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Durable and Modified Foam for Cleanup of Oil Contaminations and Separation of Oil-water Mixtures

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Abstract

With the continuous exploitation and utilization of oil resources, the oil pollution had become increasingly serious, which not only caused the economic loss, but also damaged the living environment of human beings. Herein, oleic acid coated Fe_3O_4 particles and PS microspheres were introduced into the surface of pure foam through an inexpensive two-step immersion method, we obtained a durable and modified magnetic polystyrene foam (DMMPF) with high efficiency and selectivity. The as-obtained DMMPF exhibited superhydrophobicity, superoleophilicity, and fast magnetic response *via* the surface chemical modification. In addition, the as-prepared DMMPF could be used for continuous separation of various oils and organic solvents from water surface. The absorption intake capacity of DMMPF was 40.1 times of its own weight and the absorbed oils/organic solvents could be collected by simple mechanical extrusion. Furthermore, the as-prepared DMMPF remained excellent absorption capacity and large water contact angle after 60 separation cycles. It's recognized that DMMPF could be suitable for large-scale oil spill processing.

Keywords: Foam, Durable, Superhydrophobicity, Recyclability, Modified

Introduction

In the past half century, oil spills which occur on the ocean have become a serious global problem.[1] The adverse impacts on human health and environment have raised great concern.[2-4] It is reported that a thin oil film on the water surface could cause serious damage to water organism.[5-7] That is because that the oil film prevents oxygen from entering the water body. What's worse, the toxicity of oil results in a sharp deterioration of the ecological environment and the vast majority of unsettled oils will continue to remain in the ocean. Organic vapors generated by oil evaporation pollute the

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Electronic Supplementary Information (ESI) available: [Information on EDS spectra, stress-strain curves, situation of immersed in the water bath, optical image after floating on HCl and NaOH solution, experiment of removing deionized water, collection of oil and organic solvent, weight percentage of the as-prepared samples; three videos showing the magnetic property, unsinkable property and oil absorption process of the sample.]. See DOI: 10.1039/x0xx00000x atmosphere environment and lead to the chemical smog.[8-10] In order to address these environment issues caused by oil spills, many approaches have been employed to clean up the oils, such as physical absorption,[11-14] enhanced bioremediation[15,16] and chemical reaction.[17] Among the above-mentioned methods, physical absorption using oil absorbing material with superhydrophobic and superoleophilic is considered as the most useful measure which has the advantages of low cost, being convenient and no secondary pollution, *etc.*[18-22] However, most leaked chemicals such as crude oil, diesel oil, benzene, and dichloromethane can perform emulsification reaction in the oil-water mixture, making it difficult to clear up.[23,24] Considering that, it is necessary to develop a kind of physical absorption material which should have the following functions. Firstly, the material should have the selective absorption capacity and can absorb various oils and organic solvents. Secondly, the material should have excellent hydrophobicity and oleophilicity. Last but not least, the material should still remain high absorption capacity and water contact angle after many cycles.[25-28]

In recent years, the functionalized foams and sponges with many superior performances have attracted extensive attention.[29-31] Due to the mutual connection of 3D network structure, these materials have an excellent absorption capacity and good oil holding capacity. However, high energy consumption, low selective absorption capacity and low recycling rate limited their practical applications.[32,33] As a kind of high oil absorption material with 3D structure, durable foam has a very large space for successive use.[34-38] In this article, a durable and modified magnetic polystyrene foam (DMMPF) with high efficiency and excellent absorption capacity was successfully synthesized by a simple and inexpensive two-step immersion method. Combination of effective absorption, superhydrophobicity, superoleophilicity and good magnetic response, the as-prepared foam with 3D network structure could be used for selective oil absorption and continuous oil-water separation. More importantly, the absorbed oils and organic solvents could be collected by mechanical squeeze before the next cyclic operation of DMMPF. The study may provide a facile and novel preparation method to prepare the durable and functionalized foam, which could be used to deal with the large scale of the oil spills.

Experimental section

1. Materials and Chemicals.

All chemicals were of analytic reagent grade and used without further treatment, and all solutions were prepared with deionized water. Polyethylene (PE) shock absorption foam and vinyltriethoxysilane (VTES) were obtained from Aladdin. Absolute ethanol (C_2H_5OH) was bought by Nanjing Chemical Reagent Co. Ltd., Nanjing, China. Azobisisobutyronitrile (AIBN) and acetone (C_3H_6O) were gained from Shanghai No.4 Reagent & HV Chemical Co. Ltd., Shanghai, China. Sodium hydroxide (NaOH) was received from Xilong Chemical Reagent Co. Ltd., Shantou, China. Hydrochloric acid (HCl) and n-hexane (C_6H_{14}) were purchased by Sinopharm Chemical Reagent Co. Ltd., Shanghai, China.

2. Preparation of Durable and Modified Magnetic Polystyrene Foam.

In a typical synthesis, shock absorption foam (3 cm×1.5 cm×1.5 cm) was purified in deionized water and acetone with mechanical stirring at 60 °C for 3 h successively. Initially, a piece of the pure foam was immersed in 15 mL of absolute ethanol containing 25 mg of the homogeneously dispersed oleic acid coated Fe_3O_4 particles which were prepared through our previously reported.[39] Then, oleic acid coated Fe_3O_4 particles were attached to pure foam under the ultrasonic oscillation along with mechanical vibration at room temperature. Durable magnetic polystyrene foam (DMPF) was obtained via introducing PS microspheres which were prepared by dispersion polymerization in ethanol onto the surface of the magnetic foam using 50 mg of AIBN as initiator at 50 °C for 3 h. After that, the durable and modified magnetic polystyrene foam (DMMPF) was fabricated by immersing an n-hexane solution containing VTES (7% v/v) for 1 h. Finally, the durable and modified magnetic polystyrene foam with superhydrophobicity and superoleophilicity was prepared after being dried at 60 °C for 3 h. The preparation procedures are exhibited in Fig. 1.

Fig. 1. Illustration for the synthesis of DMMPF.

3. Characterization of Durable and Modified Magnetic Polystyrene Foam

X-ray diffraction (XRD) analysis was performed on a D8 advance (Bruker D8 Super Speed) X-ray diffractometer with Kα radiation. The surface morphologies of the as-prepared foams were observed by field-emission scanning electron microscope (FESEM, Model-S4800, Hitachi, Japan). All samples were fixed on aluminum stubs and coated with gold to obtain optimum efficiency. Surface chemical compositions were investigated using the energy-dispersive X-ray spectroscopy (EDS, OXFORD INCA Energy Dispersive Spectrometer). The mechanical properties of the as-prepared samples were measured by a dynamic mechanical analyzer (DMAQ800, TA Instruments) at room temperature. Thermal gravimetric analysis (TGA) was performed with Model TA2100 (TA Instruments, USA) in the range from 50 °C to 650 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Contact angles were detected by using a Drop Shape Analyzer SL200B (CAs, SL200B, Solon Tech. Co. Ltd., China). Water and lubricating oil droplets with a volume of 4.0 μL were dropped carefully onto the surface of the as-prepared samples. The magnetic properties of the samples were investigated in fields by a vibrating sample magnetometer (VSM, Lake Shore 735).

4. Oil-Absorption Experiments.

The oil-absorption capacities of the as-prepared samples were measured by weight measurements at ambient temperature. In a typical procedure, nine kinds of oils and organic solvents including lubricating oil, diesel oil, salad oil, dichloromethane, cyclohexane, benzene, DMF, ethylene glycol and tetrahydrofuran along with water were poured on the surface of water in a beaker, respectively. Then, a piece of sample was weighed and immersed in mixture solution. The oils and organic solvents were selectively and fast absorbed by the as-prepared foams after several seconds, drained and wiped to remove excess oils or organic solvents. Later, the absorbed oils and organic solvents together with foam were collected by a magnet bar or a simple external force. The absorption capacity was calculated using the following formula: S=(M_a-M_b)/M_b, where S is the absorption capacity of the as-prepared foams, M_a and M_b are the weight of the foam after and before absorption, respectively.

5. Regeneration of absorbent

After absorption process, the oils and organic solvents were collected by simple mechanical squeezing. After being dried at 60 °C for 3 h, the regenerate DMMPF was reused to remove oils and organic solvents from water surface. The absorption-desorption procedure was repeated 60 times. For each cycle, the water contact angle and oil absorbency were measured.

Result and discussion

The as-prepared DMMPF was fabricated through a facile two-step immersion method. First, the composition of the sample was confirmed by XRD analysis (Fig. 2a), exhibiting the characteristic patterns of DMMPF. The intensive peak at 2θ = 30.1°, 35.7°, 43.1°, 57.2° and 62.6° represent the (220), (311), (400), (511) and (440) reflection of Fe_3O_4 **(**JCPDS file No. 19-0629**)**, respectively. It was obviously seen that the curve showed no characteristic peak of any other crystallite, indicating only oleic acid coated Fe_3O_4 particles were attached onto the surface of pure foam. To further confirm the surface chemical composition of the as-prepared samples, we conducted EDS measurement to test the existing elements. The element of C, Fe, and O could be seen clearly in the spectrum of the oleic acid coated Fe_3O_4, DMPF and DMMPF. According to the reaction conducting, the percentage composition of C present an increasing trend which was attributed to the PS layer attached into the surface of the magnetic foam. (see the Supporting Information, Fig. S1a, S1b and Table S1). The additive element of Si was ascribed to the hydrophobic surface modification by VTES (Fig. S1c). The changes of chemical composition could improve the wettability of the as-prepared foam.

In order to study the hydrophobicity of the as-prepared foams, the surface morphology, which was the important factor to evaluate surface wettability, was taken into account. As shown in Fig. 2b, the pure foam possessed a 3D hierarchical porous structure and the surface was very smooth without any distributed microscale protrusions. From Fig. 2c and 2d, it was obviously seen that the smooth foam skeleton was covered by many uniformly dispersed particles i.e. oleic acid coated Fe_3O_4 particles, whose size were about 300 nm. As the coated reaction conducting, the surface of DMPF exhibited random roughness, which was very important to the hydrophobicity of the foam (Fig. 2e and 2f).

Interestingly, when DMMPF was compressed to 30 % of its original shape under extra force, it could recover 98 % of its original dimension when extra force was released, as shown in Fig. 3. Moreover, it was

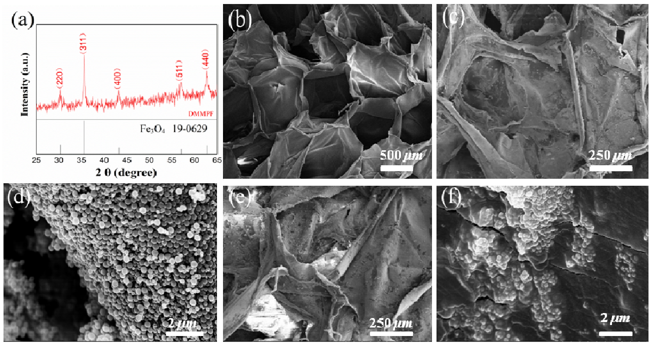

Fig. 2. (a) XRD pattern for DMMPF. SEM images of pure foam (b), magnetic foam (c, d), DMPF (e, f,) at different magnifications.

found that the as-prepared foam retained its elasticity after several cycles of compression test. The cyclic compressing tests of pure foam, DMPF and DMMPF were conducted to evaluate the mechanical property and the results were summarized in Fig. S2. Compared with Fig. S2a and 2b and 2c, it was evidenced that the stress of DMMPF at 80% compressing strain increased after modification. In particular, pure foam reached a stress of 8.5 KPa at 80% and the stress increased to 46 KPa at 80% strain for DMPF after coating by OA-Fe_3O_4 and PS. Among them, DMMPF exhibited superior structural stability and the stress for DMMPF could reach up to 48 KPa at 80% strain. It was noted that the compressing stress of DMMPF decreased slightly even after 60 compressing cycles, which confirmed the excellent mechanical property. There were probably two reasons for excellent mechanical property. Firstly, the interconnected three-dimensional network structure of the as-prepared foam improved the structural stability. Secondly, chemical bonds and van deer Waals forces were enhanced by introducing magnetic particles and PS layer, and grafting hydrophobic groups on the surface of pure foam. Therefore, when DMMPF was used for oil and organic solvent absorption, the absorbed oil and organic solvent could be easily extruded out of DMMPF pores.

The thermal decomposition behavior of the as-prepared samples was investigated by TG-DSC techniques. The TG and DSC curves of pure foam, DMPF and DMMPF were exhibited in Fig. 4a and 4b, respectively. It can be observed from the TG curves in Fig. 4a that the difference in residual content between curve a and curve c was about 26.1 wt%, indicating 26.1 wt% of the PS layer was introduced onto the surface of DMPF. Obviously, the 10.9 % weight loss which was obtained from curve b and curve c was attributed to alkyl hydrophobic groups on the surface of DMMPF. Owing to high content of alkyl hydrophobic groups, DMMPF exhibited the excellent hydrophobic property. From Fig. 4b, we could observed that an endothermic process presented in all samples at about 449.1 °C could be ascribed to the thermal decomposition of pure foam, during which pure foam was decomposed to generate some gaseous products. The low temperature decomposition peak at 95.2 °C was attributed to the glass transition temperature of PS, as exhibited in curve b and curve c. After modification by VTES, the high temperature decomposition peak appeared at 415.8 °C (curve c), which could be attributed to the grafting alkyl hydrophobic groups. The TGA and DSC curves of as-prepared samples exhibited the same information.

Moreover, oleic acid coated Fe_3O_4 on the surface ensured magnetism, which allowed the oil-absorbed

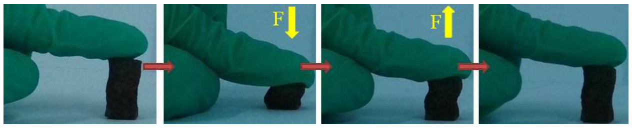

Fig. 3. Images showing compression and recovery for DMMPF.

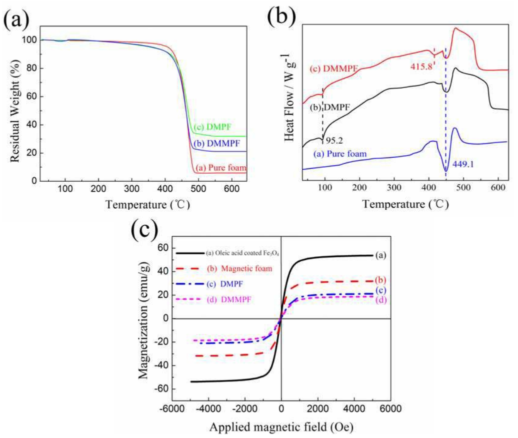

Fig. 4. (a) TGA and (b) DSC curves of pure foam, DMMPF and DMPF. (c) Magnetic curves of oleic acid coated Fe_3O_4, magnetic foam, DMPF and DMMPF.

foam to be easily collected under the magnetic field (Movie S1). The superparamagnetic property of oleic acid coated Fe_3O_4 had not been changed after modification by PS and VTES. Representative hysteresis curves of oleic acid coated Fe_3O_4, magnetic foam, DMPF and DMMPF were illustrated in Fig. 4b. It could be obviously seen that all the samples showed the superparamagnetic properties between -5 and +5 kOe at room temperature as indicated by the absence of reminance and coercivity on removing an external applied magnetic field. The saturation magnetization values of oleic acid coated Fe_3O_4, magnetic foam, DMPF and DMMPF were 53.7, 31.9, 21.1 and 18.7 emu/g, respectively. The results showed that the saturation magnetization decreased after modification. There were two reasons accounted for this phenomenon. One reason was that mass fraction of oleic acid coated Fe_3O_4 decreased after modification. The other reason was that coating layer increased after modification. When the coating layer became thicker, the saturation magnetization decreased. This result was in good agreement with the TGA results.

The superoleophilicity and superhydrophobicity of the as-prepared foams were estimated by the measurement of the contact angles. When a lubricating oil droplet was placed on the surface of pure foam, DMPF and DMMPF, it could immediately spread into the 3D structure of foams, as shown in Fig. 5(a, b, c). It was noteworthy that the oil contact angle decreased in turn, indicating the oleophilicity of the samples increased successively. What's more, the oil contact angle of DMMPF was almost 0°, exhibiting that the sample was superoleophilic. As exhibited in Fig. 5d and 5e, the water contact angles of pure foam and DMPF were about 114.5° and 131.5°, respectively. The increase in the contact angle was attributed to the PS layer on the surface of the magnetic foam. However, the water contact angle value of DMPF hardly satisfied the conditions of the superhydrophobic. In order to achieve the conditions, we utilized the silane coupling agent (VTES) as hydrophobic surface chemical modification agent and the water contact angle could be up to 150.5° (Fig. 5f). Interestingly, the pure foam sank beneath the surface of water. However, when DMMPF was immersed in water under an external force, and the foam surface was surrounded by air bubbles, which was the Cassie-Baxter nonwetting behavior owing to a signature of the composite solid-liquid-air interface[40] (Fig. S3). DMMPF immediately floated on the water surface after release of external force, and no water uptake was observed (Movie S2). Moreover, the as-prepared DMMPF displayed a stable hydrophobicity, even though floating on 1.0 M HCl and NaOH solution for 72 h, respectively, as illustrated in Fig. S4.

The as-prepared DMMPF could be used for absorbing oils and organic solvents. The absorption capacities under different conditions were also measured by weight measurement. The lubricating oil absorption process (dyed by Sudan I) was illustrated in

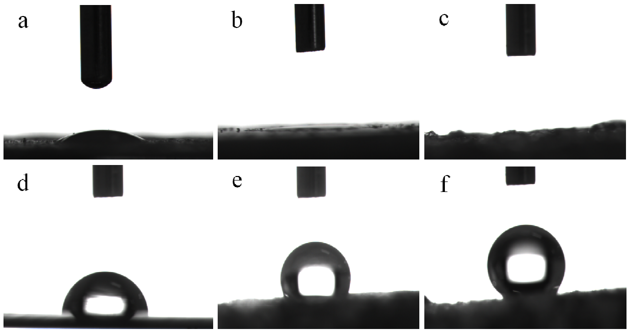

Fig. 5. Optical images of a lubricating oil droplet (a, b, c) and a water droplet (d, e, f) placed onto the surface of pure foam, DMPF and DMMPF, respectively.

Fig. 6 and Movie S3. When DMMPF was placed on the mixture, it selectively absorbed lubricating oil from the mixture in 60 s and still floated on the water surface, indicating the excellent hydrophobicity. After absorption, the oil-soaked DMMPF could be readily removed with a magnet bar and collected before the next cyclic operation. Interestingly, DMMPF could also absorb organic solvents. A benzene absorption experiment was shown in Fig. 7 and the photographs were taken in intervals of 20 s. When a piece of DMMPF was placed on the surface of benzene-water mixture, the benzene labeled by Sudan Red for clear observation was quickly absorbed by DMMPF. The organic solvent absorbed DMMPF could be easily collected by a simply extra force. It only took 60 s for DMMPF to reach its maximum absorption capacity, demonstrating that DMMPF could be oil absorbent with high efficiency. However, whether the water would be absorbed was studied, as exhibited in Fig. S5 a-f. When a piece of DMMPF was forced into the deionized water which labeled by copper sulphate for clear observation, it exhibited a silver mirror-like surface, and water could not spread into DMMPF. We put DMMPF immersed in water on a napkin and also tested the quantity. More interestingly, we found that there was no water droplet on a napkin (Fig. S5 e, f) and the mass of the napkin hardly increased, indicating excellent hydrophobicity and selectivity of DMMPF.

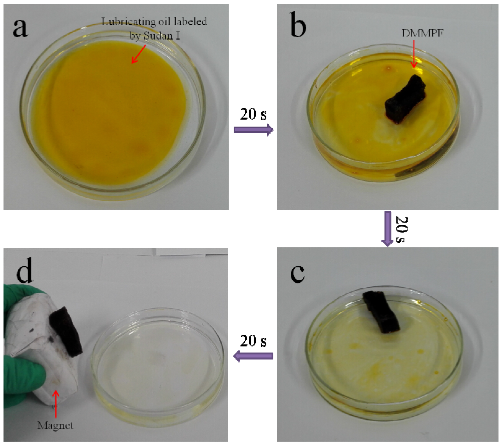

Fig. 6. Lubricating oil removal from water surface with DMMPF under magnetic field.

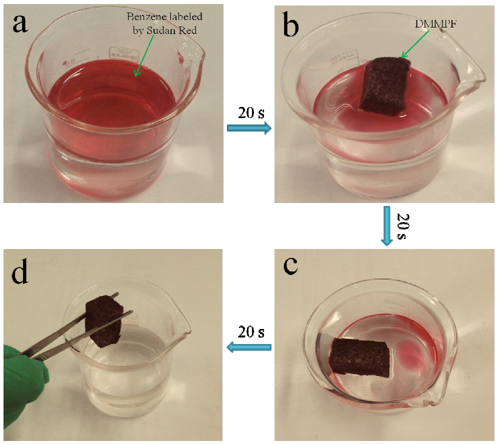

Fig. 7. Benzene removal from water surface with DMMPF under extra force.

The absorption capacities of pure foam, DMPF and DMMPF were investigated by employing water, lubricating oil, diesel oil, salad oil, dichloromethane, cyclohexane, benzene, DMF, ethylene glycol and tetrahydrofuran as absorbing targets. As shown in Fig.

8a, pure foam gained more than 6 times of its own weight after absorbing water and it also exhibited a certain absorption capacity to oils and organic solvents. It was demonstrated that pure foam without modification was not suitable for oil absorption. Therefore, the pure foam should be modified, and we introduced oleic acid coated Fe_3O_4 and PS onto the surface of pure foam to obtain DMPF. The intake capacity of DMPF exhibited that the *S* values of DMPF could reach a maximum of 37.9 g/g for dichloroform, as shown in Fig. 8b. It was obviously seen that the absorption capacity for various oils and organic solvents increased and the intake capacity of water decreased after modification. The above results displayed that the absorption capacity and selective ability of DMPF were both improved. However, it was difficult to meet the requirement that only oils and organic solvents could be absorbed. Hence, we modified DMPF and the as-obtained DMMPF could satisfy the above-mentioned requirement. The absorption capacities of DMMPF for lubricating oil, diesel oil, salad oil, dichloromethane, cyclohexane, benzene, DMF, ethylene glycol and tetrahydrofuran were about 22.7, 17.2, 20.1, 40.1, 20.5, 22.9, 18.3, 20.9 and 25.1 g/g, respectively. It should be noticed that water absorption capacity of DMMPF decreased to less than 0.3 g/g, as shown in Fig. 8c. The absorption capacity depended on the density, the viscosity and surface tension of absorbing objects. For example, lubricating oil had a higher density (0.923 *vs.* 0.843 g/cm^3), viscosity (61.2 *vs.* 6.2 cP) and surface tension (31.7 *vs.* 13 mN/m) than diesel oil, the absorption capacity of lubricating oil was larger than that of diesel oil accordingly.[41] As expected, DMMPF had high absorption capacity, which was higher than magnetic grapheme foam[42,43] and grapheme/carbon cryogels.[44] The superior absorption property was attributed to the interconnected 3D network structure along with attached PS layer in DMMPF. What's more, the absorption capacity of DMMPF was higher than DMMP, that's because DMMPF had fewer polar function groups.

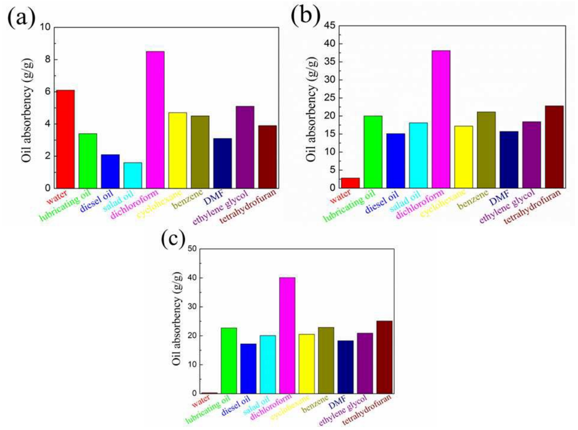

Fig. 8. Absorption capacity of (a) pure foam, (b) DMPF, and (c) DMMPF for water, various oils and organic solvents.

In practical applications, the as-obtained material could be regenerated through a simple squeezing process. As could be seen in Fig. S6, DMMPF still remained an excellent and stable mechanical property. The compressing stress only exhibited 9% loss after 60 absorption-desorption cycles (Fig. S6a) and the mechanical property of DMMPF was enough for regenerating oils/organic solvents in absorption-desorption process. Moreover, we could obviously see in Fig. S6b and S6c that a three-dimension hierarchical porous structure still existed after 60 absorption-desorption cycles, suggesting its stable mechanical property. Therefore, the absorbed oils/organic solvents could be easily reclaimed through a mechanical force for the next absorption operation, as shown in Fig. S7. To our surprise, there was no droplet in the collecting oil and organic solvent, implying the outstanding

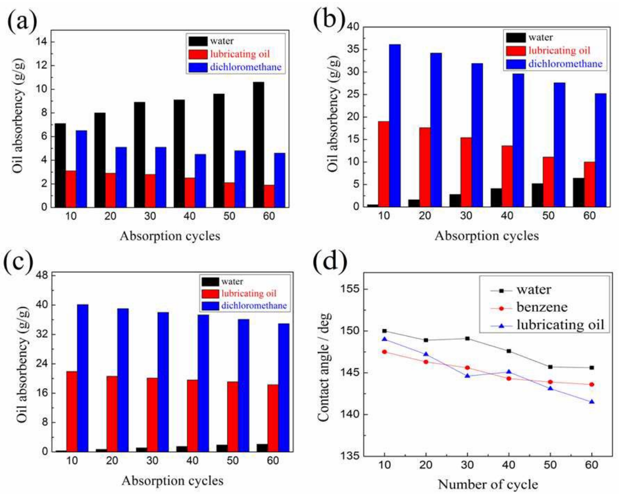

Fig. 9. Absorption capacities of (a) pure foam, (b) DMPF, and (c) DMMPF under different cycles. (d) contact angle after different water-oils/organic solvents separation cycles.

property of hydrophobicity. More importantly, DMMPF with high absorption capacity and efficiency could be reused for many times. The absorption capacities of as-prepared samples after several cycles were also investigated to evaluate the reusability, the results shown in Fig. 9. It was clearly seen in Fig. 9a and 9b that the water absorption capacity of pure foam and DMPF increased distinctly and the oils/organic solvents absorption capacity obviously decreased after 60 cycles. In contrast, the absorption capacities to water, benzene and lubricating oil and contact angle of DMMPF weakened slightly after 60 cycles, indicating a stable absorption performance and the excellent reusability of DMMPF. The similar oil absorbing foams/sponges and their performances were listed in Table S2. Compared with these absorbents, DMMPF with low cost, excellent absorption capacity and wettability has been demonstrated to be an promising absorbent for the removal of oil spills and organic solvents.

Conclusions

In summary, a durable magnetic polystyrene foam was fabricated through a facile immersion method by introducing Fe_3O_4 particles and PS layer onto the surface of pure foam. As the hydrophobic groups grafting on magnetic polystyrene foam, DMMPF showed superhydrophobicity and superoleophilicity, which was beneficial for its application in oil-water separation. In addition, the as-obtained DMMPF not only exhibited high mechanical and chemical stability, but also fast and selectively removed a variety of oils/organic solvents under the magnetic field. The maximum absorption capacity of DMMPF could reach up to 40.1 g/g of its own weight. Furthermore, we collected the oils and organic solvents by simple squeezing before the next cyclic operation. Above all, DMMPF could still maintain excellent absorption capacity and large water contact angle after 60 cycles. Due to its good properties, simple fabrication method and much lower cost than other absorption materials, we believe that this kind of durable and modified magnetic polystyrene foam is a promising candidate for removal of contaminants from water surface.

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Graphical Abstract:

DMMPF still keep excellent oil absorption capacity and large water contact angle after 60 cycles, indicating its excellent reusability.

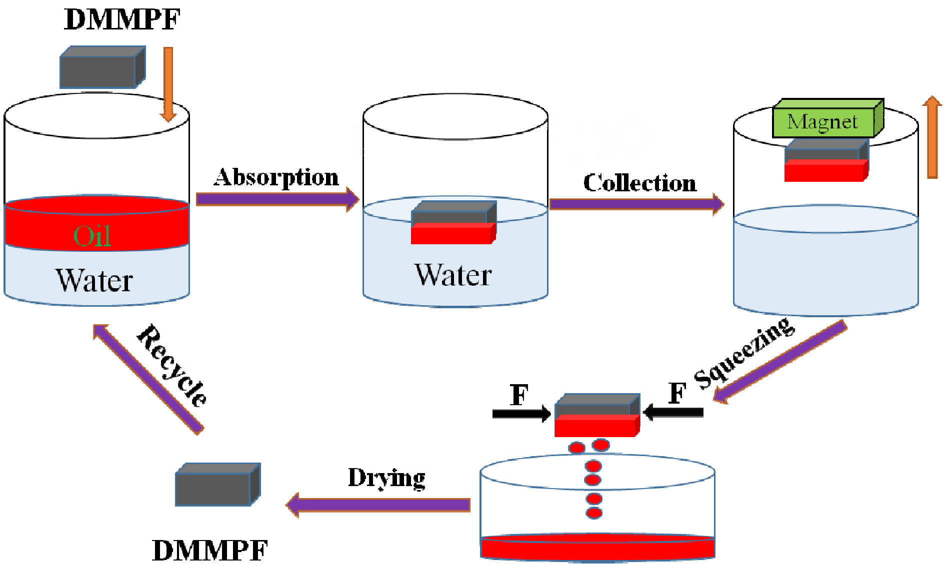

Figure. Absorption and desorption of the durable and modified magnetic polystyrene foam.