

# Polymer Chemistry

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



## Polymer Chemistry

## ARTICLE

## Ternary Silicone Sponge with Enhanced Mechanical Properties for Oil-Water Separation†

Lei Mu,<sup>a,b</sup> Sudong Yang,<sup>a</sup> Bin Hao,<sup>a,b</sup> and Peng-Cheng Ma<sup>\*a</sup>Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Silicone sponge has been developed and applied over the years for the separation of oil-water mixture. However, the material was suffered by the poor mechanical performance under the cyclic operations. In this work, we reported the preparation of ternary silicone sponge via a facile sol-gel process using methyltrimethoxysilane (MTMS), dimethyldimethoxysilane (DMDMS) and tetraethylorthosilicate (TEOS) as precursors. Special emphasis was put to illustrate the role of TEOS on governing the morphology, mechanical and thermal properties of the developed silicone sponge. The results showed that the introduction of TEOS into the binary silicone sponge resulted in a higher degree of crosslinking reactions, as verified by the chain-like structures in the sample, much enhanced mechanical properties and thermal stability of material. More importantly, the ternary sponge displayed stable superhydrophobicity, high efficiency for separating various organic liquids from water and fantabulous recyclability under the cyclic operations. The excellent structural and thermal stability of sponge make it ideal candidate be used in separation industry and environment remediation.

## Introduction

With rapid development of modern society, environmental problems arising from oil spills and chemical leakage have become increasingly prominent and happen frequently in the processes of petroleum exploitation and transportation.<sup>1</sup> For a typical example of oil spillage occurred in the Gulf of Mexico in 2010, which caused serious damage to the ecosystems of contaminated oceans and coastlines, and that the damaging effects on local environment were irreversible in a short term.<sup>2</sup> Moreover, a growing amount of similar accidents also occur in daily life and chemical industry. Materials that can effectively adsorb and transfer spilled oils and chemicals from water are in urgently needed, and the development of such materials has attracted much interest both academically and practically.

Three dimensional (3D) porous materials have been applied for oil adsorption in recent years. Compared with other types of separation media, such as inorganic or polymeric membranes,<sup>3-5</sup> metal meshes,<sup>6-10</sup> and magnetic particles,<sup>11-12</sup> the porous materials are considered to be more efficient thanks to their low density, high porosity and specific surface area and controlled hydrophobicity. Various 3D porous materials, including metal-based materials (such as nickel

foams<sup>13,14</sup>), carbon-based materials (such as carbon aerogels,<sup>15-17</sup> graphene sponges,<sup>18-19</sup> carbon nanotubes sponges,<sup>20,21</sup> and graphene-carbon nanotubes sponges<sup>22</sup>), polymer-based materials (such as polyurethane foam,<sup>23-26</sup> polyester material,<sup>27</sup> melamine sponge<sup>28-31</sup>) have been employed for oil-water separation with varying degree of success. However, the shortcomings of these materials have been highlighted that the preparation processes are excessively complicated, resulting in the high cost of materials during the practical applications. While some polymer foams have a low cost, the materials are suffered by the poor oil selectivity and unstable recyclability due to the dissolution/swelling by the organic compounds.<sup>24,28</sup> Therefore, materials that have a facile preparation process, low cost, and high recyclability are desirable for oil-water separation.

As an alternative, silicone-based polymers have been developed in recent years for oil-water separation.<sup>32-35</sup> Compared with traditional organic polymers, silicone sponge/aerogel can be achieved much easier via a sol-gel process, and the materials exhibited excellent resistance against organic liquids thanks to the -Si-O-Si- backbones. The structure and hydrophobicity of material can also be tunable by using silanes with different end groups. In addition, silane industry is a matured one, making the starting material accessible and low cost for the scale-up production of silicone sponge. Kanamori et al<sup>33</sup> reported highly flexible silicone aerogel derived from alkoxy-silane, the material showed superior oil-water separation properties and can be recovered by squeezing adsorbed liquids out of the gel. Zhang et al<sup>34</sup> prepared a magnetic silicone sponge by adding Fe<sub>3</sub>O<sub>4</sub>@silica nanoparticles into the reaction system. The material featured

<sup>a</sup>Laboratory of Environmental Science and Technology, The Xinjiang Technical Institute of Physics and Chemistry, Key Laboratory of Functional Materials and Devices for Special Environments, Chinese Academy of Sciences, Urumqi 830011, China. Tel.: +86-991-6992225; E-mail: mapc@ms.xjbc.ac.cn

<sup>b</sup>University of Chinese Academy of Sciences, Beijing 100049, China

† Electronic Supplementary Information (ESI) available: Movie S1, S2, S3, S4, S5 about the wettability of silicone sponges and the performance of oil-water separation. See DOI: 10.1039/x0xx00000x

fast magnetic responsivity, superhydrophobicity and superoleophilicity, and can selectively adsorb floating oils on water surface. While silicone sponge/foam or similar structures have been successfully prepared using different materials, there are many issues to be addressed to optimize their structural, morphological and functional properties for oil adsorption. Additionally, the collection and reuse of foams with saturated oil adsorption have become a major concern for their practical applications, which required the silicone materials outstanding structural stability and mechanical properties under the cyclic operations.

This paper is a part of a larger project in developing materials with hierarchical structures for environmental remediation. Herein, we reported the preparation of silicone sponge using silane with di-, tri- and tetra-functional groups, aiming at enhancing the mechanical properties of material. The effects of tetra-alkoxy silane on the morphological, mechanical and thermal properties of silicone sponge were studied, and the adsorption behavior of sponge for various organic liquids and oily products was evaluated and compared with those of binary silicone sponge.

## Experimental

### Materials

Silane agents with different functionalities, i.e., methyltrimethoxy-silane (MTMS), dimethyldimethoxy-silane (DMDMS) and tetraethoxy-silane (TEOS) (All from Nanjing ChenGong Silicone Material Co., China), were employed as starting materials to prepare silicone sponge. The reaction was accomplished with assistance of N-hexadecyl trimethyl ammonium bromide (CTAB) as surfactant, urea as catalyst for gelation and acetic acid as accelerator for the hydrolysis of silane (All from Sinopharm Chemical Reagent Co., China). Commercial available oil products (Gasoline, diesel, sunflower oil) and crude oil (Karamay Oilfield, China) were used as probing liquids for the oil-adsorption studies. All other chemicals were commercial products and used as received without further purification.

### Synthesis of silicone sponge

Silicone sponge (SS) was prepared via a one-pot reaction. In a typical experiment, 15 mL of aqueous acetic acid (5 mM) and CTAB (0.80 g) were mixed in a glass beaker and heated at 40 °C to dissolve the surfactant completely. Then 3.2 mL of MTMS, 1.8 mL of DMDMS and TEOS (0-0.6 mL) were added to the above solution and magnetically stirred for 30 min, producing milk-like sol in the beaker. The sol was transferred to a closed plastic box and processed at 80 °C for 9 h for gelation. The final sponge was obtained by washing the gel with water twice and following drying at 40 °C for 24 h. SS with a specific amount of TEOS was named as SS-X, where X indicated the volume of tetra-functional silane used in the starting mixture.

### Characterization

Various techniques were employed to study the properties of materials. The morphology of sponge was observed with a scanning electron microscope (SEM, Supra55VP, Zeiss). Thermal stability of samples was characterized using a thermogravimetric analyzer (TGA, STA 449F3, Netzsch) with a heating rate of 10 °C/min from 25 to 1000 °C in the nitrogen atmosphere. The hydrophobicity of sponge was evaluated by measuring the static contact angle of material against water on a goniometer (XG-CAMA, Shanghai Xuanyichuangxi) at ambient temperature. The compressive properties of material were determined on a universal testing machine (C43-104, MTS) with a constant cross-head speed of 2.0 mm/min.

The adsorption height experiment<sup>3</sup> was conducted by using strip sample (30 mm length, 1 mm width and 1 mm thickness). The sample was contacted with a specific liquid for the adsorption and the time of arriving a pre-set height of sample was recorded. The adsorption capacity of sponge was defined by  $Q$ , a ratio between the weight change of material after liquid adsorption and the initial one. The  $Q$  was calculated using the equation:

$$Q = \frac{(m_0 - m_s)}{m_s} \times 100\% \quad (1)$$

Where  $m_s$  and  $m_0$  were the weight of sponge before and after liquid sorption test. In a typical adsorption experiment, the sponge sample was put into a specific liquid and suspended for 10 minutes to reach the adsorption equilibrium. During the weight measurement, the sample was collected from the liquid using a tweezers and finely led on the edge of liquid container to remove the excessive oil droplet. All adsorption experiments were conducted three times and an average value was reported.

The porosity of sponge ( $\Phi$ ) was obtained by the following relationship<sup>36</sup>:

$$\Phi = \frac{(m_o - m_s)}{V \cdot \rho_l} \times 100\% \quad (2)$$

Where  $V$  is the volume of sponge,  $\rho_l$  is the density of probing liquid (Chloroform, 1.48 g/mL).

## Results and discussion

### Synthesis of silicone sponge

The initial study was focused on the optimization for the preparation of sponge. Fig. 1 shows the macroscopic properties of sponge with varying amount of TEOS. It is clear that the morphology of sponge is significantly affected by the TEOS content in the starting mixture (Fig. 1A). For example, the SS-0.0 exhibited a smooth bottom surface. When a fraction of TEOS (0.2 ml, SS-0.2) was added, the bottom of sponge became rough and simultaneously generated a small amount of sand-like granulars, creating a changed structure. With increasing volume of TEOS from 0.2 to 0.6 mL, the bottom of sample became much rougher and more irregular, and obvious large holes were observed in SS-0.6, leading to the structural



**Fig. 1** Digital images showing the macroscopic properties of sponge (A: Sponge prepared with various amount of TEOS; B: Two monolithic sponges of SS-0.2 with different dimensions; C: A bulk sponge of SS-0.2 was compressed and recovered to the original volume quickly by finger tips).

disintegration of sample. This was possibly due to the formation of rigid silica particles<sup>37,38</sup> in the sponge, acting as impediment for the gelation of MTMS and DMDMS. This assumption was partly confirmed by the fact that when the volume of TEOS was higher than 0.6 mL, no complete monolith of sponge can be obtained.

It should be noted here that the sponge can be prepared successfully for any designed shape and size from the wet gel (Fig. 1B), offering advantages on the processability and versatility of materials for the practical applications. Manual compression to the sample shows that the sponge displays highly structural flexibility, a bulk sample can be compressed to a large degree without breaking apart and can instantaneously recover to its original shape after releasing the applied force (Fig. 1C).

The observed changes on the macroscopic surface of sponge were accompanied with the variation on the physical properties of materials. Table 1 summarizes the density and porosity of different sponges. A slight decrease on the density of sponge was observed with increasing amount of TEOS, whereas the porosity increases by nearly 10% in SS-0.2. The increased porosity of sponge originated from the tetra-functional groups in TEOS, which provide more cross-linking sites for the gelation of di- and tri-functional silanes. The marginal effect on the density of materials suggested that the backbones from TEOS can be effectively incorporated into the sponge structure via the silanization reaction.

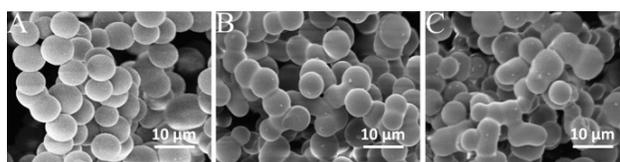
**Table 1** Density and porosity of silicone sponge with different TEOS contents

| Sample | Density (mg/cm <sup>3</sup> ) | Φ (%) |
|--------|-------------------------------|-------|
| SS-0.0 | 108.6±0.8                     | 85.88 |
| SS-0.2 | 104.7±0.9                     | 94.36 |
| SS-0.4 | 106.7±0.4                     | 92.38 |

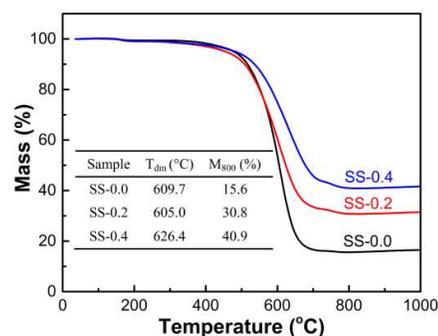
### Morphology and thermal properties of silicone sponge

The morphology of sponge was characterized by SEM, providing information on the micro-structure of materials. The results showed that without TEOS in the sponge, the material consists of nearly spherical particles with weak interactions. The diameter of these particles in SS-0 was approximately 6 μm (Fig. 2A). In sharp contrast, the primary spherical particles were linked together to form chain-like structure in SS-0.2 (Fig. 2B), suggesting a higher degree of crosslinkage in the material. The tendency for such linkage becomes more pronounced with increasing content of TEOS in silane mixture, as obvious chains were observed in SS-0.4 (Fig. 2C). The reason for these observations was that as the amount of TEOS increased, the degree of crosslinkage became dramatically higher, resulting in the coverage of crosslinked polymer on primary particles and a better connectivity among them.

Thermal analysis provides an indirect way to evaluate the crosslinking reactions in polymers. Fig. 3 shows the TGA results of sponge with various amounts of TEOS. All samples show excellent thermal stability below 450 °C. The decomposition temperature at the maximum decomposition rate obtained from derivative TG ( $T_{dm}$ ) varied marginally with 0.2 ml of TEOS in the sample. However, the  $T_{dm}$  increased to 626.4 °C in the SS-0.4, indicating that the thermal decomposition of sample was retarded by the presence of TEOS. Additionally, the residual yields of sponge at 800 °C ( $M_{800}$ ) increased with increasing TEOS content, and SS-0.4 exhibited the highest yield among the samples studied. These results were attributed to the physical barrier effect of networks in the sample arising from the higher degree of crosslinking reactions by the tetra-groups in TEOS and those from MTMS and DMDMS, which impeded the propagation of decomposition reactions in the sponge. The improved thermal stability of ternary sponge has



**Fig. 2** SEM images showing the morphologies of sponge with different amount of TEOS (A: SS-0; B: SS-0.2; C: SS-0.4).



**Fig. 3** Thermal stability of sponge samples.

practical implications in many potential applications at elevated temperatures.

### Mechanical properties of silicone sponge

The mechanical property of polymer is one of the most important parameters when selecting suitable material for application. Fig. 4 summarizes the compressive properties of sponge affected by the TEOS content. The stress-strain curves of SS-0.2 at set strain of 80% exhibit two distinct regions (Fig. 4A): i) A linear-elastic region where the stress increases linearly with increasing strain by up to 60%; and ii) A densification region with dramatically increasing slope when the strain is more than 60%. For the moderate compressive strains of 40% and 60%, the unloading curves can recover completely (Inset in Fig. 4A), indicating an elastic deformation of material. In contrast, the unloading curve of large-degree compression with 80% strain appears a significant hysteresis loop, suggesting the substantial energy dissipation due to the friction between the skeleton of sponge and entrapped air inside.<sup>20,31</sup>

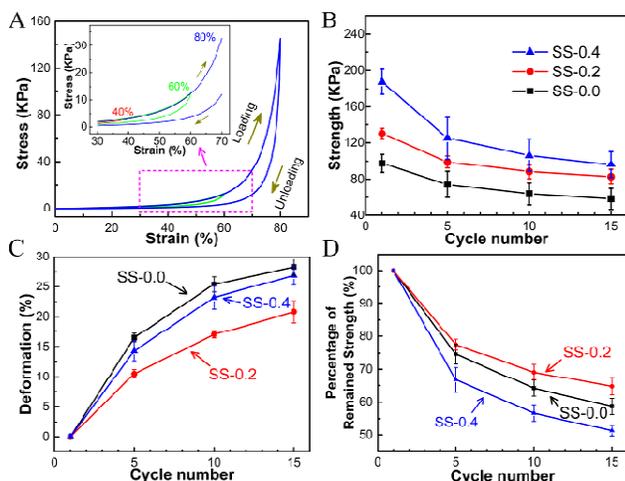
With 0.2 ml of TEOS, the strength of sponge increased by more than 30% from 97.4 to 130.4 KPa, and further increase on TEOS can enhance the strength of sponge (SS-0.4) with 92% increase to 187.4 KPa (Fig. 4B). The significant enhancement on compressive strength may associate with the interconnected particle by TEOS in sponge structure, as observed in Fig. 2 (SEM results). The excellent miscibility of TEOS with MTMS and DMDMS endowed the uniform distribution of tetra-backbones in the sponge, thus facilitated the formation of chain structures in polymers. While TEOS can enhance the strength of sponge, the material exhibited significant degradation on the strength as well as obvious deformation under the cyclic loadings. Fig. 4C compares the

changes on the sample dimension under the cyclic compression for 15 times at 80% strain. Repeated harsh compression produced obvious deformation in the sponge, and this becomes more pronounced in SS-0.0 and SS-0.4. For example, after 15 cyclic loadings, the deformation for SS-0.0, SS-0.2 and SS-0.4 are 28%, 19% and 26%, respectively, and SS-0.2 always exhibited lower deformation under the same experimental conditions than that of its counterparts. The reason for these results are two-folds: i) Proper amount of TEOS functions as a linker to connect spherical particles generated from MTMS and DMDMS, making the whole structure become more rigid and resistance to the mechanical load than the binary sponge. On the macroscale, such crosslinkage makes the material resistant to the plastic deformation along with a lower deformation. ii) Excessive amount of TEOS in the sample leads to an significant increase on the stiffness of sponge due to the formation of rigid silica particles in the sponge,<sup>38</sup> making the material loss its flexibility to maintain its original dimension under the cyclic compression. Therefore, permanent plastic deformation was observed in the sample of SS-0.4. Additionally, the quantitative analysis on the strength reduction of materials shows pretty similar results (Fig. 4D), i.e., TEOS plays an important role in maintaining the strength of sample, and SS-0.2 exhibits the best capability as verified by nearly 68% remained original strength after 15 cyclic loadings in contrast to 56% and 52% for SS-0.0 and SS-0.4, respectively.

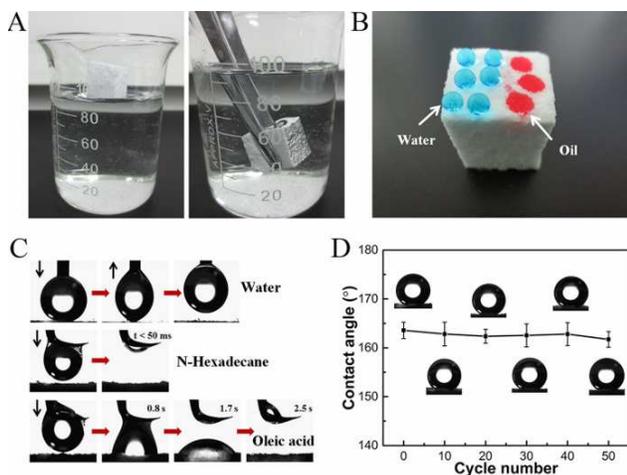
### Wettability of silicone sponge to various liquids

Wettability of material to water and oil is one of the most important considerations when selecting suitable adsorbent for the separation of oil-water mixture. Fig. 5 shows the hydrophobic and adsorption properties of sponge. The ternary sponge (SS-0.2) can float on water because of low density as well as high porosity of greater than 92%. The material exhibits a silver mirror-like surface when immersed into water through an external force (Fig. 5A), suggesting its inherently hydrophobic nature. The result on the measurement of contact angle shows that the sample displays a superhydrophobic surface with water contact angle of  $163.6 \pm 1.7^\circ$ . As a result, water droplets (dyed with Brilliant Blue) present typical spherical shapes on sample surface, whereas droplets of hexadecane (dyed with Oil Red O) are instantly absorbed into the sample in less than one second (Fig. 5B, Movie S1, ESI<sup>†</sup>).

The wetting behavior of sample to liquids was further investigated by employing two organic solvents, hexadecane and oleic acid with the viscosities of 3.34 and 26 cP, to compare qualitatively the adsorption rates of sponge. The continuous wetting progress was presented by a series of consecutive photographs as shown in Fig. 5C. A water droplet contacted with SS-0.2 could easily leave it instead of being absorbed (Movie S2, ESI<sup>†</sup>), indicating the extremely low adhesion and surface energy of sponge sample to water. However, once the spherical hexadecane and oleic acid droplets came into contact with the sample, the droplets were



**Fig. 4** Effect of TEOS content on the mechanical properties of silicone sponge (A: Stress-strain curves of SS-0.2 at set strains of 40%, 60% and 80%; B: Strength of samples under the cyclic loadings; C: Deformation of samples after cyclic loadings; D: Percentage of remained strength of samples after cyclic loadings).



**Fig. 5** Hydrophobic and oleophilic properties of sponge (A: Hydrophobicity of sponge with water; B: Wettability of sponge to water and hexadecane; C: Wetting behavior of liquid droplets on SS-0.2 surface; D: Variation on the contact angles of SS-0.2 against water after cyclic adsorption to hexane).

adsorbed into the porous sponge within 0.05s and 2.5s, respectively (Movie S2, ESI†). Apparently the absorption rates were associated to the viscosity of organic liquids, and a lower viscosity of adsorbate led to a faster adsorption.

Various polymer foams/sponges have been applied for oil-water separation, thanks to their low cost and controllable porosity.<sup>24,25,28,30,31</sup> There is a concern that most polymers can be dissolved/swelled by the organic liquids, resulting in a negative effect on their hydrophobic properties. Fig. 5D presents the changes of contact angles for SS-0.2 after absorption-drying cycles using hexane as a probing organic liquid. Over fifty cycles, the water contact angles of sample always remain at a steady value of above 160°, suggesting the stable superhydrophobic property of ternary silicone sponge.

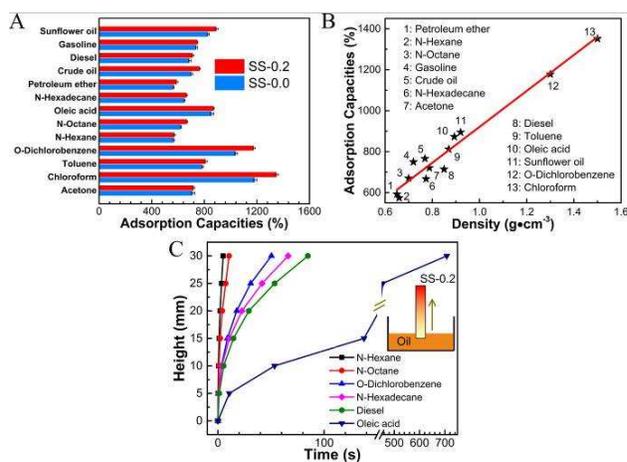
#### Adsorption behavior of silicone sponge to organic liquids

The adsorption capacities of ternary silicone sponge were compared with those of binary one (Fig. 6A). Various organic liquids, including commonly used organic solvents (such as acetone, toluene, chloroform, hexane, etc.), crude oil and commercial oil products (such as gasoline, diesel, sunflower oil, etc.) are considered as the common oily pollutants from both industry and ordinary life. SS-0.2 showed its absorption capacities ranging from 6 to 14 times of its own weight, which were comparable with those reported in references,<sup>33,34</sup> and much higher than that of the polydimethylsiloxane sponge (3–10 times).<sup>39</sup> The adsorption capacity of material was primarily ascribable to the physical absorption of organic liquids and depended on the unoccupied volume in the porous sponge. Obviously, SS-0.2 exhibited a higher absorption capacity than that of SS-0.0, and this difference became more pronounced when the probing liquids with higher densities, such as dichlorobenzene ( $\rho=1.30$  g/mL), chloroform ( $\rho=1.50$  g/mL), were employed. The reason for this is mainly due to the

increased porosity and hydrophobicity of SS-0.2, which provide more space for the retention of liquids.

An interesting observation is that when plotting the absorption capacity of SS-0.2 as a function of liquid density, the obtained result is approximately linear with reasonable scattering (Fig. 6B). It is understandable that for a given sample, the porosity is a fixed one, thus providing certain space for the adsorbed liquids. In other words, the polymer structure of SS-0.2 is independent to the type of liquids, suggesting the excellent capability of materials to resist the dissolution and swelling by organic liquids.

Fig. 6C shows the diffusion height of liquid in a sponge sample as a function of time. When putting one end of strip sponge into the liquid, a spontaneous diffusion process occurs in the sample due to the capillary effect. The capillary force is related to the pore size and framework structure of sample, the characters of liquids and wetting properties of interface between the oil and sponge.<sup>21</sup> Accordingly, the capillary pressure is different for various organic liquids, causing different diffusion speeds and adsorption behavior. Hexane diffused faster than all other organic liquids with an adsorption time of 4.9 s to reach the height of 30 mm, whereas the oleic acid needed longer time of 707.4 s to get the same height. On the basis of this feature, the sponge could be used for the separation of miscible organic liquids, which can be potentially employed as stationary phase for liquid chromatography.



**Fig. 6** Adsorption behaviour of sponge to oily compounds (A: Absorption capacities of sponge for various organic liquids. B: Relationship between the densities of organic liquids and adsorption capacity of SS-0.2; C: Correlation between the diffusion height and time of sample with different organic liquids).

#### Capability of silicone sponge for oil-water separation

The feasibility of employing silicone sponge for oil-water separation was further investigated. Hexadecane, crude oil and chloroform, chemicals which were either floating on water surface or under the water, were used as typical model pollutants. Fig. 7 shows the snapshots of collecting these

liquids from water using SS-0.2 through a facile absorption-squeezing process. When the sponge was dropped into the container, the oily liquids were immediately adsorbed and saturation was observed within a few seconds (Movie S3 and Movie S4, ESI†). The rapid adsorption was derived from the synergistic effects of sponge sample arising from its hydrophobic-oleophilic nature, high porosity and low density. The adsorbed hexadecane and crude oil in the sample could be easily removed and collected by mechanical squeezing, and no obvious damage to the sample was found during this recycling process (Fig. 7A and B). Moreover, chloroform sunk in the bottom of water due to the higher density than water was also adsorbed and recycled efficiently using the silicone sponge (Fig. 7C). It should be noted here that a small amount of organic liquid was remained in the sample, resulting in the colour change of sponge from white to red and black after adsorbing hexadecane, chloroform and crude oil, respectively.



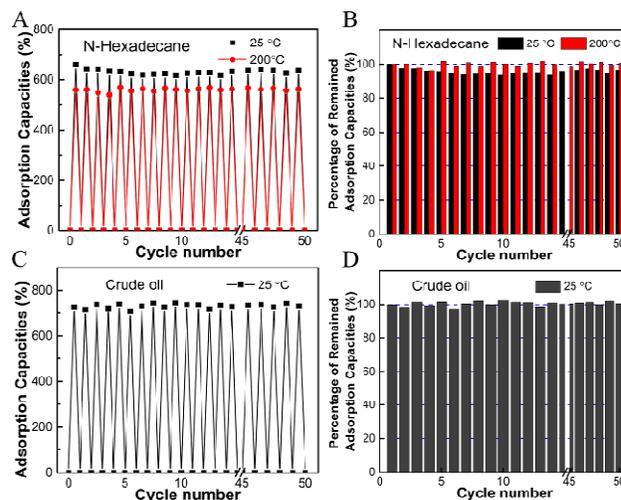
**Fig. 7** Snapshots showing the collection of oily liquids on/in water using SS-0.2 (A: Hexadecane dyed by Oil Red; B: Crude oil; C: Chloroform dyed by Oil Red).

#### Cyclic adsorption performance of silicone sponge

For a versatile adsorbent, not only should it effectively separate organic liquids from water, but also exhibit fantabulous recyclability for practical applications. Fig. 8 shows the adsorption performance of SS-0.2 under the cyclic operations. It is clear that the adsorption capacity of SS-0.2 remained essentially identical under the cyclic runs for both hexadecane (Fig. 8A and B) and crude oil (Fig. 8C and D) at room temperature. A bottleneck of polymer foams/sponges for oil-water separation is that the materials can be dissolved/swelled by the organic liquids, resulting in a loss on maintaining their original adsorption capacities under the cyclic applications.<sup>24,28</sup> However, this was not the case in our sample, for example, the material remained more than 95% and 98% of its original adsorption capacity for hexadecane and crude oil under the cyclic operation for 50 runs, respectively.

The excellent thermal stability of sponge endows the material to be used under the high temperature. Fig. 8A compares the weight gain of SS-0.2 during the absorption-squeezing processes for 50 cycles in room temperature and 200 °C. Nearly 10% decrease on the adsorption capacity of sample was observed between the one at room temperature and that in high temperature, mainly due to the density change of adsorbate (the density of hexadecane at 25 and 200 °C are 0.77, 0.64 g/mL, respectively). The adsorption capacity

had no apparent deterioration after 50 cycles at 200 °C, demonstrating the excellent recyclability of material at high temperature (Movie S5, ESI†). The practical applications of silicone sponge can be further extended for the separation of oil fluid collected using the enhanced oil recovery technique, where the temperature of oil-water mixture can be as high as 80 °C. Further evaluation on the reliability of material will be the subject for our forthcoming reports.



**Fig. 8** Cyclic performance of sponge for the adsorption of hexadecane (A and B) and crude oil (C and D).

#### Conclusions

In summary, ternary silicone sponge were obtained from silane mixture consisting of MTMS, DMDMS and TEOS through a facile one-pot reaction. The sponge exhibited low density, high porosity and controllable crosslinking structures by changing the amount of TEOS. A large number of methyl groups on the skeleton of sponge make the material superhydrophobic with water contact angle greater than 160°. Compared with its binary counterpart, the ternary silicone sponge showed enhanced mechanical properties and stable adsorption capacities for various organic liquids ranging from 6 to 14 times of weight gain, as well as excellent recyclability under the cyclic operations. The outstanding thermal stability of sponge extended the application of material for oil-water separation under the conditions of high temperature.

#### Acknowledgements

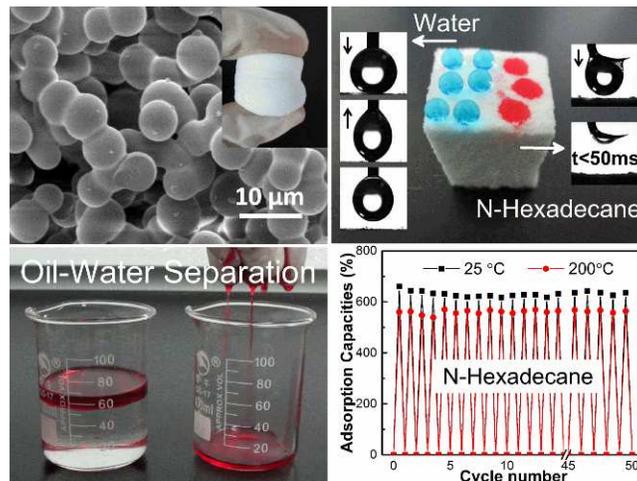
This project was supported by the Research Fund for Distinguished Young Scientist in Xinjiang Uyghur Autonomous Region (Project No. 2013711005), the National 1000-Talent Program (Recruitment Program of Global Expert, In Chinese: Qian-Ren-Ji-Hua), as well as the Technology Foundation for Selected Overseas Chinese sponsored by the Ministry of Human Resources and Social Security of China.

## Notes and references

- 1 M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Mariñas and A. M. Mayes, *Nature*, 2008, **452**, 301.
- 2 R. M. Atlas and T. C. Hazen, *Environ. Sci. Technol.*, 2011, **45**, 6709.
- 3 J. K. Yuan, X. G. Liu, O. Akbulut, J. Q. Hu, S. L. Suib, J. Kong and F. Stellacci, *Nat. Nanotechnol.*, 2008, **3**, 332.
- 4 Y. W. Shang, Y. Si, A. Raza, L. P. Yang, X. Mao, B. Ding and J. Y. Yu, *Nanoscale*, 2012, **4**, 7847.
- 5 X. Li, M. Wang, C. Wang, C. Cheng and X. F. Wang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 15272.
- 6 L. Feng, Z. Y. Zhang, Z. H. Mai, Y. M. Ma, B. Q. Liu, L. Jiang and D. B. Zhu, *Angew. Chem.*, 2004, **116**, 2046.
- 7 C.-F. Wang, F.-S. Tzeng, H.-G. Chen and C.-J. Chang, *Langmuir*, 2012, **28**, 10015.
- 8 F. Zhang, W. B. Zhang, Z. Shi, D. Wang, J. Jin and L. Jiang, *Adv. Mater.*, 2013, **25**, 4192.
- 9 C. R. Crick, J. A. Gibbins and I. P. Parkin, *J. Mater. Chem. A*, 2013, **1**, 5943.
- 10 J. W. Zeng and Z. G. Guo, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2014, **444**, 283.
- 11 L. Zhang, J. J. Wu, Y. X. Wang, Y. H. Long, N. Zhao and J. Xu, *J. Am. Chem. Soc.*, 2012, **134**, 9879.
- 12 L. P. Xu, X. W. Wu, J. X. Meng, J. T. Peng, Y. Q. Wen, X. J. Zhang and S. T. Wang, *Chem. Commun.*, 2013, **49**, 8752.
- 13 M. J. Cheng, Y. F. Gao, X. P. Guo, Z. Y. Shi, J. F. Chen and F. Shi, *Langmuir*, 2011, **27**, 7371.
- 14 R. Gao, Q. Liu, J. Wang, J. Y. Liu, W. L. Yang, Z. Gao and L. H. Liu, *Applied Surface Science*, 2014, **289**, 417.
- 15 N. Xiao, Y. Zhou, Z. Ling and J. S. Qiu, *Carbon*, 2013, **59**, 530.
- 16 N. Chen and Q. M. Pan, *ACS Nano*, 2013, **7**, 6875.
- 17 S. D. Yang, L. Chen, L. Mu, B. Hao and P. C. Ma, *RSC Adv.*, 2015, **5**, 38470.
- 18 H. C. Bi, X. Xie, K. B. Yin, Y. L. Zhou, S. Wan, L. B. He, F. Xu, F. Banhart, L. T. Sun and R. S. Ruoff, *Adv. Funct. Mater.*, 2012, **22**, 4421.
- 19 H. Hu, Z. B. Zhao, W. B. Wan, Y. Gogotsi and J. S. Qiu, *ACS Appl. Mater. Interfaces*, 2014, **6**, 3242.
- 20 X. C. Gui, J. Q. Wei, K. L. Wang, A. Y. Cao, H. W. Zhu, Y. Jia, Q. K. Shu and D. H. Wu, *Adv. Mater.*, 2010, **22**, 617.
- 21 X. C. Gui, Z. P. Zeng, Z. Q. Lin, Q. M. Gan, R. Xiang, Y. Zhu, A. Y. Cao and Z. K. Tang, *ACS Appl. Mater. Interfaces*, 2013, **5**, 5845.
- 22 H. Hu, Z. B. Zhao, Y. Gogotsi and J. S. Qiu, *Environ. Sci. Technol. Lett.*, 2014, **1**, 214.
- 23 P. Calcagnile, D. Fragouli, I. S. Bayer, G. C. Anyfantis, L. Martiradonna, P. D. Cozzoli, R. Cingolani and A. Athanassiou, *ACS Nano*, 2012, **6**, 5413.
- 24 Q. Zhu, Y. Chu, Z. K. Wang, N. Chen, L. Lin, F. T. Liu and Q. M. Pan, *J. Mater. Chem. A*, 2013, **1**, 5386.
- 25 C.-F. Wang and S.-J. Lin, *ACS Appl. Mater. Interfaces*, 2013, **5**, 8861.
- 26 G. Wang, Z. X. Zeng, X. D. Wu, T. H. Ren, J. Han and Q. J. Xue, *Polym. Chem.*, 2014, **5**, 2382.
- 27 L. Wu, J. P. Zhang, B. C. Li and A. Q. Wang, *Polym. Chem.*, 2014, **5**, 2382.
- 28 D. D. Nguyen, N.-H. Tai, S.-B. Lee and W.-S. Kuo, *Energy Environ. Sci.*, 2012, **5**, 7908.
- 29 C. P. Ruan, K. L. Ai, X. B. Li and L. H. Lu, *Angew. Chem., Int. Ed.*, 2014, **53**, 5556.
- 30 J. Ge, Y. D. Ye, H. B. Yao, X. Zhu, X. Wang, L. Wu, J. L. Wang, H. Ding, N. Yong, L. H. He and S. H. Yu, *Angew. Chem., Int. Ed.*, 2014, **53**, 3612.
- 31 Y. Yang, Y. H. Deng, Z. Tong and C. Y. Wang, *J. Mater. Chem. A*, 2014, **2**, 9994.
- 32 G. Hayase, K. Kanamori, M. Fukuchi, H. Kaji and K. Nakanishi, *Angew. Chem., Int. Ed.*, 2013, **52**, 1986.
- 33 G. Hayase, K. Kanamori, G. Hasegawa, A. Maeno, H. Kaji and K. Nakanishi, *Angew. Chem., Int. Ed.*, 2013, **52**, 10788.
- 34 L. X. Li, B. C. Li, L. Wu, X. Zhao and J. P. Zhang, *Chem. Commun.*, 2014, **50**, 7831.
- 35 Z. Wang, Z. Dai, J. J. Wu, N. Zhao and J. Xu, *Adv. Mater.*, 2013, **25**, 4494.
- 36 F. A. Shutov, *Adv. Polym. Sci.*, 1983, **51**, 155.
- 37 A. C. Pierre and A. Rigacci, *Aerogels Handbook*, Chapter 2; Springer: New York, 2011.
- 38 A. V. Rao and S. D. Bhagat, *Solid State Sciences*, 2004, **6**, 945.
- 39 S.-J. Choi, T.-H. Kwon, H. Im, D.-I. Moon, D. J. Baek, M.-L. Seol, J. P. Duarte and Y.-K. Choi, *ACS Appl. Mater. Interfaces*, 2011, **3**, 4552.

40

## Graphic abstract



Sponge-like silicone polymer was obtained from silanes with di-, tri- and tetra-functional groups. The material exhibited enhanced mechanical properties and stable adsorption capacities for various organic, as well as excellent recyclability under the cyclic operations for oil-water separation.