

Fabrication of polysiloxane-modified polyurethane sponge as low-cost organics/water separation and selective absorption material

Zhengshan Cui, Wanxia He, Jun Liu, Wei Wei, Liang Jiang, Jun Huang and Xiaomeng Lv

ABSTRACT

Through sol-gel and dip-coating processes, commercial polyurethane sponge modified by polysiloxane was fabricated under low temperature (60 °C) and atmosphere. The contact angle of the obtained polysiloxane/polyurethane sponge is $145 \pm 5^\circ$. Hence, the polysiloxane/polyurethane sponge could float on water and selectively absorb organics from the surface of the water, indicating simultaneous properties of hydrophobicity and oleophilicity. The absorbent maximum value is 50–150 times of its own weight. The polysiloxane/polyurethane sponge exhibited excellent recyclability, which could be reused by squeezing the sponge due to its high mechanical stability and flexibility. Thermogravimetry-differential thermal analysis test indicated that the polysiloxane/polyurethane sponge exhibited good thermal stability and the stable contact angle of samples tested under increasing temperature indicated its good weather resistance. Due to the commercial property of polyurethane sponge and easy-handling of polysiloxane, the polysiloxane/polyurethane sponge can be easily scaled up to recover a large-area oil spill in water and further work based on the designed equipment has been under consideration.

Key words | hydrophobic, oleophilic, polysiloxane, sol-gel

Zhengshan Cui

Liang Jiang

Jun Huang

Xiaomeng Lv

School of Chemistry and Chemical Engineering,
Jiangsu University,
Zhenjiang 212013,
China

Wanxia He

Jun Liu (corresponding author)

School of the Environment and Safety Engineering,
Jiangsu University,
Zhenjiang 212013,
China
E-mail: liujun1227@mail.ujs.edu.cn

Wei Wei

Center of Analysis and Test,
Jiangsu University,
Zhenjiang 212013,
China

INTRODUCTION

Nowadays, oil spills and chemical leakage from industrial accident have had catastrophic effects on marine and aquatic ecosystems (Corominas *et al.* 2010). Various methods have been adopted to sequester and remove oil pollutants, such as mechanical collection, combustion, absorption, acoustic, concentrating, scattering, biological treatments and membrane technology. Among these methods, absorption is regarded as an economic and effective treatment. Hence, the preparation of absorption material with superior absorption ability is an important objective of water resources remediation, especially those with hydrophobic porous materials which can selectively adsorb oily target compounds mixed with an aqueous phase, which are in wide needed.

Recently, various hydrophobic materials have been investigated, such as carbon-based materials (Inagaki *et al.* 2002; Liang *et al.* 2012), metal oxide nanowires (Lahann 2008; Yuan *et al.* 2008), biomass nanofibers (Tuteja *et al.* 2007; Korhonen *et al.* 2011), organic polymers (Nicolas *et al.* 2006; Rao

et al. 2007), and hydrophobic macroporous aerogels (Reynolds *et al.* 2001; Jin *et al.* 2011). Other materials based on polydimethylsiloxane, fluorocarbon coated materials (Yao *et al.* 2011; Wei *et al.* 2014), and materials with a biomimetic rough surface through the use of etching techniques (Liu *et al.* 2010; Sen Wei *et al.* 2014) are also widely reported to enhance hydrophobicity. However, some fabrication procedures required for these approaches are generally complicated and time-consuming. In addition, some of the as-prepared materials exhibit limited stability, flexibility and recyclability, which seriously restrict their practical applications. Therefore, the production of materials with high absorption capacity and stable unusual wettability through simple and practical approaches is highly desirable.

Polyurethane sponge, a kind of commercially available three dimensional porous materials, has been used for fabricating absorbents due to its advantages of common, cheap, and excellent microstructure. However, the amphiphilic feature

limits its further application in environmental remediation. Efforts have been made to engineer its hydrophobic surface, such as graphene based (Nguyen *et al.* 2012), metal nanoparticles (Zhu *et al.* 2011), methyltrichlorosilane (Zhu *et al.* 2013), graphene/silica hybrid material (Lü *et al.* 2015) and polytetrafluoroethylene (Calcagnile *et al.* 2012). Still, little work has been developed in the field of the hydrophobic alkyl-rich polysiloxane/polyurethane composite, especially those polysiloxane without fluorine group or other composite functional group. To find a facile strategy to fabricate sponge with high absorption capacity, high selectivity and reusability is very important, but it remains a challenge.

Here, we propose a facile approach through sol-gel and dip-coating method to fabricate hydrophobic and oleophilic sponges modified by polysiloxane (polysiloxane/polyurethane), as depicted in Figure 1. The fabricated sponges show not only high absorption capacity amounting to 160 times its own weight but also excellent recyclability which can be utilized by only extrusion/absorption. Importantly, the polysiloxane/polyurethane sponges exhibit stable hydrophobicity in the temperature range from 25 °C to 200 °C. The dual combination of hydrophobicity and oleophilicity and particular physico-chemical features of the polysiloxane/polyurethane sponges make them promising materials for the removal and collection of oil from water.

EXPERIMENT

Materials and methods

Commercial polyurethane sponges (apparent density of 0.032 g/cm³, with a void volume of more than 97%) rapeseed oil and diesel oil were obtained from a local furniture store. Acetic acid, urea, ethanol, hexamethylene, chloroform, N-hexadecyltrimethylammonium chloride (CTAC), chromium

trioxide and Sudan III were purchased from Sinopharm Chemical Reagent Co. Ltd. Vinylmethyldimethoxysilane and bis(methyldiethoxysilyl)ethane were purchased from Suzhou Yacoo Chemical Reagent Corporation. All of the chemical reagents were used as received.

Preparation of the polysiloxane/polyurethane sponge

The polyurethane sponges were ultrasonically cleaned in acetone and ethanol, successively. Then the polyurethane sponges were etched in CrO₃ (100 g/L) and H₂SO₄ (98 wt%, 100 g/L) solution in turn for a few minutes for pretreatment, and then washed with distilled water and dried in an oven.

Typically, 0.80 g of CTAC, 5.0 g of urea, 15 mL of 5 mmol/L aqueous acetic acid, 3 mL of methyltrimethoxysilane (MTMS) and 2 mL of dimethyl dimethoxysilane (DMDMOS) were mixed in a glass tube and stirred at 25 °C for 2 h. The cleaned sponge substrate was successively dipped into the solution for 10 min and withdrawn at a constant speed of less than 1 mm/s. The coated sponge was then transferred into a container with a tightly-sealed lid at 60 °C for 2–3 d for complete gelation and aging, and then taken out and washed with acetone and ethanol, each 3 times. They were dried for 24 h at 40 °C to obtain the modified polyurethane sponge in a vacuum oven.

Polysiloxane material without sponge was prepared by curing the sol at 60 °C for 2 d to obtain the gels, which were washed and dried under ambient conditions to obtain xerogels.

Organic solvent and absorption capacity of polysiloxane/polyurethane sponge

The M-PU sponges were cut into cubic specimens (5 mm × 5 mm × 2 mm) and dipped into 20 mL of organic solvent or oil (including diesel oil, rapeseed oil, motor oil, acetone, chloroform, dimethylformamide (DMF), tetrahydrofuran

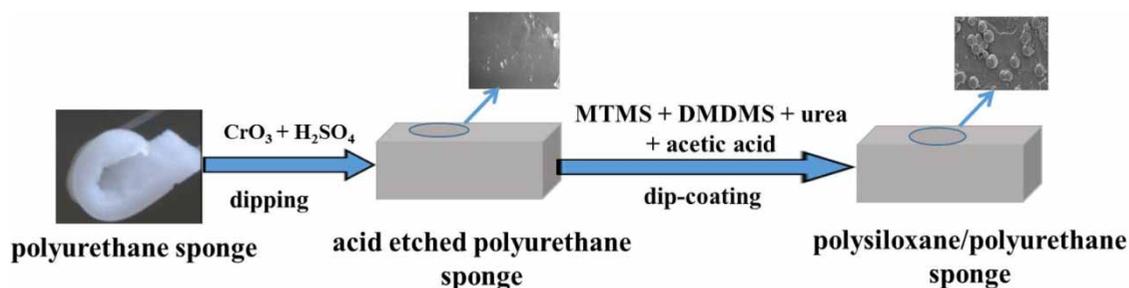


Figure 1 | The experimental process diagram.

(THF), benzyl alcohol and hexane) for 5 min. The sorption capacity Q_e (g/g) was calculated according to Equation (1).

$$Q_e \left(\frac{\text{g}}{\text{g}} \right) = \frac{(m_1 - m_0)}{m_0} \quad (1)$$

where m_0 and m_1 are the weight of the sponge before and after sorption, respectively.

Reusability

The organic solvent and oil were squeezed from the sponges by a simple mechanical compression method without solvent evaporation and we performed 10 cycles to test the mechanical performance and cyclic utilization performance of M-PU sponge. We define the Q_e' as recycle adsorption capacity during each recycle process.

$$Q_e' \left(\frac{\text{g}}{\text{g}} \right) = \frac{(m_1 - m_2)}{m_2} \quad (2)$$

where m_1 and m_2 are the weight of the sample after sorption and the weight of the sample after simple mechanical compression, respectively.

Characterization

The hydrophobicity of the polysiloxane and polysiloxane/polyurethane was measured with an optical contact angle measuring device (KSV cm200; Dataphysics Instruments, The Netherlands) using a droplet (4.8 μL) of water as the indicator.

Scanning and transmission electron microscopy (SEM and TEM) was carried out on both a Hitachi S-5200 SEM equipped with a TE detector (JEOL-6700F ESEM, Japan), operating at 30 kv and a Hitachi HD-2000 dedicated STEM equipped with an SE detector (JEOL, Japan) operating at 200 KV to observe the porous structure of the polyurethane sponge and the polysiloxane/polyurethane.

Fourier transform infrared (FT-IR) spectra of the polysiloxane and the polysiloxane/polyurethane was tested. A FT-IR spectrometer (Paragon-1000, Perkin Elmer, USA) was used to confirm the deposition of the polysiloxane on the polyurethane sponge.

Thermogravimetry-differential thermal analysis (TG-DTA) of the polyurethane sponge and the polysiloxane/polyurethane were also tested. The samples were dried to a constant weight in a vacuum at 30 °C, and then the thermogravimetric diagrams of the samples were measured at a rate of 6 °C/min.

RESULTS AND DISCUSSION

Characterization

After polysiloxane precursor was transferred into a tightly-sealed container, and cured at 60 °C for 24 h, then white and marshmallow-like material was obtained. It can be flexibly bent without structural damage (Figure 2(a)). When the polysiloxane/polyurethane sponge is compressed by more than 95% of its volume, it can completely recover its original shape without structure failure in the process of repeated compression (Figure 2(b)). The intrinsic flexibility of

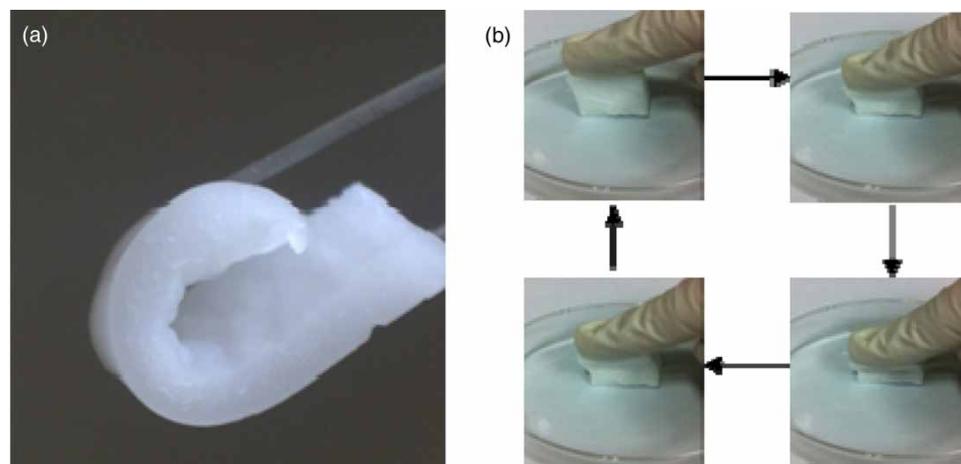


Figure 2 | Flexible performance of polysiloxane (a) and polysiloxane/polyurethane (b).

polysiloxane increases both the compressive strength of polysiloxane/polyurethane sponge and the elasticity, which may contribute to reusability by simple soaking and squeezing.

The morphologies and structures of polysiloxane and polysiloxane/polyurethane sponge surfaces were characterized by SEM and TEM. Figure 3(a) and 3(b) show the skeleton and smooth surface of polyurethane sponge. After the polysiloxane coating, lots of microspheres are loaded on the polyurethane sponge skeleton surface,

the size of which is in the range from 0.8 to 1.2 μm (Figure 3(c) and 3(d)). In addition, the polyurethane sponge skeleton surface presents a thin layer of the diaphragm. The fact could be explained from two aspects as follows. (1) Hydrolytic polycondensation of MTMS and DMDMOS occurred and formed sol seeds, the latter of which continued growing and formed microspheres during the hydrolysis and condensation of monomer. (2) After thermal decomposition of urea, large amounts of silanol material hydrolyzed in the acid conditions,

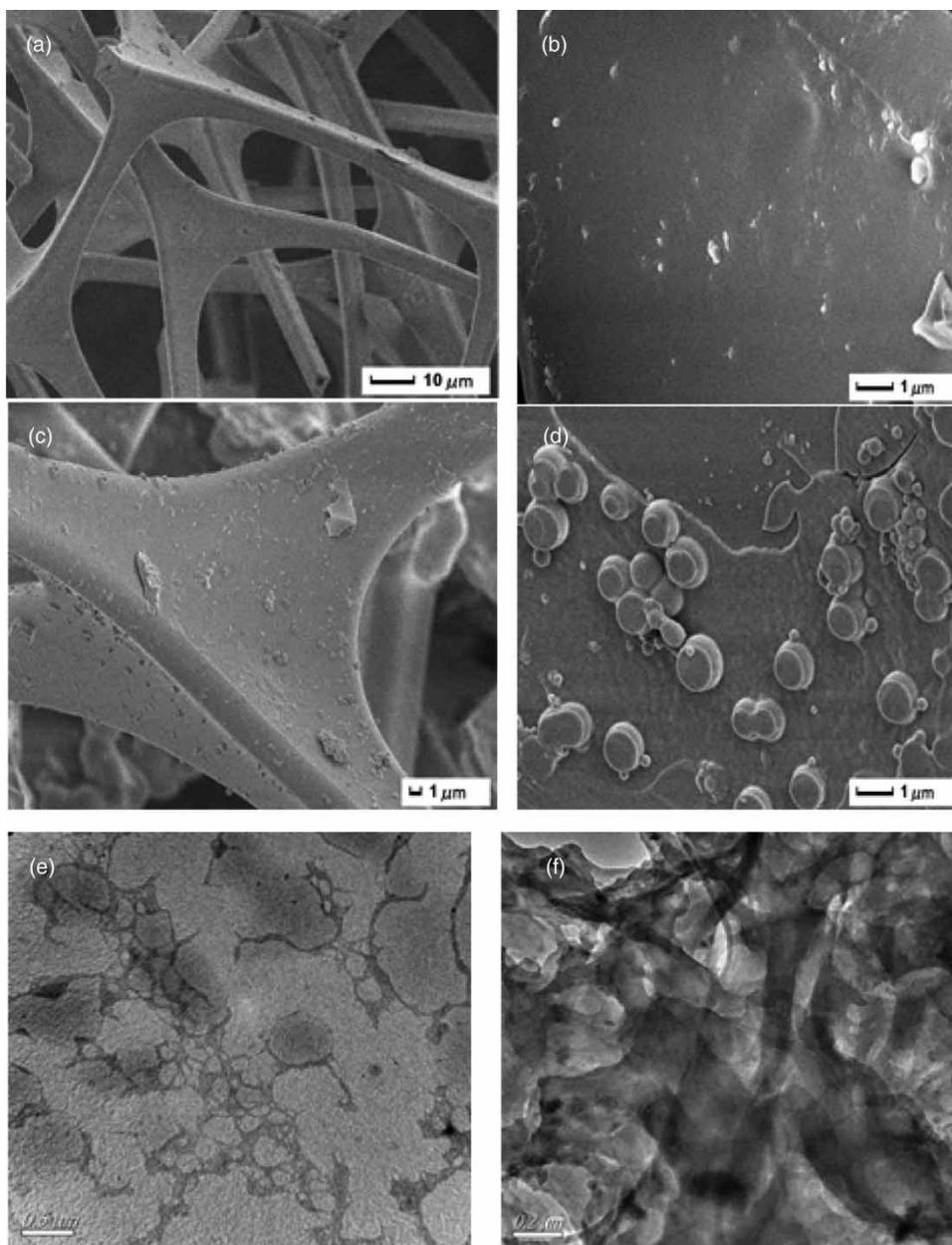


Figure 3 | SEM of the polyurethane sponge after acid etching (a), (b) and the polysiloxane/polyurethane (c), (d); TEM of the polysiloxane (e) and the polysiloxane/polyurethane (f).

crosslinked, and part of them formed into the diaphragm layer. Figure 3(e) presents the TEM image of the polysiloxane sponge, illustrating that the polysiloxane sponge has space network structure, and this pristine porous structure allows a high uptake capacity. As shown in Figure 3(f), it is also clearly seen that the morphology of polysiloxane/polyurethane sponge is similar to that of the polyurethane sponge, indicating that the process of synthesis does not change the character of the polyurethane sponge. This present method not only keeps the feature of the polyurethane sponge, but also expands the application of the polyurethane sponge as selective absorption materials.

Chemical compositions of the coatings on the sponges were identified by the FT-IR analysis. From Figure 4(b) and 4(c), peak in $1,090\text{ cm}^{-1}$ is on behalf of Si-O-Si asymmetric stretching vibration, indicating that the polysiloxane sponge did not change significantly before and after the loading. As seen from Figure 4(a), the acid-etched polyurethane sponge shows strong absorption peak at $3,480\text{ cm}^{-1}$, attributing to the hydrophilic groups such as -OH and -COOH produced in the process of the pretreatment of polyurethane sponge in oxidative $\text{CrO}_3/\text{H}_2\text{SO}_4$ solution produces. However, seen from Figure 4(b), the polysiloxane/polyurethane sponge absorption peak at $3,480\text{ cm}^{-1}$ is very weak. The reason may be that the -OH on the material surface replaced by organic groups after the modification process, leading to weak vibration. Peaks in $2,987\text{ cm}^{-1}$, $1,390\text{ cm}^{-1}$, and 930 cm^{-1} always indicate the vicinity of the absorption peak of methyl group, their existence indicate that the polysiloxane/polyurethane

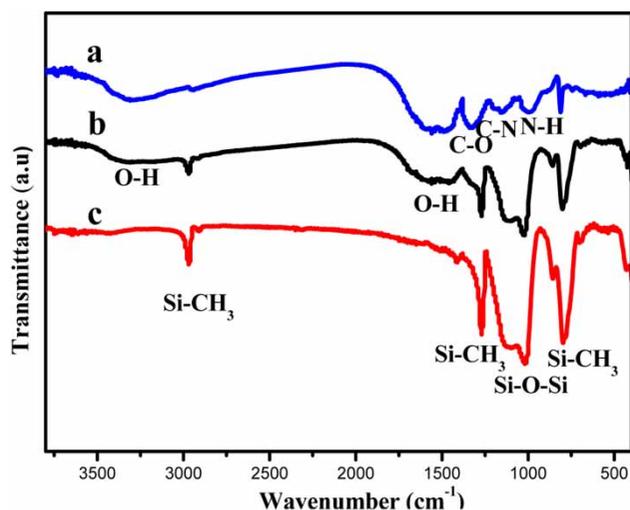


Figure 4 | FTIR spectra of the polyurethane sponge after acid etching (a), the polysiloxane/polyurethane (b), and the polysiloxane (c).

sponge contains methyl group. Infrared spectrum analysis shows that the hydroxyl group on the acid-etched polyurethane sponge surface was replaced by organic groups in the modification process, rendering the modified sponge hydrophobicity.

To evaluate thermal stability of materials, we conducted TG-DTA under an O_2/N_2 atmosphere. The TGA curves of the polysiloxane/polyurethane sponge and the polyurethane sponge are shown in Figure 5. As seen from the curve in Figure 5(a), the total weight loss of polysiloxane/polyurethane sponge is 42.28%. When temperature is below 310°C , the weight loss of the polysiloxane/polyurethane sponge is negligible, owing to the residual solvent in the surface or pore of the composite sponge, a little amount of thermal decomposition of the precursor and the sponge. Larger weight loss appears at the temperature range from 430°C to 870°C , which corresponds to the main part of the thermal decomposition of the sponge. Keeping the heating up, the curves shows no significant changes. As seen from the curves in Figure 5(b), the polyurethane sponge decomposes at lower temperature (c.a. 220°C) and sharply larger weight loss appears at the temperature range from 380°C to 940°C , which corresponds to the main part of the thermal decomposition of the sponge. Hence, the polysiloxane/polyurethane sponge shows comparatively higher thermal stability.

The hydrophobic properties of the sample are determined by measuring the contact angle. As seen from Figure 6, the contact angle of the polysiloxane sponge and the polysiloxane/polyurethane sponge is $125 \pm 5^\circ$

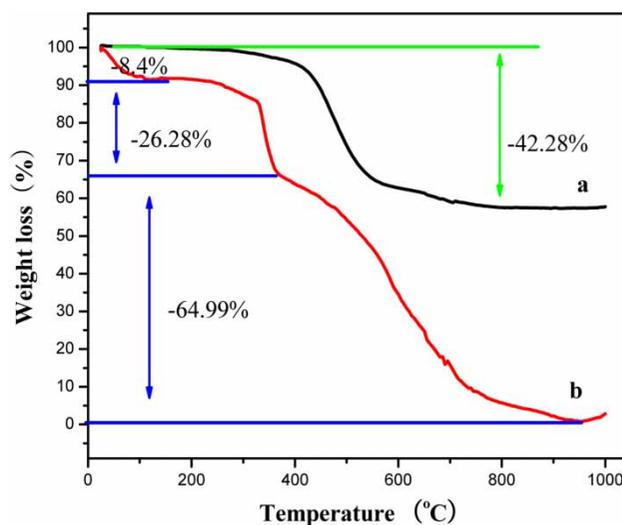


Figure 5 | TGA curves of the polysiloxane/polyurethane (a) and the polyurethane sponge (b).

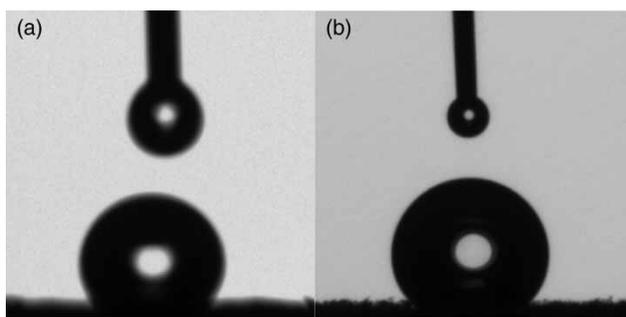
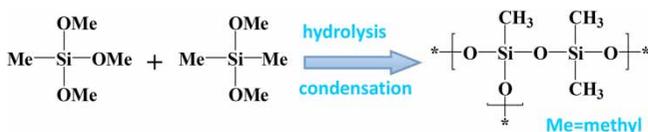


Figure 6 | Contact angle images of the polysiloxane (a) and the polysiloxane/polyurethane sponge (b).

(Figure 6(a)) and $145 \pm 5^\circ$ (Figure 6(b)), respectively. Due to the formation of $-\text{OH}$ group by hydrolysis of MTMS, DMDMOS and dehydration condensation under alkaline conditions, the polysiloxane/polyurethane sponge shows a significant reduction of $-\text{OH}$ group and increase of surface methyl group, thus leading to better hydrophobic performance. The reaction can be shown in the following reaction:



After the dehydration condensation of the $-\text{OH}$ group, the hydrophobic group formed by MTMS, DMDMOS drastically increased. Meanwhile, the sponge etched by acid also has certain roughness, which would increase the hydrophobicity of polysiloxane/polyurethane sponge.

Thermal stability of the polysiloxane/polyurethane sponge CWA

In order to examine the weather resistance of polysiloxane/polyurethane sponge, we treated samples over different temperatures (25, 60, 100, 150 and 200°C) for 24 h and then measured their contact angle. As shown in Figure 7, as the temperature increased, the contact angle of the polysiloxane/polyurethane sponge decreased slightly. Furthermore, the polysiloxane/polyurethane sponge exhibited little carbonization phenomenon before 200°C . Hence, the polysiloxane/polyurethane sponge has a potential application under harsh conditions especially under risk of fire when being used as an absorbent for flammable oils and organic compounds.

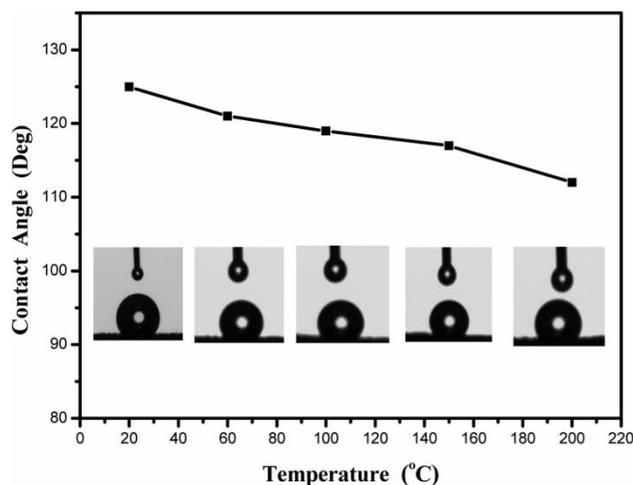


Figure 7 | Contact angle change with the temperature variation.

Oil-water separation capacity

The above characterizations show that the polysiloxane/polyurethane sponge is highly porous and hydrophobic, thus may exhibit excellent absorption capacity for oil and organic liquids. When a certain piece of polysiloxane/polyurethane sponge was placed on the surface of rapeseed oil-water mixtures, the polysiloxane/polyurethane sponge selectively absorbed the oil from the mixtures immediately as the arrows indicated (Figure 8(a)). When a high-density organic solvent (chloroform, dyed with Sudan III) was used, the polysiloxane/polyurethane sponge could also effectively absorb it from water. Seen from Figure 8(b), when a piece of polysiloxane/polyurethane sponge was forced into contact with chloroform, the chloroform was quickly sucked into the polysiloxane/polyurethane sponge within a few seconds due to the porosity, capillary action and oleophilic property. Moreover, the adsorbed chloroform could be collected through a simple mechanical squeezing process. This collection method is more eco-friendly than the reported method of burning off and heat treatment processes.

High porosity, hydrophobicity, oleophilicity, and robust stability guarantee that the polysiloxane/polyurethane sponge is a perfect candidate for the quick removal of various oils and nonpolar organic solvents. We define the Q_e value as the absorbent maximum value. Various types of organic liquids were tested, such as diesel oil, lubricating oil, rapeseed oil, ketones, DMF, THF, hexane and ethanol. The polysiloxane/polyurethane sponge shows high absorption capacity for all above-mentioned organic solvents no matter whether they are heavier or lighter than water

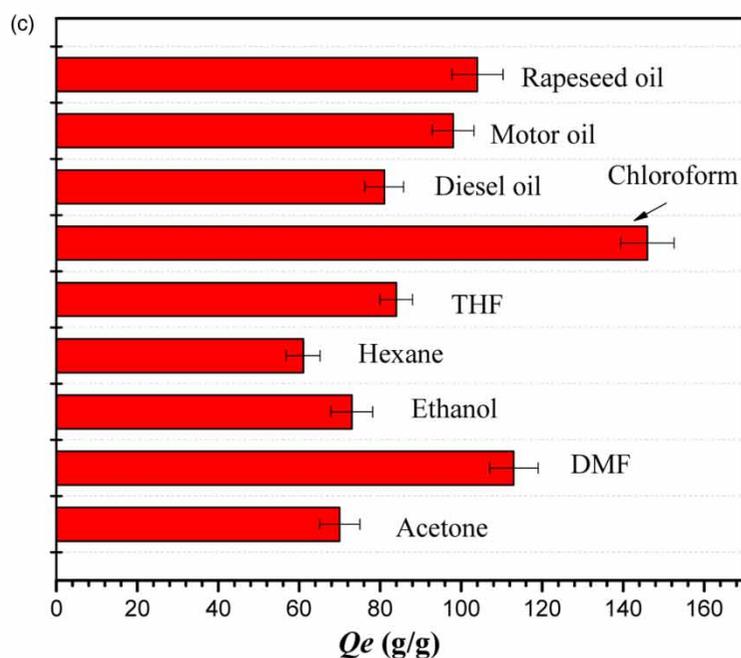
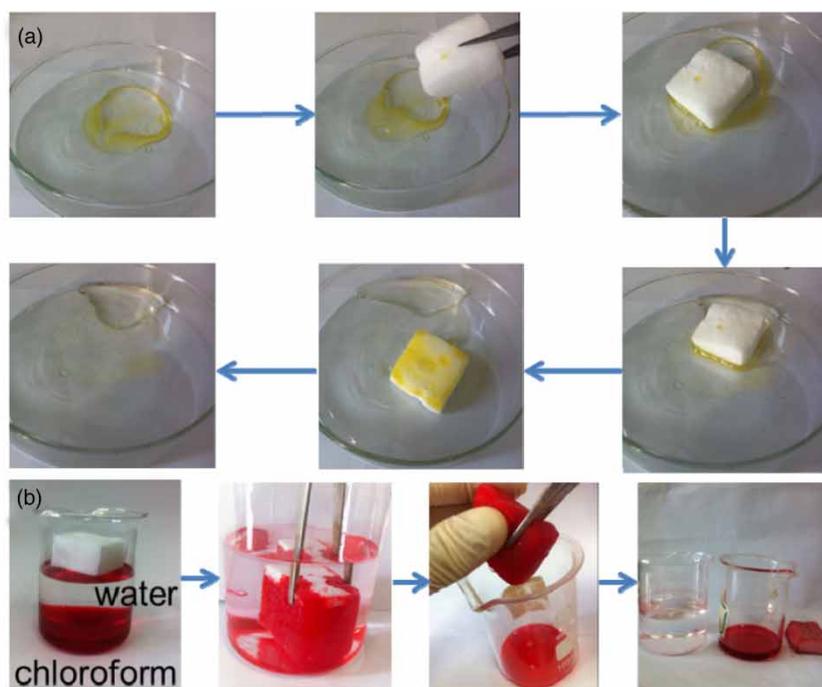


Figure 8 | Selective absorption of rapeseed oil on water by the polysiloxane/polyurethane sponge (a), selective absorption of chloroform (dyed with Sudan III) in water by the polysiloxane/polyurethane (b) and the various organic liquids absorption capability (Q_e) of the polysiloxane/polyurethane (c).

(Figure 8(c)). Specifically, the polysiloxane/polyurethane sponge can uptake these organic liquids 50–150 times its own weight. Table 1 lists the absorption capacity of previously reported adsorption. The polysiloxane/polyurethane sponge shows much higher absorption than the reported sorption materials, such as active carbons

(<1 time) (Lillo-Rodenas *et al.* 2005), wool-based nonwoven (9–15 times) (Radetic *et al.* 2003), polymers (5–25 times) (Li *et al.* 2011), metal nanoparticles foam (10–40 times) (Wang *et al.* 2005) and nanofibrillated cellulose (NFC) (40–100 times) (Zhang *et al.* 2014). Furthermore, the absorption capacity of polysiloxane/polyurethane sponge is also

Table 1 | Comparison of various absorbent material

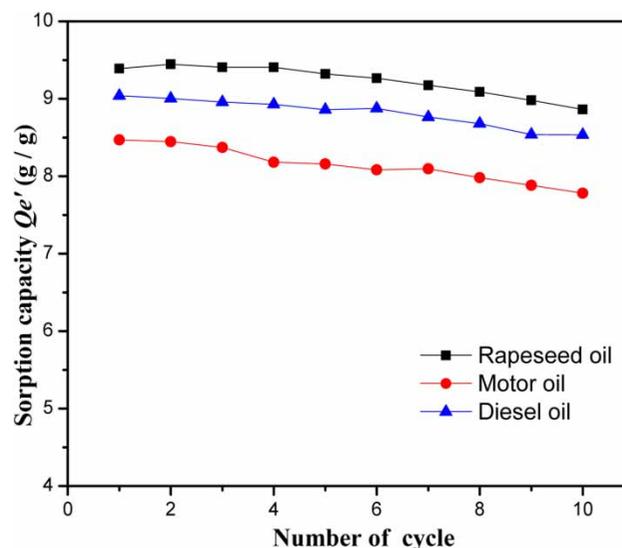
Absorbent	Absorbed substance	Absorption capacity (g/g)	Cost	Ref.
Wool-based nonwoven	Diesel, crude oil, SN 150	9–15	Low	22
Polymers	Oils and organic solvents	5–25	Medium	23
Activated carbons	Benzene, toluene	<1	Low	21
Metal nanoparticles foam	Hexane, chloroform, edible oil, <i>etc.</i>	10–40	High	24
Graphene/CNT foam	Compressor oil, organic solvents	80–140	High	26
Graphene sponge	Oils and organic solvents	60–160	High	28
NFC	Oils and organic solvents	40–100	High	25
CMB aerogel	Oils and organic solvents	56–188	Low	29
Polysiloxane aerogels	Oils and organic solvents	80–150	High	27
TCF aerogel	Oils and organic solvents	50–192	Low	30
Graphene aerogel	Oils and organic solvents	120–250	High	31
CNF aerogels	Oils and organic solvents	106–312	Low	32
Polysiloxane/polyurethane sponge	Oils and organic solvents	50–150	Low	Present work

comparable to that of materials with high absorption capacity, for instance, graphene/CNT foam (80–140 times) (Dong *et al.* 2012), polysiloxane aerogel (80–150 times) (Hayase *et al.* 2013), graphene sponge (60–160 times) (Liu *et al.* 2013), carbon microbelts (CMB) aerogel (56–188 times) (Bi *et al.* 2013a, 2013b) and twisted carbon fiber (TCF) aerogel (50–192 times) (Bi *et al.* 2013a, 2013b). Meanwhile, the absorption capacity of polysiloxane/polyurethane sponge is still lower than other novel materials, for example, graphene aerogel (120–250 times) (Li *et al.* 2014) and cellulose nano-fibers (CNF) aerogels (106–312 times) (Wu *et al.* 2013). Furthermore, we also investigated the pH value (3–11) which influence the absorption of the polysiloxane/polyurethane sponge, the results indicate the pH value has not made significant effect on absorption of the polysiloxane/polyurethane sponge. All in all, the polysiloxane/polyurethane sponge serves as one of the most efficient and promising absorbent materials for the actual removal of environmental organic pollutants.

Stability and recyclability

The recyclability of an absorbent and the recoverability of the absorbed oil and organic solvents are the key requirements in practical oil clean-up applications (Choi *et al.* 2011). Noting that, to test the recyclability of the polysiloxane/polyurethane sponge, we chose three kinds of nonvolatile solvents (diesel oil, rapeseed oil and motor oil) to test the recycling capacity of the polysiloxane/polyurethane sponge. We test the recycle capacity through

continued extrusion/absorption and define the value Q_e' as cycle absorption capacity in our work. As shown in Figure 9, the polysiloxane/polyurethane sponge also could uptake these liquids at 8–10 times its own weight during 10 recycle processes. Meanwhile, no obvious decrease of recycling absorption capacity is found after 10 cycles, indicating a stable absorption and recycling performance of the polysiloxane/polyurethane sponge. The decreased absorption capacity may attribute to the calculated 8–10% of residual organic solvents remaining in the polysiloxane/polyurethane sponge after each cycle. The excellent

**Figure 9** | Recyclability of the polysiloxane/polyurethane.

reusability may be the mechanical durability of the polysiloxane coatings, as well as the flexible performance of polyurethane sponge, making the polysiloxane/polyurethane sponge an attractive candidate for the clean-up of oil spills, recovery and purification.

CONCLUSIONS

We demonstrated a facile approach sol-gel and dip-coating process for fabricating hydrophobic and oleophilic polysiloxane/polyurethane sponge. The obtained polysiloxane/polyurethane sponge exhibited high absorption capacity, excellent elasticity and mechanical durability. Furthermore, the polysiloxane/polyurethane sponge exhibited little carbonization phenomenon before 200 °C and has a potential application in harsh conditions, especially under risk of fire and explosion. Due to its easy fabrication, commercial availability of raw materials, excellent reusability, as well as good mechanical hydrophobic, polysiloxane/polyurethane sponge would be a very promising potential absorbent for the treatment of oil spills and oil/water separation. A facile equipment using polysiloxane/polyurethane sponge might be an effective and potential approach for clean-up of large-area oil spills, which has been under consideration.

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