)	Superhydrophobic sponge(Wt％)
C	61.42	71.04
N	9.00	02.83
O	28.63	08.90
Cu	0	08.24
S	0	08.16

3.9 Analysis of surface wettability

Fig.9 is the static contact angle for the sponges. The contact angle is 93° for pristine sponge (Fig.9.A) and 166° for superhydrophobicity sponge (Fig.9.B).From the change of contact angle, it can be seen that the hydrophobicity of the sponge has been improved dramatically with reaching the requirement of superhydrophobicity.

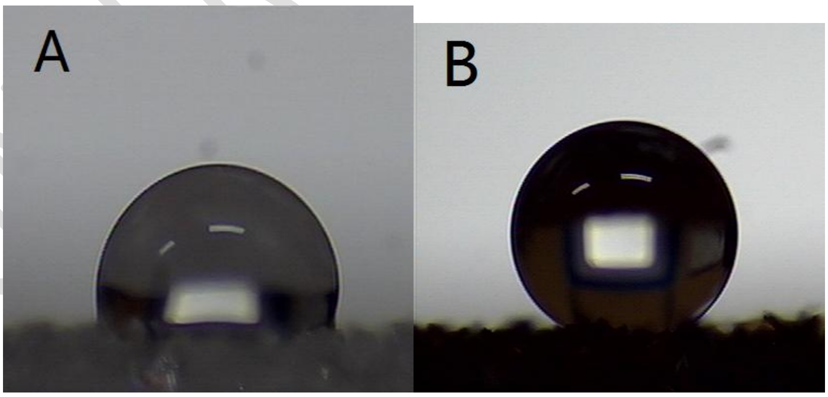

Fig.9 Static contact angle of sponge before and after treatment.

3.10 The application of the hydrophobic sponge

The superhydrophobic sponge has a potential application in the separation of oil and water. Firstly, the superhydrophobic sponge prepared according to 3.1-3.6 was explored in the separation of oil and water, compared with the pristine sponge.

Dimethylbenzene, 1, 2-dichloroethane, isocinol and hexane were used as oil phases respectively, and Deionized water as another phase. To mark the oil phase, a little Sudan red is dissolved in it. 20 mL water and 20 mL organic solvent with sudan red were added into a 50 mL beaker,then the superhydrophobic sponge(2cm×2cm×1cm) was fully compacted put at the surface of oil and water. The sponge was taken out from the beaker after the sponge absorbed fully the mixture. In the next step, the liquid in the sponge was squeezed out completely into the measuring cylinder and observed the oil and water in the measuring cylinder. The result was shown in Fig.10,from the Fig.10,the pristine sponge shows no obvious selectivity in the separation of oil and water while the superhydrophobic sponge only absorb the oil for the four organic solvent in the investigation.

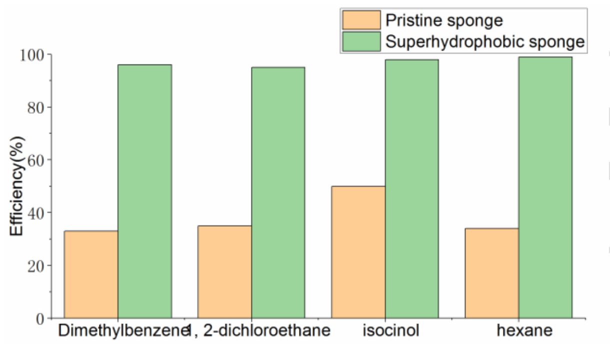

Fig.10 The efficiency of pristine and superhydrophobic sponge to absorb the oil phase.

For some reasons,the wettability of the superhydrophobic sponge will decrease after repeated use. To learn how many times the sponge can be used, the relationship between the contact angle and the number of separation times of oil and water for sponge was studied. Using dimethylbenzene as the oil phase. The process[13] of the study was carried out as show in Fig.11,(A)Add 50 mL water to a clean beaker;(B) Add 1 mL dimethylbenzene in the beaker, containing a little sudan red;(C)Put a piece of superhydrophobic sponge(2cm×2cm×1cm) in the beaker to absorb the oil phase.(D)Took the sponge absorbed the oil out the beaker,the water in the beaker was clear without the oil phase;(E)The sponge squeezed out the oil with tweezers and used to absorb the dimethylbenzene again, as described in step C,then repeat D and E；(F)When the number of repetition for the absorption reached 1、2、4、7.......as shown in Fig.12. The sponge was dried in the oven at 80℃ until it evaporated fully,then measured the contact angle to identify its wettability. The result was illustrated in Fig.12,from the Fig.12, the contact angle decreases from 166° to 153° in the first 11 times and goes down slowly to 150° at the 39 th times. The repetition was reporter only about 10 times[14,15],it is believed that the the superhydrophobic sponge can be used for at least 10 times in practice.

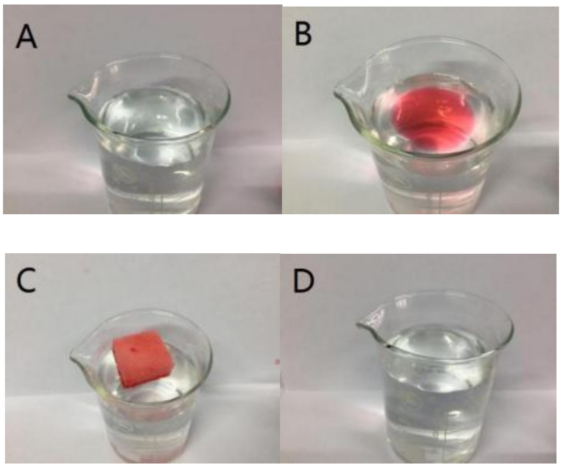

Fig.11 The process of oil and water separation .

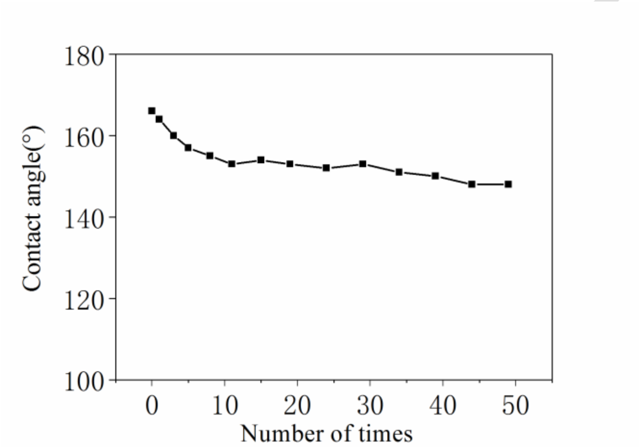

Fig.12 Relation between the number of separation and wettability.

4. Conclusion

In this paper, the complex of 1-dodecanthiol and copper chloride was prepared and attached to the surface of sponge to develop a novel superhydrophobic sponge for separation of oil and water. The surface structure and elements of the sponge were identified by SEM and EDS, showing the complex was attached to the surface of the sponge and increased the roughness of the surface. The contact angle of the sponge was measured to characterize its wettability. It was found that the superhydrophobic sponge was developed successfully with the contact angle of larger than 150 ^{o}. The superhydrophobic sponge was studied in application of separation of oil and water. The results show that the developed superhydrophobic sponge only adsorbs the oil phase and acted excellent selectivity for separation of oil and water. In the results, the sponge also was found to be used repeatedly for many times up to 39 times. The superhydrophobic sponge developed in the paper may be considered to have many advantages compared with that reported[16].

REFERENCES

1.Yang Y, Yan L I, Liu G, et al. A hindcast of the Bohai Bay oil spill during June to August 2011[J]. Acta Oceanologica Sinica, 2017, 36(11):21-26.DOI：10.1007/s 13131-017-1135-7

2.Choi H M, Cloud R M. Natural sorbents in oil spill cleanup[J]. Environmental Science & Technology, 1992, 26(4):772-776.DOI：10.1021/es00028a016

3.Dalton T , Jin D．Extent and frequency of vessel oil spills in US marine protected areas [J] ．Marine Pollution Bulletin , 2010,60（11）：1935-1945．DOI：10.1016/j.marpolbul.2010.07.036

4.Schaum J , Cohen M , Perry S , et al．Screening level assessment of risks due to dioxin emissions from burning oil from the BP deep water horizon gulf of mexico spill[J] ．Environmental Science and Technology , 2010,44（24）：9383-9389．DOI：10.1021/es103559w

5.Xue Z, Cao Y, Liu N, et al. Special Wettable Materials for Oil/Water Separation[J]. Journal of Materials Chemistry A, 2014, 2(8): 2445-2460.DOI10.1039/C3TA13397D

6.Liu K, Yao X, Jiang L. Recent Developments in Bio-Inspired Special Wettability[J]. Chemical Society Reviews, 2010, 39(8): 3240-3255.DOI：10.1039/b917112f

7.Qian C, Chen G H, Yan F, et al. Super-hydrophobic characteristics of butterfly wing surface[J]. Journal of Bionic Engineering, 2004, 1(4):249-255.

8.Zhang J, Huang W, Han Y. A Composite Polymer Film with both Superhydrophobicity and Superoleophilicity[J]. Macromolecular Rapid Communications, 2006, 27(10):804–808.DOI：10.1002/marc.200500842

9.Liu Y, Ma J, Wu T, et al. Cost-effective reduced graphene oxide-coated polyurethane sponge as a highly efficient and reusable oil-absorbent[J]. Applied

Materials & Interfaces, 2013, 5(20):10018.DOI：10.1021/am4024252

10.Patankar N A. Transition between Superhydrophobic States on Rough Surfaces[J]. Langmuir, 2004, 20(17):7097-102.DOI：10.1021/la049329e

11.Zhou X, Zhang Z, Xu X, et al. Facile Fabrication of Superhydrophobic Sponge with Selective Absorption and Collection of Oil from Water[J]. Industrial & Engineering Chemistry Research, 2013, 52(27):9411-9416. DOI：10.1021/ie400942t

12.Jiang G, Hu R, Xi X, et al. Facile preparation of superhydrophobic and superoleophilic sponge for fast removal of oils from water surface[J]. Journal of Materials Research, 2013, 28(4):651-656.DOI：10.1557/jmr.2012.410

13.Zhang L, Li H, Lai X, et al. Thiolated graphene-based superhydrophobic sponges for oil-water separation[J]. Chemical Engineering Journal, 2017, 316:736-743.DOI：10.1016/j.cej.2017.02.030

14.Saha P, Dashairya L. Reduced graphene oxide modified melamine formaldehyde (rGO@MF) superhydrophobic sponge for efficient oil–water separation[J]. Journal of Porous Materials,2018, 25(5):1475-1488.DOI:10.1007/s10934-018-0560-0

15.Yang X, Shuai Q, Luo Y, et al. Fabrication and Application of the Superhydrophobic Sponge Modified with Poly(dimethylsiloxane) /Silver Micro/Nano-particles/Polydopamine[J]. Chinese Journal of Applied Chemistry, 2015, 32(6):726-732.DOI：10.11944/j.issn.1000-0518.2015.06.140365

16.Zhang L, Xu L, Sun Y, et al. Robust and Durable Superhydrophobic Polyurethane Sponge for Oil/Water Separation[J]. Industrial & Engineering Chemistry Research, 2016, 55(43):11260-11268.DOI：10.1021/acs.iecr.6b02897