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Nontraditional oil sorbents: Hydrophilic sponges with hydrophobic skin layer for efficient oil spill remediation

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ABSTRACT   Advances in the use of porous materials for oil-water separation offer a promising avenue for solving oil spill problems. Conventionally, to realize selective oil absorption, porous sorbents need to be fully hydrophobized with low-surface-energy chemicals. However, such exhaustive hydrophobization brings about problems of excessive chemical consumption, high cost and increased environmental hazards, hindering the practical applications of sorbents. Here, an innovative type of oil sorbent is developed *via* a facile liquid film-based dip coating technique. Unlike conventional fully-hydrophobized sorbents, only the outmost layer of our sorbent is modified with hydrophobic polydimethylsiloxane (PDMS) coating while the inner part remains hydrophilic, thus achieving 80% reduction in low-surface-energy chemical consumption. The prepared sorbent allows highly selective oil absorption from oil-water mixture, as the hydrophobic skin layer blocks water entrance and the hydrophilic inner part drives oil absorption. More importantly, our sorbent significantly speeds up oil absorption, and compared with conventional hydrophobic sponges, the absorption time is reduced by 36% for absorption of the same mass of crude oil, attributed to the strong capillary absorption of its hydrophilic inner channels. This sorbent also shows larger specific absorption capacity than its fully hydrophobized counterpart. Our study provides a general strategy to develop cost-effective and environmental-benign sorbents with enhanced oil spill absorption performances.

Keywords: oil spill remediation, surface engineering, porous materials, oil sorbents, wettability

INTRODUCTION

An increasing number of oil spills and industrial oily wastewater are threatening public health and terrestrial ecosystem [1–8]. Combustion, gravity separation and biochemical methods have proven effective in treating oil-water mixtures, but disadvantages such as secondary contamination and low efficiency limit their applications under harsh practical conditions [9–13]. As promising candidates, porous materials such as sponges [14–16], wood foams [17–19] and aerogels [20–24] have been successfully applied to oil-water separation *via* selective oil absorption. Among them, highly-porous and low-density poly-

mer sponges (e.g., melamine and polyurethane) are commercially available, and have become the substrates of choice for most liquid separation materials [25–27]. The oil-absorbing sponges can be recovered by simple squeezing and cleaning with water or ethanol for recycling [28].

To enable selective oil absorption, the sponges need to be hydrophobic (water repellent) and oleophilic (oil attractive) simultaneously [29]. For this purpose, exhaustive hydrophobization has generally been employed to functionalize the sponges, in which all the porous channels of the sponges are fully hydrophobized by low-surface-energy chemicals like alkyl silanes [30–32] and fluorosilanes [33–35]. Although such hydrophobized sponges can achieve selective absorption of oil, the exhaustive hydrophobization of sponges with high specific surface area requires excessive consumption of low-surface-energy chemical reagents, which inevitably leads to lengthy fabrication process, high cost and increased environmental hazards. In addition, the absorption speed of fully hydrophobized sponges is relatively low, especially for high-viscosity oils. Current methods to improve the absorption speed of porous materials towards high-viscosity oils mainly utilize the photothermal or Joule heating effect to reduce the viscosity of oils [36–40]. Such methods can effectively promote the oil-absorption speed and have been successfully applied in the cleanup of crude oil spills. However, they require external energy supply or complex device construction, which limits their practical application range. Therefore, it is highly desired to develop advanced sorbents that can selectively absorb oil from oil-water mixtures with integrated advantages of low fabrication cost, reduced environmental impact and enhanced absorption speed.

Here, we report an innovative type of sorbent, i.e., hydrophilic sponges with hydrophobic skin layer, for highly efficient oil spill remediation. The skin-hydrophobized sponges are prepared *via* a facile liquid film-based dip coating method, of which only the outmost layer is hydrophobized with low-surface-energy coating, while the major inner core remains hydrophilic. As a result, the consumption of chemical reagents is drastically reduced in comparison with the fully hydrophobized sponges. Such a new type of sorbent exhibits excellent selective oil absorption from oil-water mixtures due to the water barrier effect of the hydrophobic skin layer, and more importantly, enables significantly enhanced oil absorption speed due to the fast capillary absorp-

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tion of the hydrophilic inner channels.

EXPERIMENTAL SECTION

Preparation of skin-hydrophobized hydrophilic sponges (MS@PDMS)

The melamine sponge (MS) was first cut into 2 cm × 2 cm × 2 cm cubes, cleaned in ethanol and water successively assisted by ultrasonication and then dried in an oven at 60°C for 6 h. The cleaned MS was subjected to oxygen plasma treatment for 10 min to hydroxylate its surface before further treatment. The oxygen plasma treatment can increase the surface energy of the polymer and help to improve the bond strength of the poly-dimethylsiloxane (PDMS) coating. A mixed solution (1 mL) prepared by dissolving PDMS prepolymer in n-hexane at a concentration of 1 mg mL^{-1} was dropped onto a plastic Petri dish, which would automatically spread into a thin liquid film. The MS sponge was then let to contact the liquid film side by side so that each side was evenly coated with a thin layer of PDMS prepolymer solution, and subsequently heated at 80°C for 2 h to form the outmost hydrophobic skin layer. Finally, the sponge was repeatedly rinsed with n-hexane, and then dried at 60°C overnight to remove excess unreacted PDMS.

Preparation of fully hydrophobized sponges

The pristine MS sponge was first treated with air plasma for 10 min and then immersed in a solution of 0.1 wt% PDMS/n-hexane for 20 min, followed by curing at 80°C for 2 h. The hydrophobized sponge was washed with n-hexane to remove residual reagent and dried at 60°C. Other fully hydrophobized control samples were prepared with similar procedures except that the 0.1 wt% PDMS/n-hexane solution was replaced with 0.1 vol% octadecyl trichlorosilane (OTS)/n-hexane or 0.1 vol% trimethylchlorosilane (TMSCL)/n-hexane solution. The above hydrophobized MSs are denoted as PDMS-MS, OTS-MS, and TMSCL-MS, respectively.

Measurement of the oil absorption speed

The oil absorption speed was measured with a self-built setup. The sponge was connected to a force sensor with a metal wire. A crude oil reservoir placed on a lifting platform was moved upwards slowly until the oil surface came in contact with the sponge. At the same time, the sensor began to record the mass change due to the absorption of crude oil by the sponge. The weights of MS@PDMS and the PDMS-MS during the absorption test were measured by a pressure transducer equipped with a 0.5-N load cell (ME KD34S, Germany).

Oil/water separation efficiency

Water (40 mL) and the tested oil (4 mL) were added into a beaker, and the sponge was then put into the beaker to clean up the oil spill. After absorption, the residual oil was extracted with CCl$_4$. The oil content in CCl$_4$ was measured with a Fourier transform infrared (FT-IR) oil meter (OIL-6A, Suyuan), and the separation efficiency was then calculated.

Oil absorption capacity

The oil was poured into a beaker, and the sponge sample was placed into the oil for about 2 min to reach a saturation absorption. The mass change of the sponge was measured quickly to avoid evaporation of the absorbed organic liquids.

The gravimetric absorption capacity Q was calculated following Equation (1):

$$Q = (m_1 - m_0)/m_0, \qquad (1)$$

where m_0 and m_1 are the masses before and after absorption, respectively.

Instruments and characterization

The surface structure and morphology of the sponges were characterized with a scanning electron microscope (SEM, Quanta 400F, Oxford) at an acceleration voltage of 20.0 kV. Chemical and elemental analyses of the shell and the core of MS@PDMS and the hydrophobized PDMS-MS were conducted with X-ray photoelectron spectroscopy (XPS, ESCALab250, Thermo Fisher Scientific) and X-ray energy-dispersive spectroscopy (EDS). The surface chemistry was analyzed using FT-IR spectroscopy (Thermo Fisher NICOLET iS10). Static contact angles were tested with a DSA100S Drop Shape Analyzer (KRÜSS, Germany) at 25°C. Advancing contact angles were measured by a tilting plate method, in which a 6-μL droplet was deposited on the surface and the substrate was tilted with a speed of 15° min^{-1}. The contact angles are the average values measured at three different places of the samples. The viscosities of different oils at room temperature (25°C) were tested by a rotational rheometer (MCR302, Anton Paar GmbH).

RESULTS AND DISCUSSION

Our strategy of using skin-hydrophobized hydrophilic sorbents for selective and enhanced oil absorption is illustrated in Fig. 1. Conventional oil sorbents are fully hydrophobized from inside to outside to ensure the rejection of water and the selective absorption of oil (Fig. 1a). In the absence of external forces, the absorption of liquid into the porous sorbent is driven by the capillary force: $F \sim \gamma l \cos\theta_1$, where γ is the liquid surface tension, l is the perimeter of the capillary channel and θ_1 is the oil contact angle of the hydrophobic material. However, from the viewpoint of liquid absorption dynamics, the hydrophobic capillary channel is not a preferred choice for oil absorption as it is not able to generate a maximized capillary force for rapid liquid transport. The liquid absorption speed of porous sorbents can be calculated from Equation (2) [41]:

$$m_s = K_s t^{1/2}, \qquad (2)$$

where m_s is the liquid suction mass per unit area in the vertical suction direction, K_s is the absorption coefficient, and t is the time. K_s can be further expressed as

$$K_s = (\gamma d^2/\mu)^{1/2}(\varepsilon^* r_0/\lambda)^{1/2}(\cos\theta/2)^{1/2}, \qquad (3)$$

where d and μ are the density and viscosity of the liquid, respectively, ε^* is the porosity of the sorbent, λ is the average bending factor of the capillary channels ($\lambda > 1$), r_0 is the average pore radius, and θ is the oil contact angle of the sorbent material. While the first and the second parentheses indicate the effects of the inherent liquid properties and the geometrical parameters of the sorbent, respectively, the third one indicates how the liquid-material interface interaction (i.e., the contact angle) affects the absorption dynamics. Since the liquid transport inside capillary channels is a dynamic process involving contact line advancing, it is more appropriate to use the advancing angle instead of the contact angle in Equation (3) [42]. It can then be concluded that the smaller the advancing angle is, the faster the absorption speed is, which is verified by our experimental investigation (Fig. S1). However, there exists a dilemma, that is, hydrophilic sorbents can promote rapid oil transport but are not suitable for
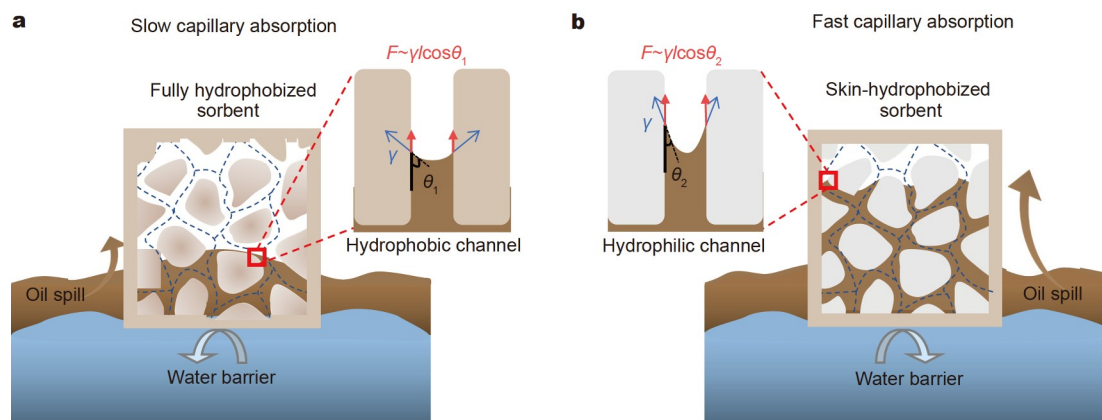
Figure 1 Schematic comparison of the absorption behaviors of (a) conventional fully hydrophobized sorbent and (b) the skin-hydrophobized sorbent. While the hydrophobic skin layer blocks water and allows only oil entrance, its hydrophilic inner channels promote capillary absorption of oils due to the small oil advancing contact angle, thus enabling selective and fast oil absorption.

selective oil absorption, whereas hydrophobic ones are able to perform selective oil absorption but not preferred for rapid oil transport.

To combine the properties of selective oil absorption and rapid capillary transport together, an innovative type of sorbent is proposed in this study (Fig. 1b). Only the outmost layer of the sorbent is hydrophobized, and the major inner part keeps its intrinsic hydrophilic characteristics. When coming in contact with an oil-water mixture, the hydrophobic skin layer acts as a water barrier, whereas oil can transport through the skin layer effortlessly, thus endowing the sorbent with selective oil absorption property. Once the oil penetrates through the hydrophobic skin layer and touches the hydrophilic inner channel, an enhanced capillary force begins to work on the oil: $F \sim \gamma l \cos \theta_2$, where $\theta_2 < \theta_1$. Since the skin layer is very thin and the major part is hydrophilic, a significantly promoted oil absorption dynamics could be realized, as anticipated from Equations (2) and (3). Therefore, the skin-hydrophobized sorbent is expected to achieve both excellent oil selectivity and rapid oil transport properties.

To verify the above strategy, we prepared the skin-hydrophobized sorbent and the fully hydrophobized counterpart using MSs as the substrate material and PDMS as the modifier, which are denoted as MS@PDMS and PDMS-MS, respectively. MSs were selected because of their high porosity, low cost and desired hydrophilicity, which have been widely used to prepare oil sorbents [43,44]. MS@PDMS was fabricated through a facile liquid film-based dip coating method, as illustrated in Fig. 2a. Briefly, a cubic pristine MS (2 cm × 2 cm × 2 cm) was subjected to oxygen plasma treatment to hydroxylate the surface and then put onto a very thin liquid film of 0.1 wt% PDMS prepolymer solution. The liquid would rise to a certain height under capillary force and cause the skin layer of MS to be infused with the prepolymer solution. The thickness of the skin layer can be controlled by adjusting the height of the liquid film. The above procedures were repeated to wrap all six sides of MS with a thin layer of PDMS prepolymer solution, and MS@PDMS was obtained after curing the prepolymer solution at 80°C for 2 h (see the EXPERIMENTAL SECTION for details). PDMS-MS was prepared by immersing the pristine MS entirely in PDMS prepolymer solution and then curing under the same condition. With the liquid film-based dip coating method, a thin hydro-

phobic PDMS skin layer can be formed on the MS, and its appropriate thickness is within 0.1–0.2 cm. It was found a too thin skin layer could hardly prevent water from breaking into the sponge due to the insufficient critical wetting pressure, whereas a too thick skin layer would be adverse to rapid liquid absorption. In our investigation, a skin layer with a thickness of 0.15 cm was adopted for MS@PDMS. Notably, the amount of PDMS prepolymer solution expended in the preparation of MS@PDMS is reduced by about 80% compared with the fully hydrophobized PDMS-MS, which means a drastic reduction of chemical reagent consumption and accompanying environmental impact.

Fig. 2b shows SEM images of three different samples, including pristine MS, PDMS-MS, and the skin-hydrophobized MS@PDMS. The pore sizes are about 100–200 μm and show no observable change after coating with PDMS, which indicates that the effect of pore size on the liquid absorption is negligible for the three samples. As shown in the insets of Fig. 2b, PDMS-MS and the skin layer of MS@PDMS have the same water contact angle (~149°), while the inner core of MS@PDMS shows the same superhydrophilic property as pristine MS (~0°). The EDS mapping (Fig. 2c) confirms the skin-layer structure of MS@PDMS. Strong Si signal and relatively weak C signal are present in the hydrophobic skin layer (I), indicating the successful coating of PDMS. In the core region (II), no Si signal is found while a strong C signal is detected. At the junction area, a clear boundary can be found from the distribution of Si elements. XPS (Fig. 2d) and FT-IR (Fig. S2) analyses further confirm the unique skin-layer structure of MS@PDMS and the chemical compositions of different samples.

The oil absorption speeds of the three different samples were investigated using viscous crude oil as a probe liquid. Spontaneous sinking tests were first conducted by placing the sponges onto the surface of a crude oil reservoir and measuring the sinking depth as a function of time (Fig. 3a, b). Clearly, the hydrophilic pristine MS sank the fastest. Though MS@PDMS sank slightly slower than pristine MS, it sank much faster than PDMS-MS. The detailed sinking dynamics of the three sponges are shown in Fig. 3c. While PDMS-MS took 225 s to get fully submerged, MS@PDMS took only 150 s to complete the submergence. The two sponges sank to almost the same depth in the first 30 s, which is due to that the crude oil did not yet submerge
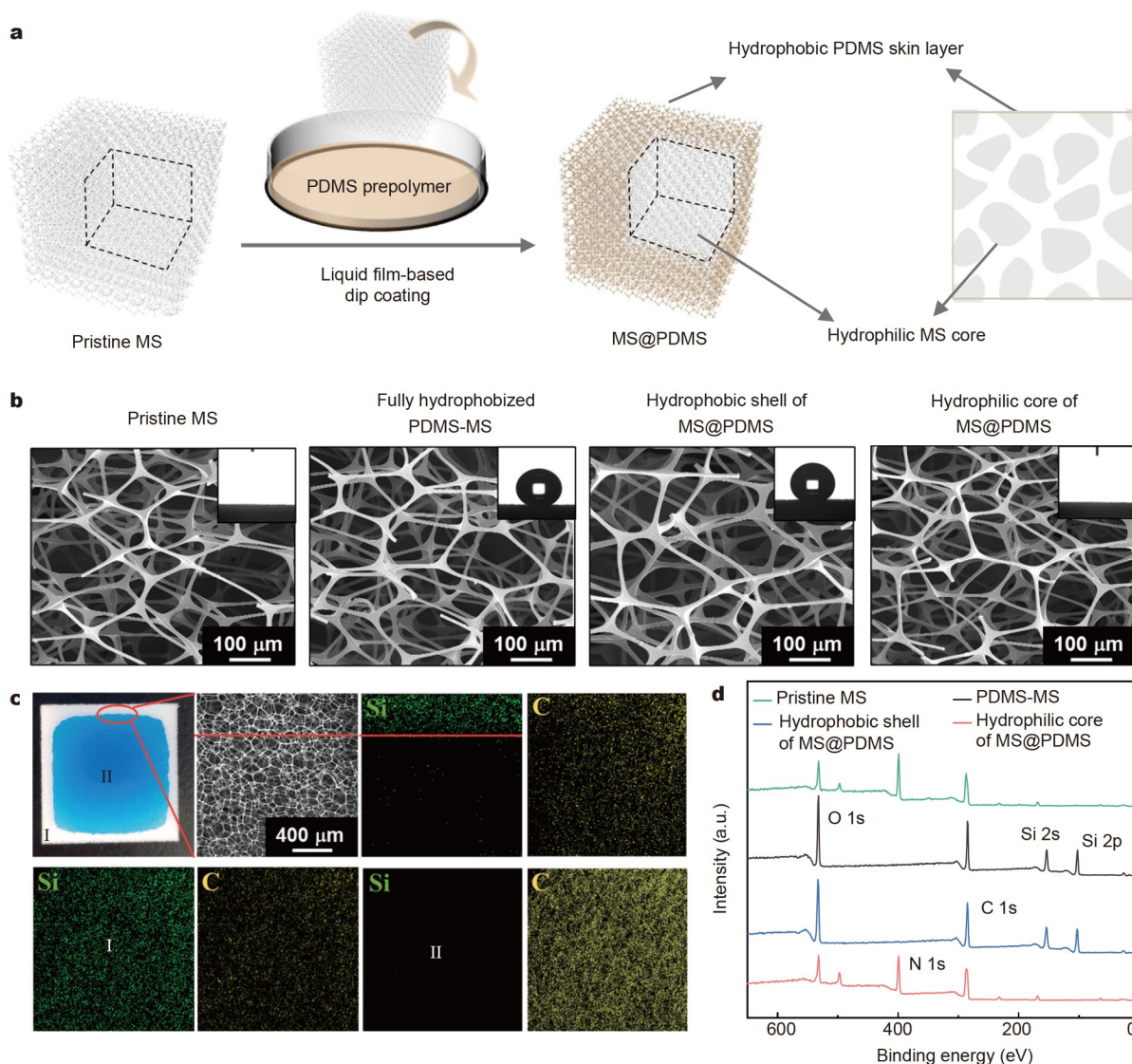
Figure 2 (a) Fabrication of MS@PDMS using a liquid film-based coating method. (b) SEM images of pristine MS, hydrophobized PDMS-MS, and hydrophobic shell and hydrophilic core of MS@PDMS, respectively. Insets show the corresponding water contact angles. (c) EDS analyses of the junction area, the skin layer (I) and the core area (II) of MS@PDMS. (d) XPS spectra of pristine MS, hydrophobized PDMS-MS, and MS@PDMS.

the hydrophobic skin layer of MS@PDMS at the beginning, and the crude oil was thus subjected to similar capillary forces in the porous channels of the PDMS-MS and MS@PDMS. However, once the crude oil submerged the hydrophobic skin layer of MS@PDMS, its internal hydrophilic channels would exert a greater capillary force and accelerate the absorption of the crude oil into the sponge, resulting in a faster sinking of MS@PDMS.

A self-built setup was constructed to measure the absorption speeds of the three sponges towards crude oil (Fig. 3d). The sponge sample connected to a force sensor was placed above a crude oil reservoir, which was gradually lifted until the oil surface was in contact with the bottom surface of the sample. Upon contact, the crude oil would be sucked into the sponge and the weight of absorbed oil was measured by the force sensor. Fig. 3e, f show the representative weight-time curves and the corresponding absorption speed-time curves obtained in the absorption process. MS@PDMS can absorb more crude oil than PDMS-MS in the same duration, and with prolonged time, the

difference in the weight of absorbed oil between them gradually increases. After tens of seconds, the absorption saturation is reached, and the absorption speeds of the three sponges gradually approach zero. Obviously, MS@PDMS exhibits a much faster absorption of crude oil than PDMS-MS.

PDMS-MS took about 28.4 s to absorb 1.1 g of crude oil, close to its saturated absorption mass. In comparison, MS@PDMS only took about 18 s to attain the same absorption mass, manifesting a 36% reduction of the absorption time. Such a difference originates from the smaller advancing angle of pristine melamine material compared with that of the PDMS coating (10° $vs.$ 60°) (Fig. S1), and confirms that the skin-hydrophobized sponges are superior to conventional fully-hydrophobized ones as oil sorbents.

Besides MSs, balsa wood sponges (WSs, another type of porous materials) were also employed to test the feasibility of this strategy of using skin-hydrophobized hydrophilic sponges for rapid oil-selective absorption (Fig. S3). Unlike the MSs, the WSs
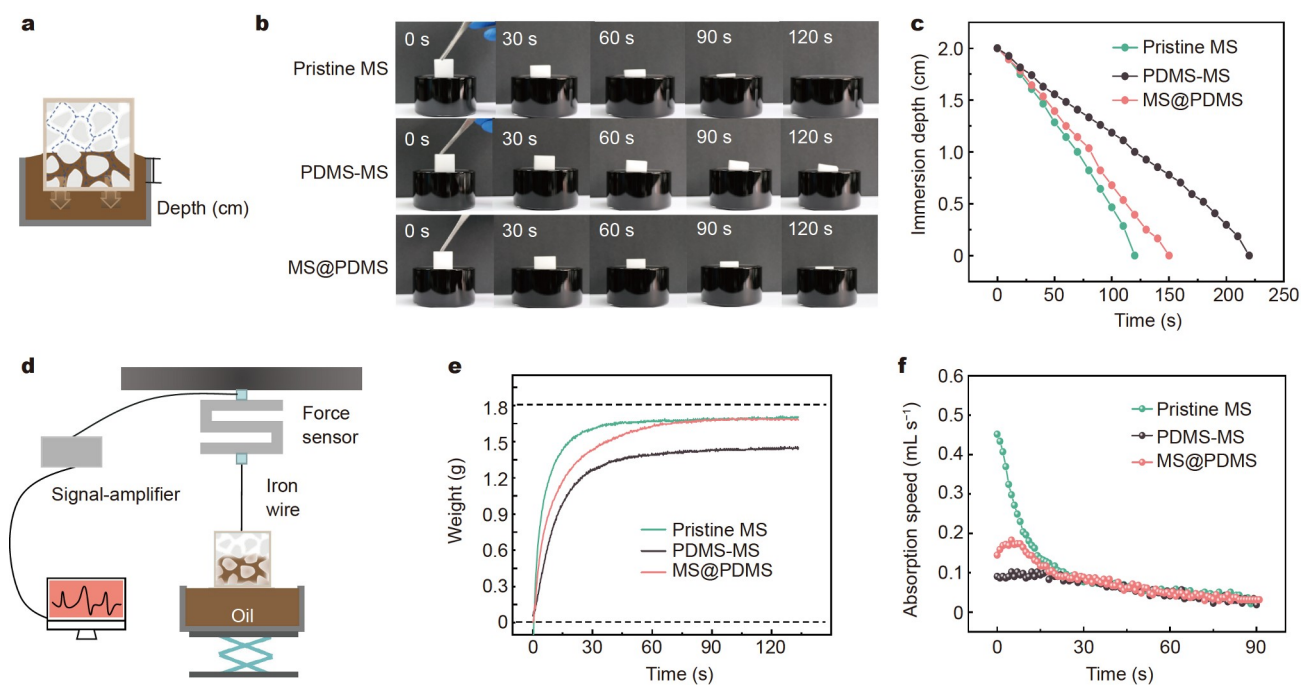
Figure 3 (a) Schematic of spontaneous sinking of sponge into crude oil. (b) Sequential images showing the sinking behavior of pristine MS, PDMS-MS and MS@PDMS, and (c) the corresponding time-dependent immersion depth. (d) Schematic illustration of the set-up for the measurement of the oil absorption speed. (e) The weight of viscous crude oil absorbed into different MSs (2 cm × 2 cm × 2 cm) *versus* the sorption time. (f) The corresponding real-time absorption speed for different samples.

have a lamellar structure with gaps of about 50–100 μm (Fig. S3a, b). Though structurally different from the MSs, the skin-hydrophobized WS (WS@PDMS) also showed much faster crude oil absorption than the fully hydrophobized WS (PDMS-WS), indicating the versatility of our strategy (Fig. S3c–f).

We further investigated the performance of MS@PDMS and PDMS-MS in the cleanup of oil spills from oil-water mixtures. The breakthrough pressure of MS@PDMS was first evaluated by pressing it into water and measuring the critical depth at which water began to penetrate into the interior of the sponge. MS@PDMS showed a breakthrough pressure of about 2.45 kPa, confirming that an effective water barrier was achieved by the hydrophobic skin layer. In the oil-water separation test, water (40 mL) and crude oil (4 mL) were added into a beaker to simulate a practical scenario of the crude oil spill. The sponge was gently put into the beaker and the oil cleaning process was recorded (Fig. 4a). After 30 s of absorption, most crude oil was absorbed by MS@PDMS. However, PDMS-MS only absorbed a small amount of crude oil in the same period. After 90 s, the crude oil was almost completely absorbed by MS@PDMS with only a minimal amount of residual slick oil, whereas more crude oil remained on the water surface after absorption by PDMS-MS. We also measured the concentration of residual crude oil in the oil-water mixture at different absorption periods and calculated the corresponding crude oil separation ratio (Fig. 4b). MS@PDMS took only 50 s to achieve a separation ratio of 80%. In contrast, PDMS-MS took nearly twice as long to reach the same separation ratio. These results clearly confirm the great advantage of MS@PDMS over PDMS-MS as a highly efficient sorbent in oil spill remediation.

To demonstrate the universality of the oil absorption speed advantage of MS@PDMS, we tested a variety of crude oils with different viscosities (Fig. 4c). The average absorption speed

decreased with the viscosity of the tested oils. Nevertheless, regardless of the viscosities of crude oils, the absorption speed of MS@PDMS was always faster than that of PDMS-MS. Fig. 4d shows the enhancement factor of the absorption speed between the two sponges, which becomes more pronounced for high-viscosity oils. This may be due to the difference in their intrinsic advancing angles θ_A. It can be inferred from Equation (3), the difference in absorption speed is mainly determined by the cosine of their intrinsic advancing angles ($\cos\theta_A$). High-viscosity oils exhibited more significant differences in $\cos\theta_A$ between the two sponges, thus leading to more pronounced differences in the enhancement factor (Fig. S4). MS@PDMS also manifested excellent recoverability and reusability as a sorbent for the cleanup of crude oil spills. Its absorption capacity showed a negligible decline and remained above 110 g g^{-1} after 10 cycles of repeated absorption/releasing tests (Fig. 4e).

MS@PDMS and WS@PDMS can not only remove the floating crude oil from the water surface, but also can clean up heavy immiscible organic solvents under water (Fig. 4f and Fig. S5). MS@PDMS can be immersed into a water reservoir, free from being wetted by water, and rapidly absorb chloroform spills deposited on the bottom of the reservoir. These phenomena indicate the great potential of MS@PDMS for eliminating oil and chemical spills from water. To quantitatively evaluate the oil-water separation efficiency of MS@PDMS, a variety of organic liquids, including diesel, cetane, mineral oil, crude oil, and silicone oil, were tested. The residual oil content in the water after absorption was measured using an FT-IR oil meter and the separation efficiency was calculated. Chloroform was not used in the quantitative investigation because it is highly volatile and the residual content can hardly be measured accurately. MS@PDMS was able to clean up the organic liquids in a highly efficient way and the separation efficiency is above 98.8% for all the tested oils
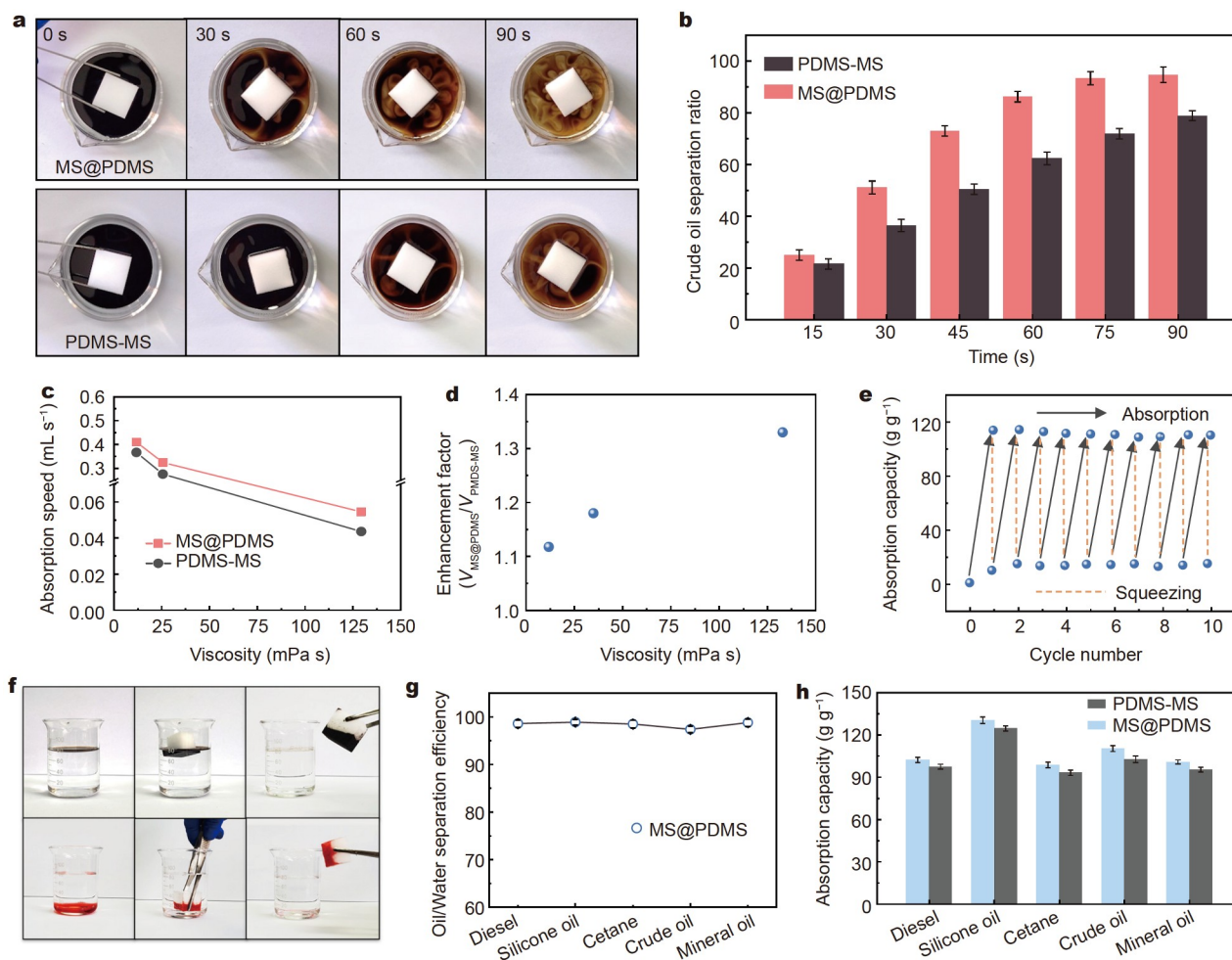
Figure 4 (a) Sequential images showing the absorption of crude oil leakage on the water surface using the hydrophobized PDMS-MS and MS@PDMS (size 2 cm × 2 cm × 2 cm). (b) Crude oil separation ratio as a function of time. (c) Absorption speed of the samples in respect to crude oils of different viscosities. (d) Enhancement factor of the absorption speed ($V_{MS@PDMS}/V_{PDMS-MS}$). (e) Absorption capacities of MS@PDMS for crude oil in cyclic absorption experiments. (f) Removal of crude oil on the water surface and chloroform under water bottom with MS@PDMS. (g) Separation efficiency of MS@PDMS for different oils. (h) Absorption capacities of PDMS-MS and MS@PDMS for different oils.

(Fig. 4g). The absorption capacity of MS@PDMS was also investigated, and MS@PDMS exhibited mildly enhanced absorption capacity than PDMS-MS for all the oils (Fig. 4h). For example, PDMS-MS has an absorption capacity of 92.2 for cetane, whereas it is 99.3 for MS@PDMS. This may be due to the fact that the initial mass of PDMS-MS is about 9% higher than that of MS@PDMS, and moreover the PDMS-modified skeleton of PDMS-MS occupies more inner space where the oil could be absorbed. Consequently, a larger specific absorption capacity is thus expected for the oil sorbent with only hydrophobic skin layer. The WS-based sorbent showed the same trend in the absorption capacity, and the skin-hydrophobized WS@PDMS exhibited improved absorption capacity than the fully hydrophobized PDMS-WS for all the tested oils, attributed to the decreased initial mass (by about 1%) and the less occupied inner space of the former sorbent (Fig. S6). The enhanced absorption capacity thus endows the skin-hydrophobized sponge with an additional advantage over its fully hydrophobized counterpart in oil spill remediation.

The skin-hydrophobized sponge can not only work as an oil sorbent, but also function as a porous filter for gravity-driven oil-water separation (Fig. 5a). While the hydrophobic skin layer

of MS@PDMS prevents water permeation, oils can penetrate through the sponge effortlessly. When a mixture of chloroform and water was fed onto the MS@PDMS filter, chloroform readily permeated through the sponge and colorless water remained above it. Besides gravity-driven separation [45], MS@PDMS can also be used for continuous oil-water separation with the assistance of an external pump (Fig. 5b) [46,47]. MS@PDMS was connected to the inlet of a peristaltic pump with a plastic hose and the outlet of the pump was connected to an oil collection beaker with another hose. Driven by the pump, MS@PDMS can continuously absorb oil spills from the oil-water mixture and release the oil to the collection beaker *via* the plastic hoses. MS@PDMS can effectively and continuously separate crude oil, mineral oil, hexadecane and other organic liquids from their oil-water mixtures with a separation efficiency of over 98% (Fig. 5c). All the above results prove the promising application potential of MS@PDMS in oil-water separation. MS@PDMS also showed excellent stability regarding the surface chemistry of its skin layer. After 12 h of ultrasonic treatment in a solvent of *n*-hexane or acetone, MS@PDMS still kept stable hydrophobicity (Fig. S7a). In response to marine oil spill accidents, the oil sorbent should have well seawater corrosion resistance. When
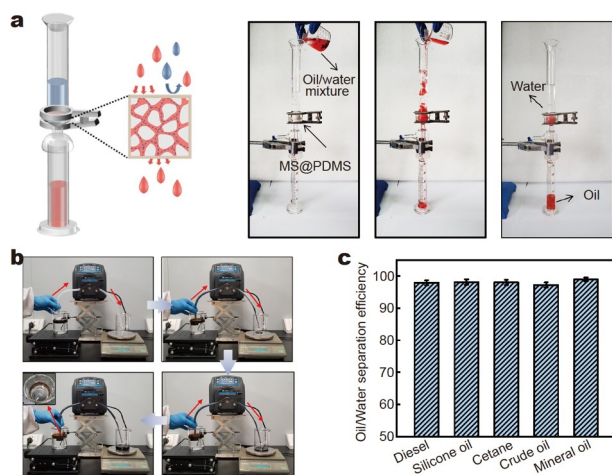
Figure 5 (a) Gravity-driven separation of chloroform/water mixture using MS@PDMS. (b) Sequential images showing the continuous removal of crude oil from a nonturbulent oil/water system. Inset: optical photograph of the interior of the beaker after continuous separation, shows no oil remaining on the water surface with only a small amount of oil adhered to the wall of the beaker. (c) Separation efficiency for different oils in continuous oil/water separation.

immersed into a simulated seawater of 3.5 wt% NaCl solution for tens of hours, MS@PDMS showed an only very limited reduction on the surface hydrophobicity. Its water contact angle remained about 146° after 72 h of immersing, verifying the durability of the hydrophobic skin layer (Fig. S7b).

CONCLUSIONS

In summary, a unique type of oil sorbent, i.e., hydrophilic sponges with hydrophobic skin layer, is developed *via* a facile liquid film-based dip coating technology. Compared with the prevailing fully-hydrophobized sponges, such skin-hydrophobized sponges only require functionalization of the outmost thin layer with low-surface-energy modifier, and thus greatly reduce the consumption of chemical reagents as well as accompanying environmental impact. The hydrophobic skin layer endows the sponges with selective oil absorption capability from oil-water mixtures. More importantly, the skin-hydrophobized sorbent exhibits a greatly enhanced oil absorption speed than its fully hydrophobized counterpart, benefitting from the strong capillary action of the hydrophilic inner channels. The specific absorption capacity is also improved, as such skin layer functionalization reduces the mass of the sorbent and allows more inner space for oil storage. We believe that the skin-hydrophobization strategy opens an environmentally friendly avenue to develop advanced sorbents for high-performance oil spill remediation.

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Supplementary information Supporting data are available in the online version of the paper.

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非传统吸油剂: 疏水皮肤层的亲水海绵用于高效溢油清理

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摘要 基于多孔材料的油水分离为解决溢油污染问题提供了一个有前景的途径. 传统上, 为了实现选择性吸油, 多孔材料需要用低表面能化学试剂进行充分的疏水处理, 以赋予其疏水/亲油特性. 然而, 这种充分的疏水处理既导致了高成本, 又由于过度的化学试剂消耗增加了环境危害, 阻碍了其实际应用. 在此, 我们通过一种简单的液体薄膜浸渍技术, 开发了一种替代性的吸油剂, 即具有疏水皮肤层的亲水海绵. 与传统的全疏水吸油剂不同, 我们制备的海绵只有最外层用疏水聚二甲基硅氧烷(PDMS)涂层进行了改性, 疏水化学试剂消耗减少达80%. 该海绵疏水皮肤层阻挡了水的进入, 而内部亲水主体促进了油的吸收, 因此可以从油水混合物中高度选择性吸收油. 更重要的是, 这种皮肤层结构海绵表现出增强的吸油速度. 与传统的疏水海绵相比, 在吸收相同质量原油时, 吸收时间可减少36%. 这主要归功于其亲水内部通道相比于传统吸油剂疏水通道具有更强大的毛细管吸收作用. 此外, 该海绵还显示出比完全疏水海绵更强的吸收容量. 这项研究提供了一个开发具有增强吸油性能的低成本、环境友好吸油剂的通用策略.