Supporting Information

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

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Experimental section

Materials

Vinyltrimethoxysilane (VTMS), dimethyldiethoxysilane (DMDEOS) and tetraethoxysilane (TEOS) were purchased from Gelest. Urea, *n*-hexadecyltrimethyl ammonium bromide (CTAB), HAc, anhydrous ethanol, toluene, *n*-hexane, $FeSO_4 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$, sodium citrate, petroleum ether, chloroform, ammonia (25wt.%), Sudan Red and methylene blue were purchased from China National Medicines Co., Ltd. Commercial petrol, diesel and crude oil were purchased from Sinopec, Lanzhou, China. All chemicals were used as received without further purification. Distilled water was used for all the experiments and tests.

Preparation of Fe_3O_4@silica NPs

The magnetic Fe_3O_4 NPs were prepared by co-precipitation of $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ using ammonia as the catalyst in the presence of sodium citrate under stirring.[1] Briefly, 50 mL of 25% ammonia solution was added into the aqueous solution containing 18 g of $FeSO_4 \cdot 7H_2O$ and 26 g of $FeCl_3 \cdot 6H_2O$ in the N_2 atmosphere under vigorous mechanical stirring. Then, 7.5 g of sodium citrate was added to the mixture and stirred for 1 h at 70 ℃. The mixture was repeatedly separated by a magnet and washed with distilled water and ethanol to neutral.

The Fe_3O_4 NPs were further modified with TEOS according to the following procedure. Firstly, 10 mL of the aforementioned Fe_3O_4 NPs dispersion was fully dispersed in 30 mL of ethanol under ultrasonication. Then, 30 mL of ethanol, 60 mL of ammonia saturated ethanol and 5.28 g of water were added into the dispersion with stirring. Finally, 2.0 mL of TEOS in 30 mL of ethanol was added in 20 min under continuous mechanical stirring and the reaction was allowed to proceed for 9 h at room temperature. The product was repeatedly separated by a magnet and washed with distilled water to neutral.

Preparation magnetic silicone sponges

The magnetic silicone sponges were prepared via HAc-catalyzed hydrolysis and polymerization of DMDEOS and VTMS in the presence of the Fe_3O_4@silica NPs, urea and CTAB. Typically, 0.4 g of CTAB and 2.5 g of urea were dissolved in an HAc aqueous solution in a glass vessel, and then 17.5 mmol of organosilanes (VTMS and DMDEOS) with proper ratio and 2 mL of aqueous suspension of the Fe_3O_4@silica NPs were sequentially added. The mixture was vibrated at 150 rpm for 1 h at room temperature in a thermostatic incubator shaker for the HAc-catalyzed hydrolysis of the precursors. Then, the mixture was kept in an oven at 95 ℃ for 24 h without any shake to promote formation of the hydrogel with three-dimensional network. The obtained soft silicone hydrogel was washed with ethanol by squeezing with hand for several times to remove the residual urea, CTAB and other chemicals, and then dried in an oven at 60 ℃.

Measurement of water shedding angle (WSA)

Owing to the fact that the surfaces of some materials such as sponges, foams and textiles are macroscopically rough, it is very difficult to detect the full drop profile for CA measurement. Therefore, the classical CA measurement (highly dependent on the method of drop shape analysis) and sliding angle measurement (highly dependent on the surface roughness near the water drop), are not suitable to reliably evaluate the wetting properties of the surfaces. Thus, WSA is used instead of CA and sliding angle according to a previous reported method.[2] Typically, the samples were fixed onto a sample holder and placed on the tilting table of the Contact Angle System OCA 20 (Dataphysics, Germany). The syringe was positioned with the needle tip 10 mm above the tilted sample. The needle with an inner diameter of 0.11 mm was used to produce7 μL water droplets. To determine the WSA, measurements were started at an inclination angle of 5 °. Water dropls were released onto the sample at a minimum of three different positions. If all drops completely rolled down the sample, the inclination angle was reduced by 1 °and the procedure repeated until one or more of the dros would not completely roll off the surface. The lowest inclination angle at which all the drops completely rolled down the surface was noted as the WSA.

Oil absorbency and oil/water separation

A piece of sample was immersed in oil at room temperature. The sample was taken out from the oil after 1 min, drained for several seconds and wiped with filter paper to remove excess oil. The oil absorbency k of the sample was determined by weighing the sample before and after oil absorption and calculated according to Eq. (1).

$$k = (M_{eq} - M_0)/M_0 \times 100\% \tag{1}$$

where M_{eq} is the weight of the wet sample at absorption equilibrium (g) and M_0 is the weight of dry sample (g).

n-Hexane was used as the model oil on the surface of water and dichloromethane was used as the model oil under water. The oil-in-water emulsion was prepared by mechanically stirring 5 mL of toluene and 95 mL of water at 1000 rpm for 1 h. The emulsion was quickly poured into the glass tube with a piece of the fixed sponge. The oil was absorbed by the sponge, while water gradually permeated through the sponge and dropped into the glass vessel below. The concentrations of toluene in water before and after separation were determined using a UV-Vis spectrophotometer (SPECORD 200, Analytik Jera AG) at 269 nm. The calibration curve was prepared by measuring the absorbency of toluene in methanol/water (3/1, v/v) solution according to the Lambert-Beer's law.

The influences of repeated absorption-desorption of oils on superhydrophobicity and oil absorbency of the sponge were investigated to evaluate its reusability. The sample was immersed in dichloromethane to reach equilibrium, and then weighted to calculate the absorbency. The sample was squeezed and washed with ethanol for three times, and then dried in an oven at 60 ℃. Afterwards, the CA_{water} and WSA were recorded. This absorption-desorption procedure was repeated for 10 times.

Characterization

The micrographs of the samples were taken using a field emission scanning electron microscope (SEM, JSM-6701F, JEOL). Before SEM observation, all samples were fixed on aluminum stubs and coated with a layer of gold film (~ 7 nm). The morphology of the Fe_3O_4@silica NPs was observed using a field emission transmission electron microscope (TEM, TECNAI-G2-F30, FEI). For TEM observation, the sample was prepared as follows. A drop of the Fe_3O_4@silica NPs dispersion in ethanol was put on a copper grid and dried in the open atmosphere. The energy dispersive X-ray analysis (EDX) was done on the attachments to SEM and TEM. The FTIR spectrum of the sample was recorded by a Thermo Nicolet NEXUS TM spectrophotometer using KBr pellets. The surface chemical composition of the sample was analyzed via X-ray photoelectron spectra (XPS) using a VG ESCALAB 250 Xi spectrometer equipped with a Monochromated AlKa X-ray radiation source and a hemispherical electron analyzer. The spectrum was recorded in the constant pass energy mode with a value of 100 eV, and all binding energies were calibrated using the C1s peak at 284.6 eV as the reference. The mechanical properties of sponge were measured using a universal testing machine (CMT4304, Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China) equipped with a 200 N load cell at room temperature. A vibrating-sample magnetometer (VSM) (Lake Shore, 735 VSM, Model 7304, USA) was used to test the magnetic properties of the samples. Thermogravimetric analysis (TGA) was carried out using a STA 6000 simultaneous thermal analyzer (PerkinElmer Instrument Co., Ltd. USA) in the range of 25 to 800 ℃ at a rate of 10 ℃/min under nitrogen atmosphere.

Fig. S1. The product formed by using the Fe_3O_4 NPs directly.

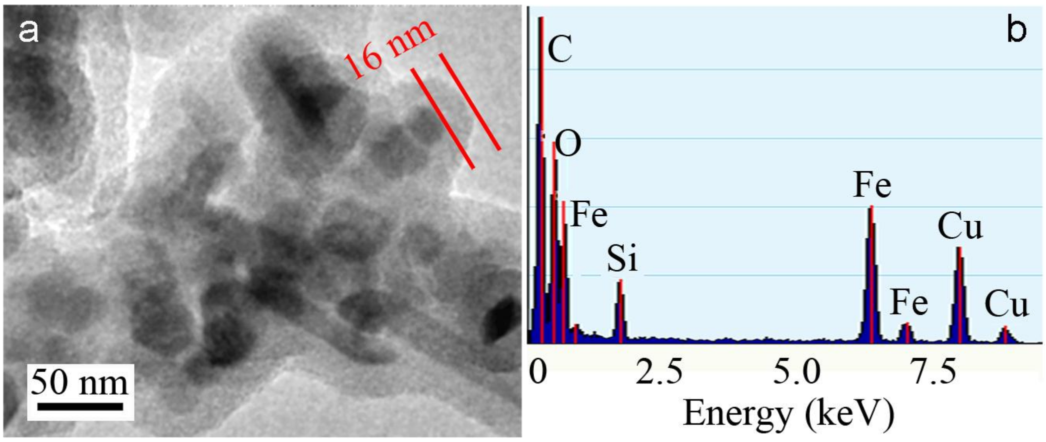

Fig. S2. (a) TEM image and (b) energy dispersive X-ray spectrum of the $Fe_3O_4@SiO_2$ NPs.

Table S1. Oil absorbency and images of the products prepared under various conditions.

No.	C_{CTAB} (mg mL^{-1})	m_{Urea} (g mL^{-1})	V_{HAc} (mL)	n_{VTMS}/n_{DMDEOS}	Oil absorbency (%)	Images
1	12.5	0.31	8	6:4	-	
2	25	0.31	8	6:4	1026	
3	50	0.31	8	6:4	1175	
4	50	0.63	8	6:4	1021	
5	50	1.26	8	6:4	-	
6	40	0.25	10	3:7	1336	
7	40	0.25	10	4:6	1279	
8	40	0.25	10	5:5	1377	
9	40	0.25	10	6:4	1367	

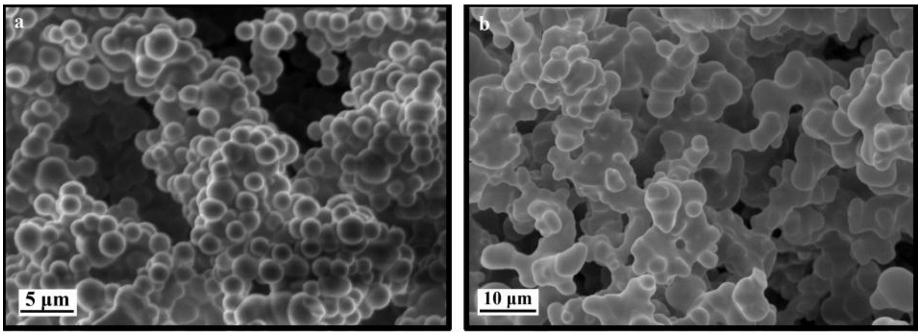

Fig. S3. SEM images of silicone sponges prepared with a CTAB concentration of (a) 12.5 and (b) 50 mg/mL.

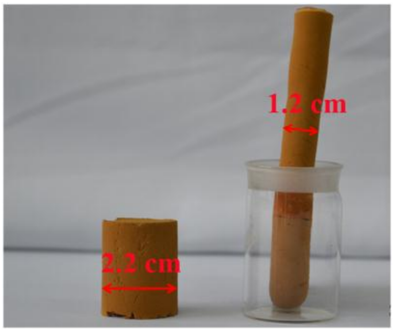

Fig. S4. Images of the silicone sponges in different shape.

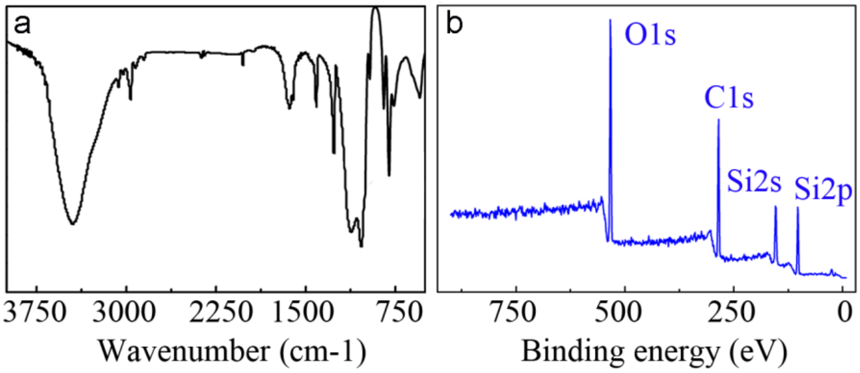

Fig. S5. (a) FTIR spectrum and (b) XPS spectrum of the silicone sponge.

In the FTIR spectrum of the sponge (Fig. S5a), the characteristic bands of polymerized DMDEOS and VTMS were observed at 2964.5 ($-CH_3$ stretching), 1608.5 (C=C stretching), 1411.9 and 1265.0 ($-CH_3$ asymmetric deformations), 1120.5 (Si-O-Si asymmetric stretching of polycyclic oligomers), 1034.4 (asymmetric stretching of linear and branched Si-O-Si), 956.4 ($=CH_2$ wagging), 847.7 and 803.4 cm^{-1} ($-CH_3$ rocking of $Si-(CH_3)_2$ and C-Si asymmetric stretching).

Table S2. EDX analysis of the silicone sponge.

Elements	Atomic (%)
C	37.55
N	26.48
O	9.24
Si	22.59
Fe	4.13

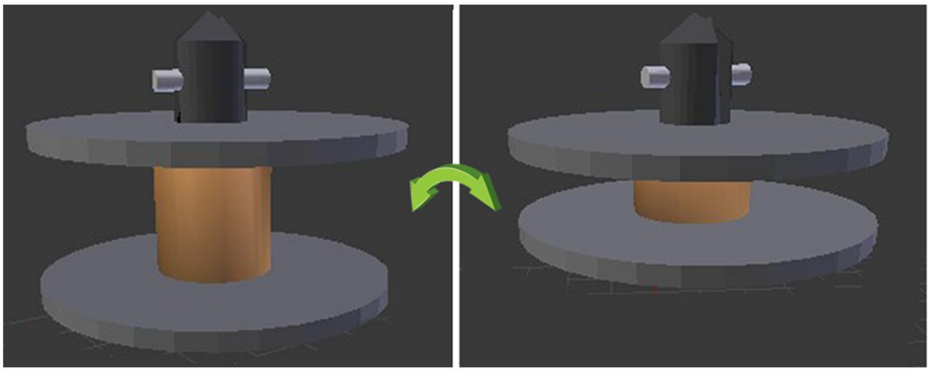

Fig. S6. Schematic illustration of the uniaxial compression tests of the sponge using a universal testing machine.

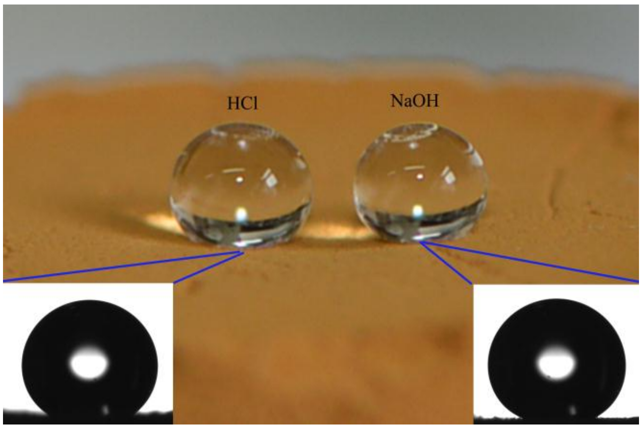

Fig. S7. Optical image of 1.0 M HCl (CA ≈ 151.3°) and 1.0 M NaOH (CA ≈ 151.8°) aqueous droplets on the silicone sponge.

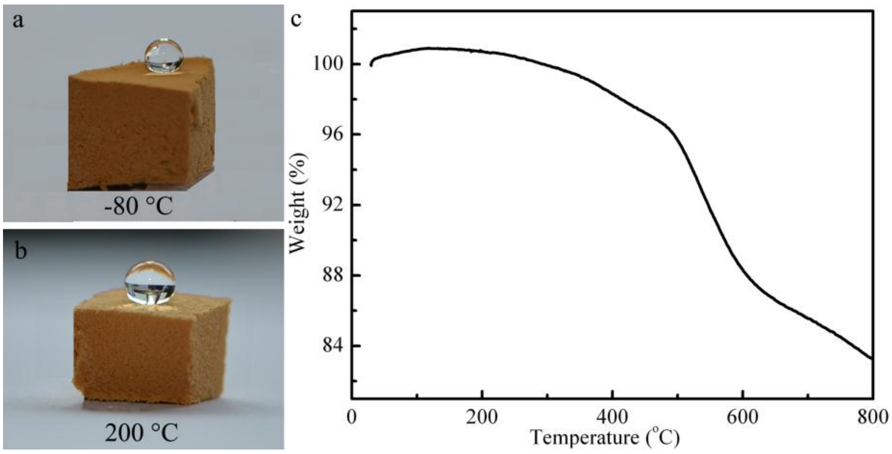

Fig. S8. Digtal images of water drops on the silicone sponges after stored at (a) -80 ℃ (CA ≈ 157.9°) and (b) 200 ℃ (CA ≈ 158.6°) for 24 h. (c) TGA curve of the sponge measured at a scanning rate of 10 ℃ min^{-1} in nitrogen.

Table S3. Weight loss of the silicone sponge, CA and WSA of water drops (7 μL) on the silicone sponge after immersed in various oils for 24 h.

Oils	Weight loss (%)	CA (°)	WSA (°)
n-hexane	0	153.6	2
dichloromethane	0	162.3	2
toluene	0	150.9	3
petrol	0	150.1	2
diesel oil	0	152.3	2

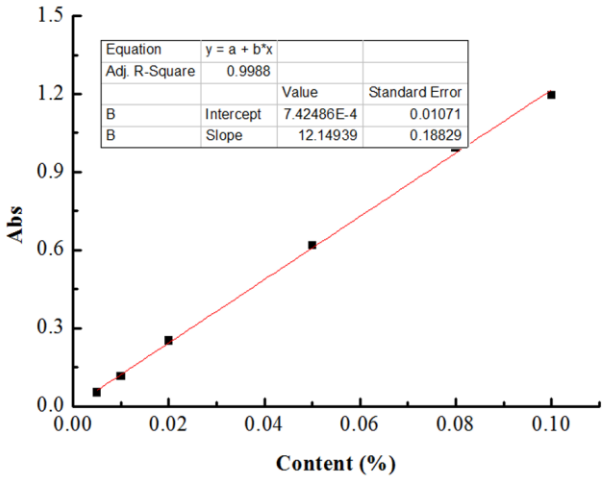

Fig. S9. The calibration curve of toluene in methanol/water (3/1, v/v) solution.

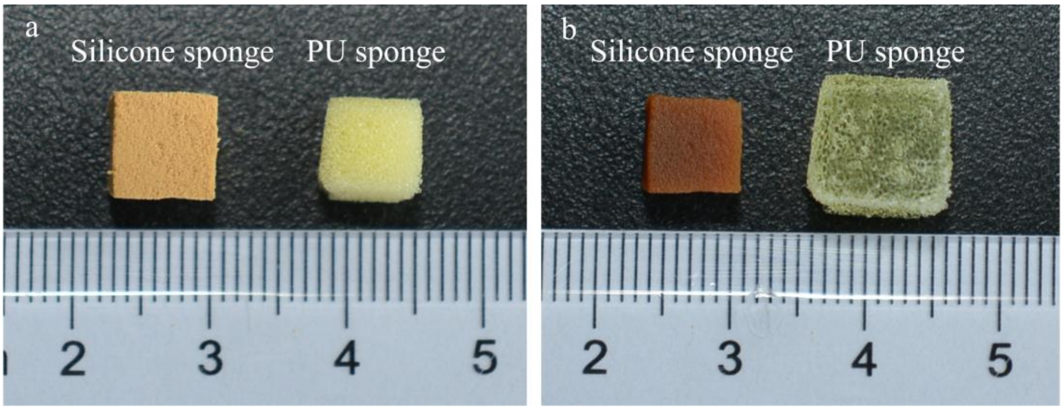

Fig. S10. Optical images of the slicone sponge and the PU sponge (a) before and (b) after immersed in dichloromethane.

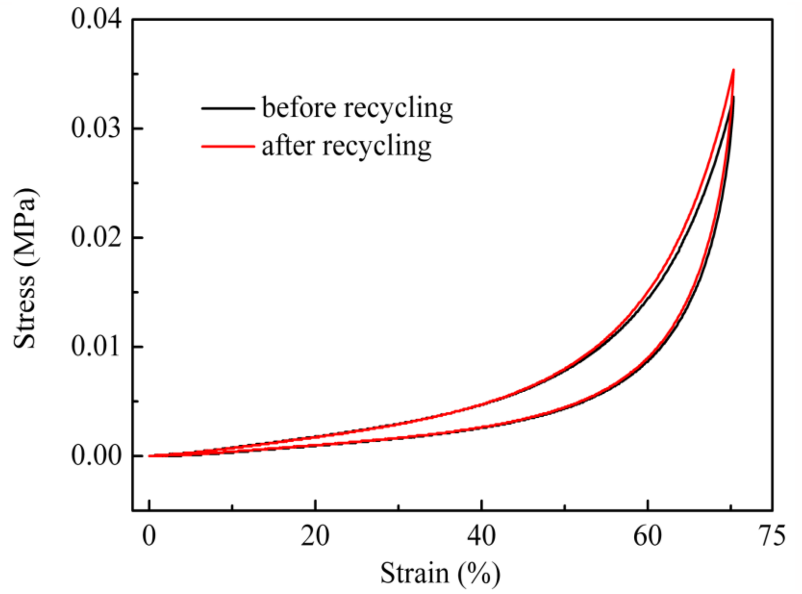

Fig. S11. Stress-strain curves (70% strain) of the silicone sponge before and after 10 absorption-desorption cycles for dichloromethane.

Movie S1. Wetting behaviors of the silicone sponge by water and oil. This video highlights the great difference in wettability of the sponge by water and oil.

Movie S2. The combustion process of the silicone sponge and superhydrophobic polyurethane sponge. This video highlights flame retardancy of the silicone sponge.

Movie S3. Selective oil absorption by the silicone sponge. This video highlights the high efficiency in oil absorption and the magnetically driven process. Oils were colored with Sudan Red.

References

1. a) K. El-Boubbou, C. Gruden, X. F. Huang, *J. Am. Chem.Soc.*, 2007, **129**, 13392; b) F. Y. Cheng, C. H. Su, Y. S. Yang, C. S. Yeh, C. Y. Tsai, C. L. Wu, M. T. Wu, D. B. Shieh, *Biomaterials*, 2005, **26**, 729; c) H. N. Gao, J. He, L. Deng, X. Q. Gao, *Appl. Surf. Sci.*, 2009, **255**, 7974.
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