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## COMMUNICATION

# Magnetic, superhydrophobic and durable silicone sponges and their applications in removal of organic pollutants from water

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**Porous silicone sponges are fabricated by polymerization of organosilanes in the presence of Fe<sub>3</sub>O<sub>4</sub>@silica nanoparticles. The sponges feature fast magnetic responsiveness, superhydrophobicity/superoleophilicity, high compressibility and stability. The sponges can selectively absorb floating oils on water surface, heavy oils under water and even emulsified oils.**

3D porous materials have drawn great interests in many fields, *e.g.*, electrodes and absorbents, because of their low density, high porosity and specific surface area.<sup>1</sup> Porous materials in the forms of aerogel, sponge and foam have been prepared using carbonaceous materials, biomass and synthetic polymers, etc.<sup>2, 3</sup> In spite of excellent properties, the preparation often has problems such as harmful and expensive precursors, complicated and lengthy processes, and complex devices, which hamper their practical applications. For example, the expensive templates must be removed and the samples should be carefully dried via special methods, *e.g.*, freeze drying and supercritical CO<sub>2</sub> drying, to retain the porous structure. In addition, many of the porous materials are fragile owing to the high porosity. Moreover, multifunctional porous materials are rare and should be developed to meet diverse practical applications. All these push us to explore a facile approach to fabricate multifunctional and robust porous materials.

With the rapid development of the marine transportation and the expansion of offshore oil fields, oily wastewater pollution becomes serious all over the world, which has turned into environmental and social concerns. Thus, there is a high demand for excellent materials for oil/water separation.<sup>4</sup> The wettability of materials has great influences on their performance in oil/water separation. It is promising to design novel oil absorbing materials with high selectivity by regulating the wettability. Recently, superhydrophobic/superoleophilic materials, characterized by high water contact angle ( $CA_{\text{water}} > 150^\circ$ ) and ultralow  $CA_{\text{oil}}$ , have drawn much attention for cleaning oily wastewater.<sup>5</sup> For example, Li et al. prepared superhydrophobic sponges with high absorption capacity for various organics using conjugated microporous polymers.<sup>3</sup> The

pioneering work is encouraging but still has some problems, *e.g.*, high cost, poor stability and difficulties in recycling.

Here we report a simple approach for fabricating magnetic, superhydrophobic and durable silicone sponges. The structure and property of silicones are determined by many factors including reactive groups of organosilane, alkyl group structure and reaction conditions.<sup>6, 7</sup> Thus, there are many chances to tailor their properties. We have prepared superhydrophobic and superoleophobic silicone nanofilaments using methyltrichlorosilane.<sup>8, 9</sup> We also have recently fabricated novel silicone nanoparticles which endow various textiles with durable superhydrophobicity.<sup>10</sup> The silicone sponges in this study are prepared by polymerization of organosilanes in the presence of silica coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@silica NPs). The sponges feature fast magnetic responsiveness, superhydrophobicity/superoleophilicity, high compressibility, temperature stability and oil/water separation efficiency.

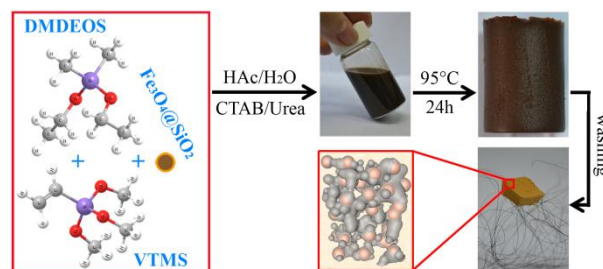
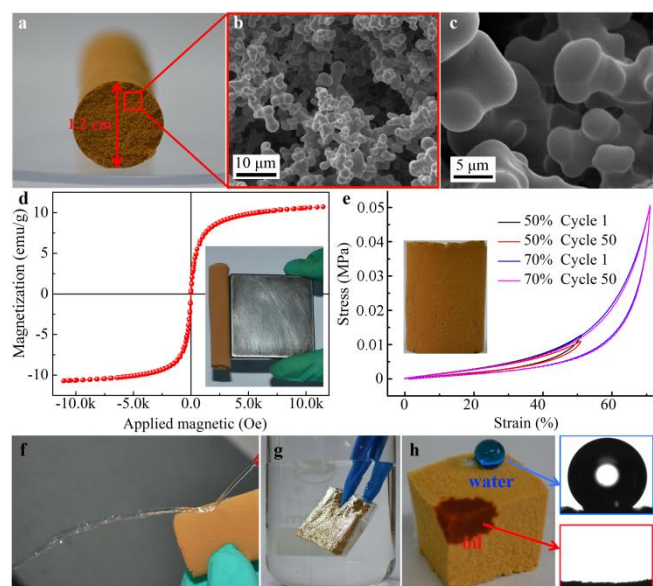


Fig. 1. Schematic illustration for preparing the silicone sponges.

The sponges are fabricated by hydrolysis and polymerization of dimethyldiethoxysilane (DMDEOS) and vinyltrimethoxysilane (VTMS) catalyzed with HAc in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> NPs by using *n*-hexadecyltrimethyl ammonium bromide (CTAB) and urea as the pore-forming agents (Fig. 1). Firstly, CTAB and urea were dissolved in HAc aqueous solution in a vial, and then DMDEOS, VTMS and the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> NPs were sequentially added. The sealed vial was shaken at 150 rpm for 1 h at room temperature for the hydrolysis of organosilanes, and then left to stand in an oven at

95 °C for 24 h to accomplish their polymerization. The homogeneous brown aqueous suspension finally transformed into a brown hydrogel. After repeated washing with ethanol by squeezing with hand to remove CTAB, residual urea and other impurities, the light porous (0.12 g/cm<sup>3</sup>, porosity > 92%) and flexible sponge which could even stand stably on hairs was obtained.

The Fe<sub>3</sub>O<sub>4</sub> NPs must be modified with a SiO<sub>2</sub> shell in advance in order to make them compatible with the organosilanes and to obtain the uniform sponge, or else phase separation is inevitable (Fig. S1). A silica shell with a thickness of ~16 nm was formed on the surface of the Fe<sub>3</sub>O<sub>4</sub> NPs after modified with tetraethoxysilane, which was further confirmed by the presence of C and Si elements in the EDX spectrum (Fig. S2). The CTAB concentration, urea concentration and molar ratio of VTMS to DMDEOS have great influences on formation of the sponge (Table S1). The product is composed of spherical microparticles and is fragile when the CTAB concentration is less than 25 mg/mL (Fig. S3a). The sponges are composed of interconnected irregular microparticles with increasing the CTAB concentration to 25 and 50 mg/mL (Fig. 2b and S3b). The sponge can only be formed at a urea concentration of not more than 0.63 g/mL, or else the product is pasty and partly soluble. Only fragmentary product is formed at  $n_{VTMS}/n_{DMDEOS} = 3:7$ . Sponges with excellent porous structure are formed at  $n_{VTMS}/n_{DMDEOS} = 6:4$ .



**Fig. 2.** (a) Digital and (b, c) SEM images of the sponge, (d) magnetic curve and the sponge held by a magnet, (e) stress-strain curves (2.2 cm in diameter, successive 50% strain for 50 cycles and 70% strain for 50 cycles) and the sponge after tests, (f) a jet of water bouncing off, (g) immersed in water, (h) drops of water (dyed with methylene blue) and oil (dyed with Sudan Red) on the cross section.

The sponge can be fabricated in any shape, *e.g.*, cylinder, stick and sheet, using different containers (Fig. 2a and S4). The sponge is composed of interconnected irregular microparticles with spaces among them (Fig. 2b, c). The Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> NPs distribute uniformly in the sponge and no exposed ones were observed via SEM. This means the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> NPs are further covered with the silicone microparticles during the polymerization of DMDEOS and VTMS.

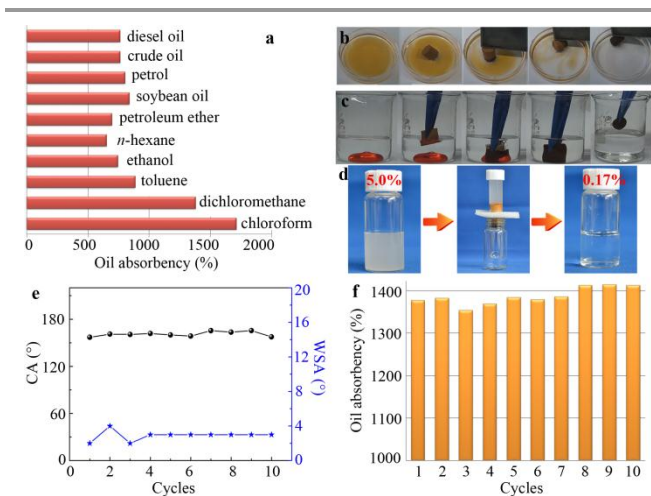
In the FTIR spectrum of the sponge (Fig. S5a), the characteristic bands of polymerized DMDEOS and VTMS were observed.<sup>6, 11</sup> The

absorption bands of Fe<sub>3</sub>O<sub>4</sub> NPs at 3413, 2924, 1044 and 987 cm<sup>-1</sup> overlap with those of polymerized DMDEOS and VTMS. In the XPS spectrum of the sponge (Fig. S5b), the peaks of Si2p (103 eV), C1s (285 eV) and O1s (532 eV) were detected, whereas the Fe peak of Fe<sub>3</sub>O<sub>4</sub> NPs was undetectable. As is well known, the XPS spectrum only gives chemical composition of a surface with a detecting depth of less than 10 nm. So, it is reasonable that Fe cannot be detected by XPS since the Fe<sub>3</sub>O<sub>4</sub> NPs are covered with the silica shell and polymerized organosilanes. The EDX analysis with a greater detecting depth confirmed the existence of the Fe<sub>3</sub>O<sub>4</sub> NPs in the sponge (Table S2). The integrated XPS peak intensities show an atomic ratio of 1:2.1 for Si/C on the surface of the sponge, which is in good agreement with the theoretical ratio of 1:2.

The sponge shows standard paramagnetic characteristic curve with no hysteresis after removal of the magnetic field. The saturation magnetization of the Fe<sub>3</sub>O<sub>4</sub> NPs is 52.9 emu/g at 300K. The sponge with a saturation magnetization of 10.0 emu/g can be neatly manipulated using a magnet (Fig. 2d). The sponge is highly compressible according to the results of uniaxial compression tests (Fig. S6). The stress of the sponge is about 0.013 MPa at 50% strain and 0.05 MPa at 70% strain (Fig. 2e). Compared with the first cycle, no obvious change in the stress-strain curves was detected after 100 cycles of cyclic compression tests. In addition, no fracture or collapse of the sponge was observed during the tests. The deformed sponge can completely recover to their original shape after the tests (Fig. 2e).

The sponge is superhydrophobic ( $CA_{water} \approx 161.5^\circ$ ) because the vinyl and methyl groups tend to appear on the surface of the silicone microparticles to decrease the surface energy.<sup>9</sup> Water drops on both the surface and the cross section are spherical in shape (Fig. 2h), indicating again uniformity of the sponge. Water drops could easily roll down the slightly tilted sponge (water shedding angle (WSA) = 2 ~ 3°). A jet of water from a pipette or a tap could bounce off the sponge without leaving a trace (Fig. 2f). A 7 μL water droplet released from a height of 10 mm could bounce 4 times on the sponge (Movie S1, part 1). In addition, the sponge tends to float on the surface of water. Once immersed in water by an external force, the sponge is surrounded by an air cushion, exhibiting a silver mirror-like surface (Fig. 2g). The sponge could float immediately on water surface and remains completely dry after releasing the external force. Moreover, the sponge exhibits superior repellency towards corrosive liquids such as 1.0 M HCl and 1.0 M NaOH aqueous solutions besides water (Fig. S7). The sponge is also superoleophilic ( $CA_{oil} = 0^\circ$ ; Fig. 2h). Oils could wet and be absorbed by the sponge quickly (~ 6 ms, Movie S1, part 2).

The sponge shows excellent stability in a wide range of temperature (Fig. S8). No weight loss was detected at temperature below 300 °C according to the TGA curve of the sponge. The 16.71% weight loss in 300 ~ 800 °C is owing to the decomposition of the methyl and vinyl groups. The magnetic property, flexibility and superhydrophobicity of the sponge remain unchanged after kept at -80 °C or 200 °C for 24 h. When ignited by an alcohol lamp, the silicone sponge shows fire retardant property and the carbonaceous sponge still keeps its skeleton intact, whereas the superhydrophobic polyurethane (PU) sponge that we fabricated burns down quickly (Movie S2). No other porous materials with such high temperature stability besides the excellent magnetic, mechanical and superhydrophobic properties have been reported.



**Fig. 3.** (a) Absorbency of the sponge for organics. Removal of (b) *n*-hexane (dyed with Sudan Red) on water surface controlled by a magnet, (c) dichloromethane (dyed with Sudan Red) under water and (d) emulsified oil using the sponge. Variation of (e)  $CA_{\text{water}}$  and WSA, and (f) absorbency for dichloromethane with absorption cycles.

The applications of the sponge in removal of organic pollutants from water were studied. The sponge absorbs organics very quickly owing to its porous structure and superoleophilic property. The equilibrium absorbency can be achieved within a few seconds regardless of density and viscosity of the organics. The absorbency of the sponge is in the range of 700% to 1700% depending on density of the organics (Fig. 3a). The absorbed organics are stored in the abundant micropores of the sponge and can be completely squeezed out by hand. No dripping of the absorbed organics was observed in the handling process indicating firm absorption.

The sponge can be used to absorb floating oils on water surface, heavy oils under water and even emulsified oils in water (Fig. 3b-d and Movie S3). Controlled by a magnet, the sponge can be driven to the water zone with floating oils on its surface, and then rapidly absorb the oils (Fig. 3b). In addition, the sponge can firmly absorb heavy oils under water and take out of water without leaving a trace (Fig. 3c). The sponge remains completely dry in water before contacting oil owing to the existence of the air cushion (Fig. 3c). Once contacting the oil under water, the heterogeneous sponge/water interface with entrapped air automatically converts to the homogeneous sponge/oil interface owing to the low surface tension of oil. Moreover, the sponge can absorb emulsified oil in water (Fig. 3d). The sponge is wetted when the oil-in-water emulsion (5% v/v) is poured onto the surface of the sponge fixed in a glass tube. The oil is absorbed by the sponge, while water gradually permeates through the sponge and drops into the glass vessel below. No external force is employed during the separation process, only their own weight. The concentration of oil in water determined using a UV-Vis spectrophotometer at 269 nm (Fig. S9) decreases from 5% to below 0.17% after separation, indicating that more than 96.6% of oil in the emulsion is eliminated.

As far as superhydrophobicity and oil absorbency are concerned, the sponge is also reusable besides the excellent performance in removal of organic pollutants from water. The sponge is the same as the new one after simply squeezed out the absorbed oil, washed with ethanol and dried in an oven. The  $CA_{\text{water}}$  is above  $160^\circ$ , the WSA is  $2 \sim 4^\circ$  and water drops could easily roll off the samples in ten

absorption-desorption cycles, indicating excellent superhydrophobicity (Fig. 3e). The oil absorbency of the sponge is very stable and remains in the range of 1300% ~ 1400% for dichloromethane after repeated oil absorption (Fig. 3f). In addition, long time immersion in various organics has no influence on the weight, superhydrophobicity and shape of the silicone sponge, whereas the superhydrophobic PU sponge swells in dichloromethane (Table S3 and Fig. S10). Moreover, the silicone sponge retains its compressibility after ten absorption-desorption cycles (Fig. S11).

In summary, we have reported synthesis of porous silicone sponges. The sponges show fast magnetic responsivity, high compressibility, flexibility, superhydrophobicity/superoleophilicity, temperature stability and efficiency for removal of organic pollutants from water. The sponge can be used to, driven by a magnet, selectively absorb a large amount of floating oils on water surface, heavy oils under water and even emulsified oils in water, and is reusable. We can envisage that the silicone sponges are very promising materials in efficiently treating oily wastewater under various conditions owing to simplicity of the method and excellent properties of the sponge.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: [Materials, experimental details, oil absorbency, digital images, SEM images, EDX analysis, TGA analysis and videos]. See DOI: 10.1039/b000000x/

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