Multi-functional Porous and Magnetic Silicone with High Elasticity, Durability and Oil-water Separation Properties

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Abstract

Frequent oil spills and industrial emissions of organic solvents cause serious environmental problems. Therefore, finding a high-performance absorbent material is necessary but also challenging. Here we present a very simple method to fabricate a magnetic porous silicone that exhibits excellent absorbency, fast magnetic responsiveness, high elasticity, stretchability and high chemical stability. The porous silicone instantly adsorbs any oil floating on water in a complex environment under magnetic field driving, without human operation, and can also separate the oil/water mixture automatically and quickly at high efficiency using an external pump. The oil absorption capacity and mechanical properties, such as compressibility and stretchability, were robust even under corrosive conditions or UV exposure. The robust reusable magnetic porous silicone is a promising candidate for a large-scale industrial separation of organic solvents/water mixture in harsh conditions.

Keywords: Magnetic silicone; Robust; Elastic; Porous; Oil/water separation

Introduction

Leakage of oils/organic solvents leads to great harm to human health and ecological environments.[1-4] To remove leaked oils/organic solvents under harsh and dangerous conditions, current traditional cleaning methods require a significant amount of time, as well as human and financial resources, resulting in a worldwide challenge.[5] Therefore, it urgently requires the development of highly efficient and low-cost adsorbent materials.

Common absorbent materials, including cotton fabrics,[6-10] meshes[11, 12] and various inorganic absorbents,[13] tend to suffer from low selectivity and absorption capacity. For example, Crick et al. [14] reported silica wool with an oil absorbency of 5.4 mL/g by chemical modification method. In recent years, various 3D porous materials such as silicones,[15-17] foams[18, 19] and aerogels[20, 21] have been used for oil-water separation and adsorption of oils/organic solvents. These high porosity 3D absorbent materials are one of the most promising strategies. Porous materials can absorb large amounts of leaked oil into the pores for easy storage and transportation. Carbonaceous porous materials, such as carbon nanotubes and graphene silicones, have been proposed for oil absorption because of their very low density and high porosity. For example, Gui et al.[22] prepared carbon nanotube silicones with an oil absorbency of 56 g/g by chemical vapor deposition approach. Li et al.[23] fabricated 3D graphene/polypyrole foams via a multistep route through the cross-linking, polymerization reactions and hydrothermal reduction of graphene oxide, and this material could be used for oil spill cleanup. In addition to their superior performances in oil-water separation and oil adsorption, most of these materials have drawbacks, such as complex synthetic steps, poor durability and high cost, which limit their practical applications.

Porous polydimethylsiloxane (PDMS) silicones have been selected as good candidates for oil adsorption and oil-water separation because of the high hydrophobicity, flexibility, thermal stability, mechanical and chemical stability, low cost and easy preparation.[24-27] Recently, porous PDMS silicones have been successfully prepared for oil-water separation and adsorption of oils/organic solvents. Zhang et al. [28] synthesized 3D interconnected porous PDMS sponge by using p-xylene as the solvent and sugar particles as the templates, which could be used for oil-polluted water cleanup. Despite the excellent oil mass absorption of these materials, the compressive stress of the 3D interconnected porous PDMS silicones remains to be improved. Zhao et al.[29] fabricated a superhydrophobic PDMS sponge, which was used for selective oil absorption and plugging oil leakages. However, the preparation process required the use of centrifuges, which hampers the large-scale preparation of these materials in practical applications. Furthermore, although the sponge showed excellent oil mass absorption there was evidence of low stress strain.

Smart controllable adsorption materials[30] have become a trend in the field of oil-water separation and oil adsorption, for example, by controlling pH, temperature, light, electricity and magnetism to control the adsorption capacity of materials. Among them, magnetic-controllable materials have attracted wide attention in recent years because the materials can be remotely manipulated to remove oil waste under dangerous or harsh conditions, and it also greatly reduces costs and manpower. In the development of porous magnetic materials, porous sponges have rarely been reported until now because of difficulties in maintaining the mechanical properties of the framework after modifications required to incorporate magnetic properties.[31]

Here, we report a simple method for the preparation of porous magnetic silicone by curing magnetic $ZnFe_2O_4$ nanoparticles and polydimethylsiloxane (PDMS, commonly called silicone) using NaCl as a hard template. The obtained magnetic silicone demonstrated high compressibility and stretchability even after immersion in organic solution for a few hours, showing excellent chemical and mechanical stability. In addition, the silicone is hydrophobic and superoleophilic and can be driven by a magnet to absorb the floating oil on the surface of water or heavy oils under water. If connected with a vacuum pump, it can be used to separate oil/organic solvent and water automatically and quickly at a high efficiency.

Experimental section

Materials and chemicals

The PDMS precursor (Sylgard 184) and a curing agent were purchased from Dow Corning. Zinc chloride ($ZnCl_2$), iron(III) chloride hexahydrate ($FeCl_3$•$6H_2O$), sodium chloride (NaCl), sodium acetate (NaAc), ethanol, sodium hydroxide (NaOH), ethylene glycol (EG), polyethylene glycol (PEG), methylene chloride, toluene, xylene, n-hexane, paraffin oil, silicone oil, dimethyl sulfoxide (DMFO) and acetone were provided by Tianjin Kermel Chemical Reagent Company (Tianjin, China). Hydrochloric acid (HCl) were provided by Luoyang Haohua Chemical Reagent Company (Luoyang, China). Motor oil (Chery, 10W-40) and PU silicone (PU25) were purchased at local supermarket.

Preparation of magnetic $ZnFe_2O_4$ nanoparticles

First, 20 mmol of $Zn(NO_3)_2 \cdot 6H_2O$ and 40 mmol $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in 100 ml distilled water, and the pH value of the solution was adjusted to 12 by adding 5 mol/L NaOH solution. After that, the solution was continuously stirred at 70 °C for 2 h. The precipitate was filtered and washed with distilled water several times and dried at 60 °C for 3 hours to obtain a precursor. The precursor was calcined at 400 °C for 4 h to get the magnetic $ZnFe_2O_4$ (ZFO) powder.

Preparation of magnetic porous silicone

4.0 g of the PDMS precursor, 0.4 g of $ZnFeO_4$ and an amount of NaCl were placed into a teflon box. After being intensively stirred for 5 min, 0.4 g of the thermal curing agent was added and stirred for another 5 min. The as-prepared mixture was then placed in a mold and cured in an oven at 200 °C for 1 hour. After cooling to room temperature, the cured sample was immersed in hot water (90 °C) for 24h to completely remove the NaCl to obtain the 3D porous magnetic silicone. Finally, the porous silicone was dried in a blast oven at 80 °C. The silicone could be easily prepared in various shapes with different molds.

Oil Absorption Capacity and Oil/Water Separation Efficiency

To test oil adsorption capacity, the porous silicone was immersed in various oil/organic solvents at room temperature for 3 min, and then removed from the oil to measure its weight without dripping. The oil adsorption capacity (*M*) was determined by measuring the weight before and after adsorption and evaluated by using the following equation:

$$M = \left(\frac{m_t}{m_0} - 1\right) \times 100\% \qquad (1)$$

where m_0 and m_t are the weight of the porous silicone before and after adsorption, respectively. For the highly viscosity oils, weight measurements were performed once removed after 1 min and no dripping was observed on the silicone. However, to avoid the evaporation of highly volatile organic solvents, weight measurements were performed immediately after taking out. The oil adsorption capacity was measured five times and then averaged. Oil/water separation efficiency (η) of sample was determined by a peristaltic pump at a rate of 7 mL min^{-1} and after separation and evaluated by using the following equation:

$$\eta = \left(\frac{a_t}{a_0} - 1\right) \times 100\% \qquad (2)$$

where a_0 and a_t are the total mass of oil and water and the quality of the separated oil.

Characterization

The surface morphology of the porous silicone was examined with a field emission scanning electron microscope (FESEM, JSM-6701F). X-ray photoelectron spectrometer (XPS, AXISULTRA) was conducted to confirm the surface chemical composition of the porous silicone. Thermogravimetric (TG) measurements were carried out on a NETZSCH STA 449 C thermogravimetric analyzer from room temperature to 800 °C at a rate of 10 °C min^{-1} under N_2 atmosphere. The water and other liquids contact angle (CA) and sliding angle (SA) tests were measured on a DSA-100S optical contact-angle system (Kruss Company, Germany) at room temperature. The volume of all liquids was 4–10 μL when the CA and SA were measured. All optical photos were taken with a digital camera (NIKON, P600). The tensile test of silicone was measured using a universal testing machine (GOTECH TCS-2000, Taiwan, China) equipped with a 500 N load cell at room temperature. The tests were performed with a loading speed of 20 mm min^{-1}. The compression test was carried out by loading different forces. The elastic test was performed by measuring the change in height of the sample before and after compression. Magnetic measurement was performed on a MPMS3 magnetometer (Quantum Design).

Durability test

Saturated NaCl, 2 M HCl and 2 M NaOH solution were employed to evaluate the durability of the prepared porous silicone in highly acidic, alkaline, and salty environments. After the silicones were immersed in the above corrosive aqueous solutions for 3 h, the oil absorption capacity was then investigated to assess their chemical stabilities. An UV accelerated weathering tester (UV-II, Shanghai Pushen Chemical Machinery; Shanghai, China) was used to evaluate the UV resistance of the prepared porous silicone under 30 °C and 40% humidity, and the Oil Absorption Capacity of the porous silicone was measured after 48 hours of UV radiation.

Results and Discussion

Magnetic porous silicone

The magnetic porous silicone was prepared by polymerization of PDMS precursor and curing agent in the presence of NaCl and $ZnFe_2O_4$ (ZFO) nanoparticles, and the fabrication process is as shown in Fig. 1(a). Note that no organic solvents were used in this preparation and thus the process is environmentally friendly. The characterization of the ZFO nanoparticles is shown in Supporting Information (Fig. S1). It is clear that the characteristic peaks of ZFO are consistent with the standard card (JCPDS No. 22-1012) and that confirms the successful preparation of ZFO, and TEM image shows that the ZFO nanoparticles were about 20-40 nm. The content of sodium chloride addition could affect the oil absorption and mechanical properties of the porous silicone. The majority of the reported magnetic porous silicone in this work was prepared with the mass ratio of $m_{\mathrm{PDMS}}:m_{\mathrm{NaCl}}:\mathrm{m}_{\mathrm{ZFO}}$ = 1:9:0.1 (*M#9*), unless specified otherwise. The porous PDMS-ZFO silicones could be made into various shapes as shown in Fig. 1(b) and demonstrate hydrophobicity. A water droplet sitting on the silicone surface shows a spherical shape with a water contact angle of about 146° and n-hexane droplet can immerse immediately into the elastic PDMS surface (Fig. 1c). SEM images show that the porous silicone was composed of interconnected irregular pores forming a rougher surface (Fig. 1d). The obtained porous silicone had a good thermal stability and no significant weight loss was observed before 260 °C, as shown in Fig. 1e. A dramatic weight loss about 75% between 260 °C and 450 °C, which corresponds to the decomposition of the methyl group on the PDMS.

Surface chemical composition of the porous silicone was analyzed using XPS (Fig. 1f).

The C 1s, O 1s, Si 2s and Si 2p peaks were observed at 284.4, 532.6, 154.4 and 101.8 eV. The characteristic peaks of Na and Cl could not be detected, indicating that NaCl particles were completely removed. Note that Fe and Zn peaks could not be detected and it is expected that the ZFO nanoparticles surface was covered by PDMS. The SEM-EDS elemental mapping of C, O, Si, Fe and Zn is exhibited in Fig. S2 in the supporting information, and it is clear that Fe and Zn elements are distributed on the silicone. The obtained porous silicone shows superparamagnetism and can be attracted under an applied magnetic field condition (Fig. 1g). The magnetic hysteresis loops further demonstrate the superparamagnetism of the porous silicone (Fig. 1h). The magnetic saturation value of the ZFO nanoparticles and porous silicone were 0.88 and 0.065 emu/g, respectively. Due to the reduced ZFO component content of porous silicone compared to pure ZFO nanoparticles, the magnetic saturation value of porous silicone was lower than that of pure ZFO nanoparticles.

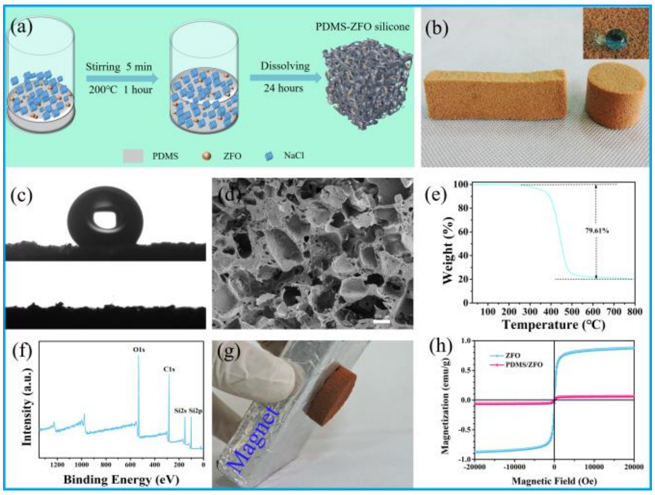

Fig. 1. (a) Schematic of the facile fabrication of interconnected porous PDMS-ZFO silicone. (b) Photograph of as-prepared interconnected differently shaped porous silicone (Inset: photo of water droplets on silicone surface dyed with methylene blue). (c) Photo shows water contact angle about 146.5° and n-hexane contact angle about 0°; (d) SEM image of the porous silicone with m_{PDMS}:m_{NaCl}:m_{ZFO} = 1:9:0.1. (e) TG curve of porous silicone measured at a scanning rate of 10 °C min^{-1} in nitrogen. (f) XPS spectra of the PDMS-ZFO silicone. (g) Photo of magnet attracting obtained silicone. (h) Magnetic curves of the ZFO and PDMS-ZFO silicone.

Mechanical properties of magnetic silicone

Currently, a major problem of superhydrophobic surfaces is the mechanical fragility of the nanostructures, which results in the degradation of the hydrophobicity in common environments (e.g., long-term air exposure, mechanical abrasion, external pressure, contamination with pollutants, acid rain, etc.).[32, 33] Herein, the porous silicone had a certain resistance to stretching with an elongation at break of 482-800 KPa according to the addition of NaCl (Fig. 2a). The tensile strength decreased with the increase of template addition since increased NaCl addition resulted in additional pores inside the silicone rubber, which makes the porous silicone less stress under external tension. Fig. 2(b) shows the compressive stress–strain curves of the magnetic porous silicone rubber with different NaCl addition. The stress increased gradually with the increasing strain to 60% and at the same stress, the strain increased with the increase of NaCl addition. The silicone can withstand 90% compressive strain and almost completely recover, as shown in Fig. 2(c). Before the strain reaches 70%, the compressive stress gradually increases with the strain, owing to the elastic bending of irregular 3D connected skeletons. After 70% strain, the compressive stress increases sharply, because irregular 3D connected skeletons collide with each other.[34] Importantly, no significant cracking or collapse of the silicone after 1000 cycles of a 60% compression test was observed. The silicone had only 5.4% of deformation after 1000 compression tests, and almost recovered its original shape, as shown in Fig. 2(d, e) and Fig. S3 in the supporting information. The prepared silicone was very stable to various organic solvents, as shown in Fig. 2(f). Insets in Fig. 2(f) shows the optical images of the prepared silicone soaked in ethanol, acetone and DMSO respectively for 3 hours and it can be seen that the silicones were still stable without being destroyed. No significant change in stress compared to original stress after 100 compressions at 70% strain was observed. The robust stability proves that the silicone has excellent recyclability, which is also very important in practical applications.

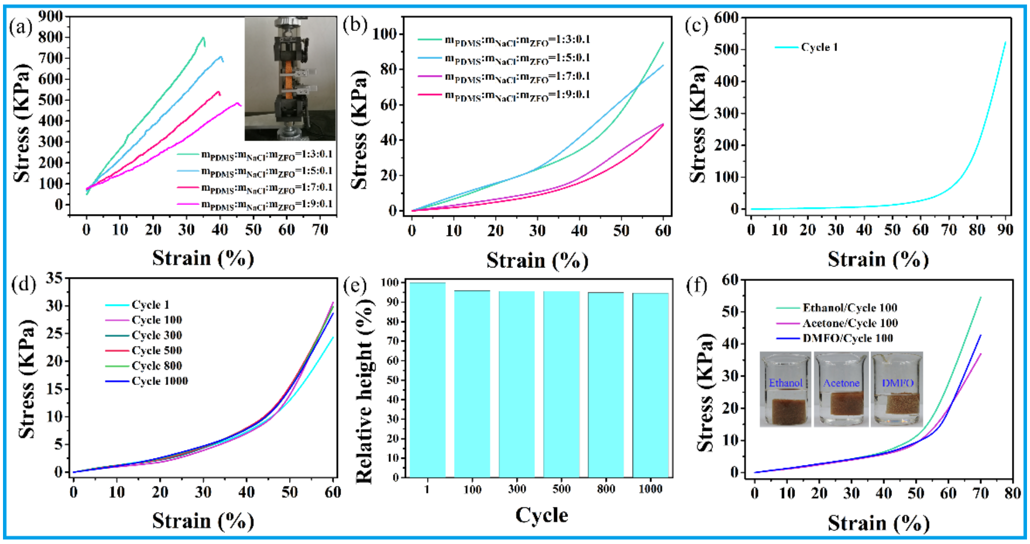

Fig. 2. (a) Tensile stress–strain curve of the porous PDMS-ZFO. (b) Compressive stress–strain curves of different porous PDMS-ZFO at successive 60%. (c) The porous silicone at 90% strain. (d) Compressive stress–strain curves of different porous silicone at successive 60% strain for 1000 cycles. (e) The relative height of the porous silicone after 1000 cycles of compression. (f) After 3 hours of soaking in ethanol, acetone and dimethylsulfoxide, the compressive stress–strain curves of the porous silicone at successive 70% strain for 100 cycles. (Inset: Photographs of the porous magnetic silicone soaked in ethanol, acetone and dimethylsulfoxide (DMSO) after 3 hours.

Oil/Water Separation

For an ideal oil absorbent, a highly porous material with 3D interconnected pores is necessary. Herein, the obtained porous silicone showed good ability to absorb heavy or light oil due to the hydrophobicity and oleophilicity, and could separate heavy oil or light oil from water quickly without residue, as shown in Fig. 3(a-j), Video S1 and Video S2 in Supporting Information. Moreover, the prepared composite silicone also exhibits magnetic responsivity. As shown in Fig. 3(k-o) and Video S3 (Supporting Information), the prepared superparamagnetic composite porous silicone could be driven under external magnetic field condition and absorbed completely n-hexane on water surface. This method of removing oil can reduce costs and clean up areas that people cannot reach. As illustrated in Fig. 3(p-u) and Video S4 (Supporting Information), the silicone could still remove the oil-water mixture under strong magnetic stirring (≈1200 r/min), and the n-hexane removal could be completed within 4 s, demonstrating efficiency oil-water separation under highly turbulent environment.

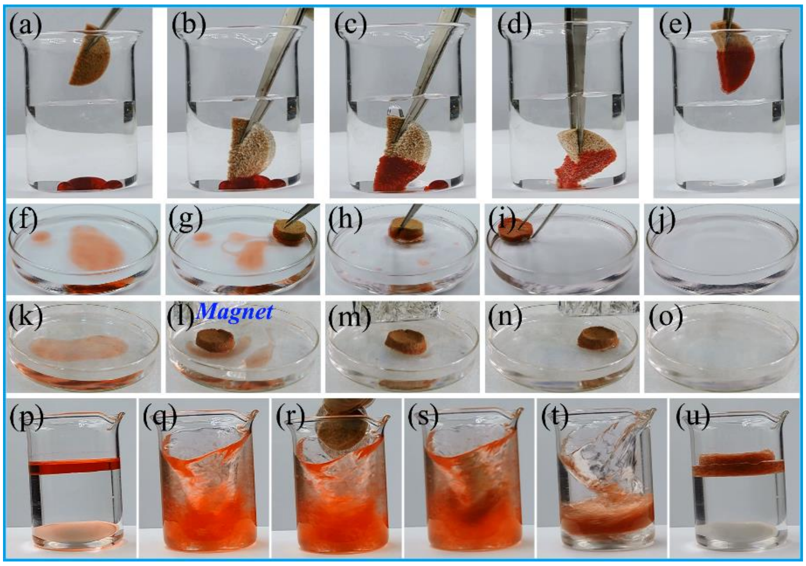

Fig. 3. (a-e) The process of the silicone removal of dichloromethane under water. (f-j) The process of the silicone adsorbing n-hexane on the surface of water. (k-o) Removal of n-hexane on the surface of water by magnetically driven. (p-u) The sequence shows n-hexane removal from water under strong magnetic stirring. The organic solvents in (a-u) were dyed with oil red.

Fig. 4(a) presents the adsorption capacity of the porous silicone toward a wide range of oils and organic solvents. The adsorption capacity ranges from 400% to 1100% and is affected by the density and viscosity of oils/organic solvents. For oils/organic solvents with low viscosity, including n-hexane, toluene, xylene and dichloromethane, the adsorption capacity was much larger than that of solvents with higher viscosity. It is expected that the oils or organic solvents with high viscosity (e.g., motor oil) tended to block the pores of the porous silicone when being adsorbed because of the slow diffusion speed, which further locked air inside the porous silicone and thus resulted in a low adsorption capacity (413.7 ± 17.2% for motor oil).[35]

In the practical application of oil cleanup, the recyclability and adsorption efficiency of the silicone are crucial. Some general methods, including combustion,[34, 36] mechanically squeezing,[35, 37-38] release in other solvent, [35, 39-40] and evaporation by heating,[34-35] were used to determine the recyclability of the oil/organic solvent adsorbents. Herein, we also used different methods to determine the recyclability of oil adsorption of the porous magnetic silicone. Fig. 4(b) shows the adsorption capacity of the silicone evaluated by the squeezing method. After the first cycle of paraffin oil adsorption, the mass of the silicone changed from 0.33 to 1.79 g, revealing an adsorption capacity of 444.4%. During the remaining nine cycles, the adsorption capacity of the silicone remains 223.4% demonstrating good reusability by a squeezing method. As illustrated in Fig. 4(c), the corresponding adsorption capacity was stable and remained about 417.1 ± 2.1% after ten cycles, which shows excellent reusability of the silicone for the adsorption of highly viscous organic solvents. The heating method was used to evaluate the cyclic adsorption capacity of the silicone for easily volatile organic solvents (Fig. 4d), and it also shows an excellent reusability after ten cycles. Fig. 4(e-i) and Video S5 (Supporting Information) show the process of removing paraffin oil from the surface of water by means of adsorption-squeezing. The reusability of the silicone to absorb high-viscosity organic solvents was determined by thoroughly washing with ethanol and drying at 80 °C for 5 min.

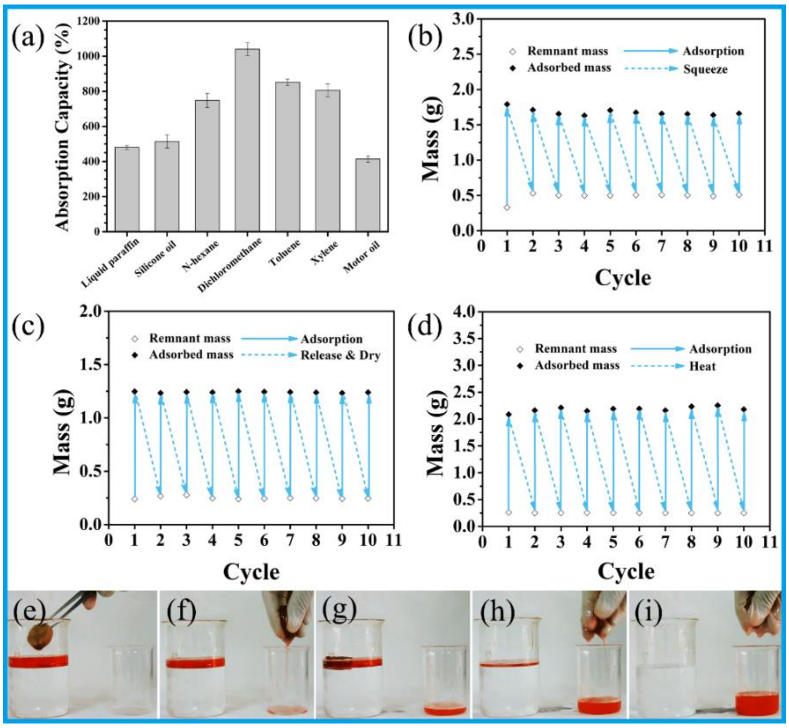

Fig. 4. (a) Absorbency of the porous silicone for various organic solvents. (b) Reusing the silicone for absorption of paraffin oil using the direct squeezing method. (c) The reusability of the silicone for paraffin oil recovery rinsing in ethanol and drying. (d) Measurement of recyclability of the silicone by heating volatilization of n-hexane. (e-i) Images sequence showing the cleaning of paraffin oil (dyed with Oil Red) floating on water by repeated squeezing.

Recently, superhydrophobic and superoleophilic meshes, films, and membranes have also attracted broad attention because of their capacity for the efficient separation of oil and polluted water.[15] However, they cannot be applied to oil spills because they require the polluted water to be accumulated first and then filtered. Therefore, it is necessary to develop novel materials for the continuous absorption and removal of oil from water with high separation capacity. Herein, the bulk magnetic porous silicone could be used for the continuous absorption and removal of oil from water surfaces, making the oil and water separation easier and faster. As shown in Fig. 5 (a-b) and video S6 in the supporting information, once the silicone touched the paraffin oil, the oil penetrated into the hydrophobic silicone immediately, and in combination with a pump allows complete removed of the paraffin oil with no obvious oil left behind. Note that the percentage of NaCl will have a great influence on the 3D connected porous structures and thus influence the separation efficiency. As the m_{PDMS}:m_{NaCl} changed from 1:3 to 1:9, the separation efficiency for paraffin oil/water increased from 91.1% to 97.4% (Fig. 5c), and the absorption capacity increased from 70.9% to 480.3% (Fig. 5d). Importantly, the interconnected porous silicone is reusable and after being washed thoroughly with ethanol and dried, the porous silicone could be reused to continue multiple oil-water separation (Fig. 5e). Note that after 10 repetitions, the separation efficiency remains above 94% and the separation efficiency tends to be stable after four repetitions, which indicates that the porous silicone could be reused more efficiently. The magnetic silicone also shows chemical stability and UV irradiation durability. Fig. 6(a) demonstrates a schematic diagram of the silicone irradiated in an UV accelerated weathering tester and no significant change was observed in contact angle after exposure to ultraviolet light for 48 hours. Fig. 6(b) is an optical photograph for silicone immersed in 2 M NaOH, 2 M HCl and saturated NaCl. It is clear that the “water mirror” can still be seen, indicating the silicone is still hydrophobic and has a good chemical resistance. As can be seen from Fig. 6(c), there was no significant change in the adsorption capacity of the silicone for various organic solvents and after UV irradiation. In addition, strong corrosive solution or saturated NaCl solution have little influence on the adsorption capacity and the adsorption capacity retains its original states after 3 hours immersion (Fig. 6d-f).

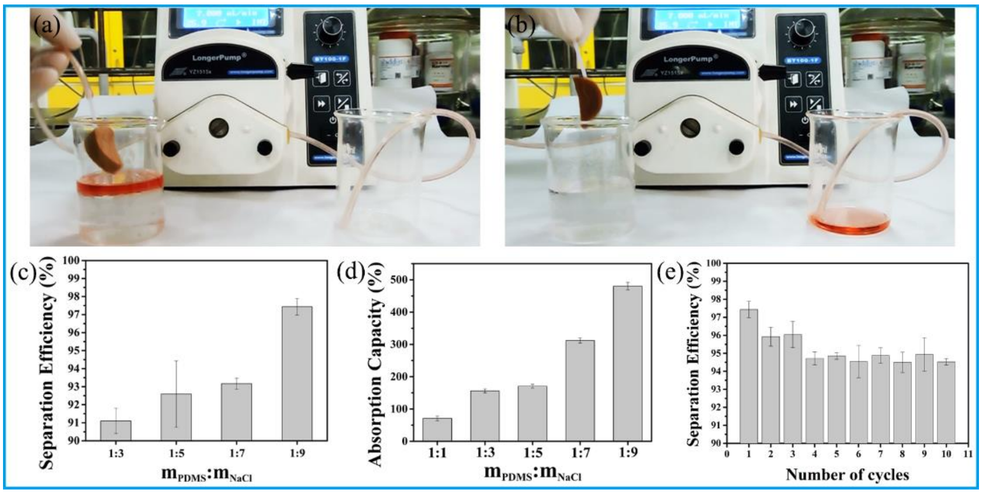

Fig. 5. (a, b) Pictures of the continuous absorption of paraffin oil (dyed with Oil Red) from water. Separation efficiency (c) and absorption capacity (d) of magnetic silicone with different mass ratio of PDMS to NaCl. (e) The relationship between separation efficiency and recyclability of the obtained silicone.

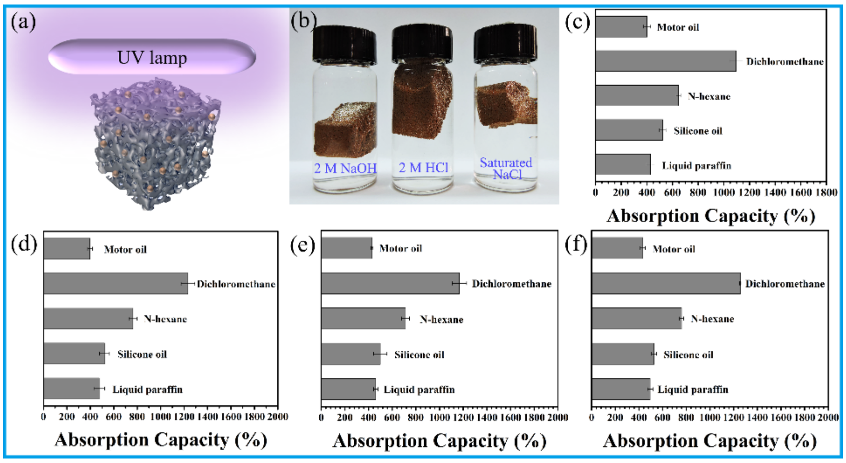

Fig. 6. (a) Schematic diagram of ultraviolet irradiation. (b) Optical photo after 2 hours soaking in 2 M NaOH, 2 M HCl and saturated NaCl. (c) Adsorption capacity of organic solvents after UV irradiation for 48 hours at 30 °C and 40% humidity. Adsorption capacity of organic solvents after 3 hours soaking in 2 M NaOH (d), 2 M HCl (e) and saturated NaCl (f).

Conclusion

In summary, we have successfully prepared PDMS-ZFO silicones using NaCl microparticles as the hard templates. The preparation process is simple and does not require special equipment for easy large-scale preparation. The silicone possesses many functional properties such as high elasticity, stretchability, rapid magnetic response, excellent oil adsorption capacity and oil-water separation capability, etc. The silicone can be used to drive by a magnet and selectively adsorb large amounts of floating oil and heavy oil underwater, and can be reused after being squeezed. Importantly, the silicone could be continuously subjected to oil-water separation with the aid of a vacuum pump, which greatly reduces costs and manpower. In addition, mechanical properties and oil adsorption capacity did not change significantly after being soaked in a variety of organic solutions for a few hours, indicating the chemical stability. It is expected that the magnetic porous silicone rubber will be a promising material for efficiently treating oil spills and industrial discharge of organic solvents, because of the simple preparation method and the outstanding properties.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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