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A Superhydrophobic Sponge with Excellent Absorbency and Flame Retardancy**

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Abstract: *Frequent oil spillages and the industrial discharge of organic solvents have not only caused severe environmental and ecological damage, but also create a risk of fire and explosion. Therefore, it is imperative, but also challenging, to find high-performance absorbent materials that are both effective and less flammable. Here we present a superior superhydrophobic sponge that exhibits excellent absorption performance through a combination of its superhydrophobicity, high porosity, and robust stability. More importantly, it inherits the intrinsic flame-retardant nature of the raw melamine sponge, and is thus expected to reduce the risk of fire and explosion when being used as an absorbent for flammable oils and organic compounds. Moreover, the fabrication of this sponge is easy to scale up, since it does not use a complicated process or sophisticated equipment. These characteristics make the sponge a much more competitive product than the commercial absorbent, nonwoven polypropylene fabric.*

With increasing industrial development, frequent oil spillages and the industrial discharge of organic solvents have caused severe environmental and ecological damage.[1] The Gulf of Mexico oil spill in 2010, the largest accidental oil release in history, greatly harmed the coastline and near-shore waters, creating a disaster for marine animals and organisms. The effects of that spillage may last for decades.[1d] Aside from environmental and ecological issues, the spilled oil and organic compounds usually create a risk of fire and explosion, since crude oil and most organic solvents are highly flammable and extremely dangerous if ignited. Therefore, it is imperative, but also challenging, to explore high-performance absorbent materials that are both effective and less flammable.

Common absorbents, including various inorganic absorbents,[2] natural organic fibres,[3] and synthetic organic polymers,[4] tend to suffer from poor selectivity and low absorption capacity. In recent years, a number of new and advanced absorbent materials have been developed which have demonstrated significantly improved absorption performance towards various oils and organic solvents. Ultralight carbon aerogels, including carbon nanofiber aerogels derived from bacterial cellulose, nitrogen-doped graphene frameworks, and ultra-lightweight carbon aerogels, exhibit superior absorption capacity because of their ultralow density (below 10 $\mathrm{mg\,cm^{-3}}$).[5] Porous boron nitride nanosheets, as prepared by Lei et al., show excellent recyclability as a result of their strong resistance to oxidation and chemical inertness.[1a] Superwetting nanowire membranes, as prepared by Yuan et al., exhibit controlled wetting behavior and a high level of selectivity for a wide range of organic solvents and oil.[1b] Hayase et al. reported the preparation of a robust marshmallow-like macroporous gel that can be used as an absorbent over a wide temperature range.[6] Although extensively implemented in research, these materials often have limitations for commercial application because of the difficulty of large-scale fabrication and their high cost. Moreover, none of these materials have been proven to have a flame-retardant nature.

The melamine sponge (melamine-formaldehyde sponge, denoted MF sponge) is an ideal flame retardant due to its high nitrogen content.[7] When exposed to heat, the MF sponge will degrade and release N_2. The released nitrogen will replace the oxygen surrounding the material, thus preventing further burning. In addition to this flame-retardant property, the MF sponge is characterized by its light weight, high porosity, and robustness, all of which are highly desirable in a high-performance absorbent.[8] With this inspiration, here we present the fabrication of a superior superhydrophobic sponge that overcomes any fundamental limitations as it uses a commercially available and low-cost MF sponge. A simple and mild two-step strategy is used to prepare the superhydrophobic sponge. First, the simple immersion of the original hydrophilic MF sponge in an aqueous solution of dopamine leads to the spontaneous deposit of a thin layer of polydopamine (PDA) films over the entire surface.[9] Subsequently, a monolayer of hydrophobic molecules with low surface energy is covalently grafted on the sponge through simple immersion of the PDA-coated sponge into an ethanolic solution of mercapto-functionalized hydrophobic molecules (1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol).[9a,b] The obtained sponge exhibits excellent absorption performance, including a high absorption capacity, excellent selectivity, and extraordinary recyclability, through a combination of its superhydrophobicity, high porosity, and robust stability. More importantly, it inherits the intrinsic flame-retardant nature of the raw sponge, and is thus expected to reduce the

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risk of fire and explosion when being used as an absorbent for flammable oils and organic compounds. Furthermore, this approach is much more convenient, economical, and environmentally friendly than conventional processes for surface modification, including dip coating with a polymer, chemical vapor deposition (CVD), additional polymerization of the organic molecule, and electrostatic deposition.[10] It does not need multistep procedures, harsh conditions, sophisticated equipment, or an aggressive etching solution, thus making it possible to synthesize on a large scale.

Scanning electron microscopy (SEM, Figure 1 a,b) images of the sponge before and after the hydrophobic modification display exactly the same microstructures, thus confirming that the mild reactions do not damage the original structure and morphology of the MF sponge. Both sponges reveal an inherent three-dimensional (3D) interconnected network and a highly porous structure. None of the pores inside the modified sponge are blocked. These characteristics will be beneficial for the rapid uptake of oil, as the open-pore network permits rapid transport of gas and liquid in the sponge.[11] The successful grafting of the hydrophobic molecules on the surface was confirmed by X-ray photoelectron spectroscopy (XPS) and ^{19}F solid-state NMR spectroscopy[12] (see Figures S1 and S2 in the Supporting Information). The surface wetting property of the modified sponge was examined by means of water contact angle measurements. As shown in Figure 1 c,d, a water droplet is absorbed by the unmodified sponge immediately after reaching its surface because of the sponge's superhydrophilicity; in contrast, the modified sponge displays a water contact angle of 163.4°, thus demonstrating its superhydrophobicity. After being placed on the surface of water, the unmodified sponge sinks to the bottom within a few seconds, because of its open-pore structure and superhydrophilicity. However, the modified sponge floats on water without sinking, as a result of its light weight, superhydrophobicity, and water-repellent nature (Figure 1 e). The water-repellent behavior of the superhydrophobic sponge is further confirmed by the photographs in Figure 1 f. A control experiment on a glass slide prepared by the same coating treatment produces a slightly hydrophobic surface, with a water contact angle of 97.3° (see Figure S3c in the Supporting Information). This indicates that the surface coating itself is not the sole contributor to the superhydrophobicity of the modified sponge. It is well known that the wetting property of the surface is determined by the fraction of air trapped on the surface, the surface roughness, and the material composition.[1b] As a consequence of the 3D interconnected network, the high porosity, and the hydrophobic coating of the modified sponge, the water drop on the sponge is supported not only by the protruding fibers of the sponge, but also by the air trapped in the sponge. Thus, it retains a quasispherical shape, yielding a large static water contact angle.[13] According to the Cassie Equation,[14] 95.2 % of the contact area between the water droplet and the sponge surface is occupied by air (see Figure S3 in the Supporting Information for details of the calculation), which is in accordance with the high porosity of the sponge (99.5 %). Furthermore, the superhydrophobicity does not occur in the absence of the PDA coating, thus confirming that the hydrophobic molecule is immobilized onto the surface of the sponge through covalent interactions with the PDA film (see Figure S3d in the Supporting Information).

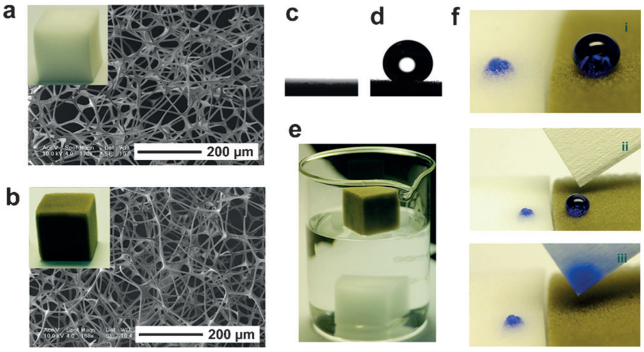

Figure 1. a) SEM image of the unmodified MF sponge. Inset: photograph of the unmodified sponge. b) SEM image of the superhydrophobic MF sponge. Inset: photograph of the modified sponge. c) The water contact angle of the raw MF sponge. d) The water contact angle of the modified sponge (163.4°). e) Photograph of the raw MF sponge and the modified MF sponge after placement on the water surface. f) The residue of the dyed water on the surface of the raw sponge, and the quasispherical water droplet on the surface of the modified MF sponge. This water droplet can be removed by a piece of filter paper without any residual dye.

Most organic solvents and crude oil are highly flammable and extremely dangerous when ignited. In 2013, the Qingdao oil pipeline blast in China caused 62 deaths. Similar accidents occur occasionally when clearing spilled oil and other flammable organic compounds. The MF resin has a flame-retardant property, and thus we believed that the superhydrophobic MF sponge might inherit this advantage and have the potential of reducing the risk of fire and explosion. To validate this assumption, the combustion behavior of the superhydrophobic MF sponge was investigated using cone calorimetry. For comparison, a commercial absorbent, nonwoven polypropylene fabric (denoted PP fabric), was also subjected to the same test. After being ignited, a bright and vigorous flame is observed on the PP fabric, and it continues to burn completely (Figure 2 a,c, the burning lasts for more than 1 min). In contrast, the flame on the superhydrophobic MF sponge is weak and extinguishes within three seconds, leaving behind a black residue (Figure 2 b,c, 21 % of the original weight). This indicates the improved flame-retardant property of the modified MF sponge.[15] As expected, the heat release rate (HRR) of the sponge is much lower than that of PP fabric (Figure 2 d). The maximum heat release rates (PHRR) are 394.2 and 36.2 $\mathrm{kW\,m^{-2}}$ for the PP fabric and the superhydrophobic MF sponge, respectively. The total heat release (THR) of the superhydrophobic MF sponge is also much lower than that of the PP fabric (Figure 2 e). Thus, the superhydrophobic MF sponge is expected to reduce the risk of fire and explosion when being used as an absorbent for flammable oils and organic compounds. To further confirm the above conclusion, 1-octadecene was used as the model material to investigate its combustion behavior in the presence of these two absorbents. The PP fabric shows no

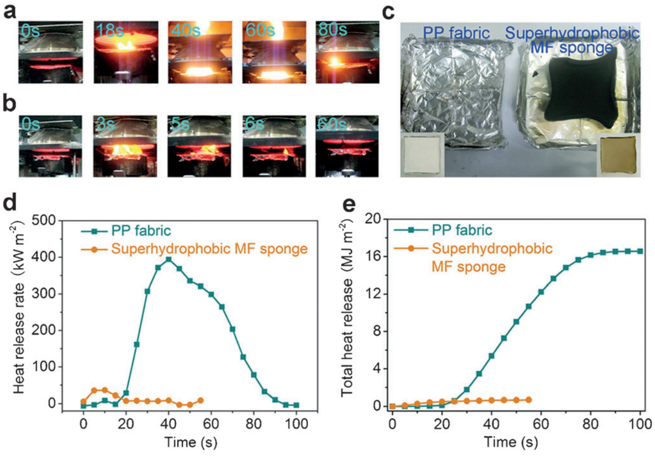

Figure 2. a) The combustion process of the PP fabric. b) The combustion process of the superhydrophobic MF sponge. c) Residues after burning. Insets: the corresponding samples before test. d) HRR curves. e) THR curves.

sign of a flame-retardant nature towards the absorbed 1-octadecene (see Figure S4a in the Supporting Information). In contrast, the 1-octadecene absorbed by the superhydrophobic MF sponge extinguishes a few seconds later after being ignited, leaving behind a half-burnt sponge (see Figure S4b in the Supporting Information). The total weight of the residue is 61 % of the original weight (both 1-octadecene and MF sponge are included), further confirming the good flame-retardant property of the superhydrophobic MF sponge.

As a result of the excellent mechanical stability of the substrate, the superhydrophobic sponge exhibits considerable robustness against various harsh conditions, including harsh compression tests and various organic solvents. As shown in Figure 3 (see also Figure S5 in the Supporting Information), the as-prepared sponge exhibits excellent flexibility and recovers its original shape after compression. Importantly, the 3D interconnected network and the high porosity of the sponge are maintained without apparent structural damage even after 1000 cycles of a 60% compression test (see Figure S6 in the Supporting Information for SEM images). In addition to its compressability, the as-prepared sponge is highly stable and robust against various organic solvents. After being immersed into various organic solvents for one hour, the sponges retain not only their surface hydrophobic property, but also the mechanical stability of the framework (see Figures S7 and S8 in the Supporting Information). The robust stability endows the sponge with excellent recyclability, which is of great significance for practical applications.

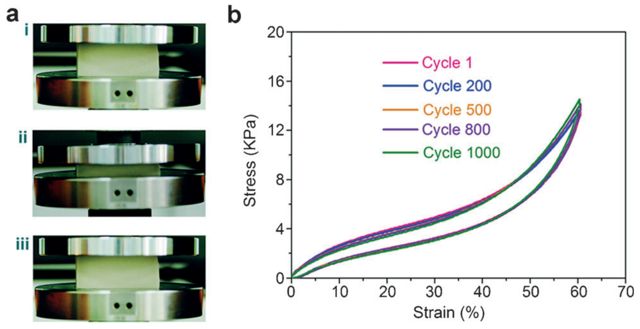

Figure 3. a) Sequential photographs of the superhydrophobic MF sponge during the compression process (60% strain). b) The compressive stress–strain curves of the superhydrophobic MF sponge over 1000 cycles.

Its high porosity, superhydrophobicity, and robust stability make the MF sponge a perfect candidate for the quick removal of various oils and organic solvents. The superhydrophobic sponge exhibits excellent absorption capacities towards a wide range of oils and organic solvents, up to 79–195 times of its own weight depending on the density of the liquid (Figure 4a). Such an excellent adsorptive property is far superior to that of commercial PP fabric (5–12 times, see Figure S9a in the Supporting Information) and many previously reported high-performance absorbents.[1a,b,6,16] Furthermore, as a result of the high porosity of the as-prepared sponge, it has a comparable volumetric absorption capacity (approximately 72–90%, see Figure S10 in the Supporting Information) to ultralight carbon aerogels.[5]

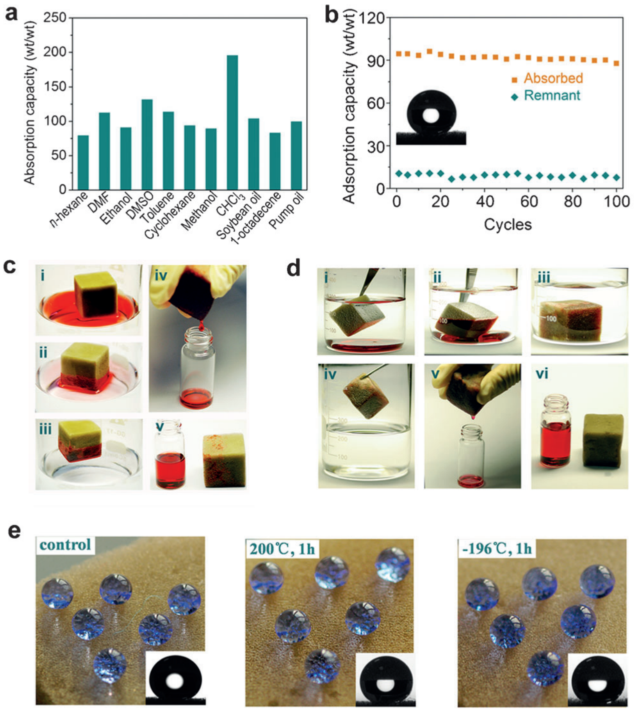

Figure 4. a) Gravimetric absorption capacities of the superhydrophobic MF sponge. b) Absorption capacity and residual amount of cyclohexane over 100 absorption/squeezing cycles. Inset: the water contact angle is 158.3° after 100 cycles of measurement. c) The absorption and recycling process of 1-octadecene. d) The absorption and recycling process of the underwater chloroform. e) Photographs of dyed water droplets (10 μL) on the surface of the superhydrophobic MF sponges before and after low-/high-temperature exposure for 1 h. Inset: the corresponding water contact angle.

The recyclability of the absorbent and the recoverability of the absorbed liquid are key criteria for the clean-up of oil spills. Cyclohexane was used as the model absorbate to investigate the cyclic absorption/squeezing behavior of the sponge. No apparent deterioration in the absorbency was observed over 100 repetitions, thus indicating its excellent recyclability (Figure 4b). Nearly 90% of the absorbed cyclohexane could be squeezed out mechanically during each cycle. Importantly, the superhydrophobicity of the sponge remained intact after 100 cycles of the absorption/squeezing test, as evidenced by the high water contact angle of 158.3° (inset in Figure 4b) and the presence of an F1s signal in its XPS spectrum (see Figure S11 in the Supporting Information). For comparison, a control experiment consisting of cyclic tests on PP fabric was performed. The PP fabric shows poor cyclic absorption/squeezing behavior (see Figure S9c in the Supporting Information) because of a lack of elasticity (see Figure S9b in the Supporting Information). Furthermore, the recovery efficiency of the absorbed solvent is very low, that is, approximately 30–40% residual cyclohexane remains in the fabric after squeezing and wringing. Besides mechanical squeezing, distillation is also used extensively to recycle organic solvents, particularly with fragile absorbents and other materials unsuitable for compression. Three types of solvents with boiling points below the melting temperature of PP (cyclohexane, toluene, and xylene) were used as model absorbates to investigate whether it is feasible to recycle these solvents using PP fabric by distillation. The PP fabric loses its structural integrity when heating a mixture of PP fabric and solvents to the corresponding boiling point of each solvent (see Figure S12a–c in the Supporting Information). In contrast to PP fabric, the superhydrophobic MF sponge is highly stable and robust against various harsh environments, including heating (200°C, 1 h), freezing (−196°C, in liquid nitrogen for 1 h), and boiling in organic solvents (at the corresponding boiling point of cyclohexane, toluene, and xylene for 1 h; see Figure 4e as well as Figures S12d–i, S13, S14, and S15 in the Supporting Information). These features may further extend the potential use of the sponge, thus making it an attractive candidate for the clean-up of oil spills, recovery, and purification.

To further verify the feasibility for practical applications, two organic solvents with different densities, 1-octadecene and chloroform, were chosen as model absorbates to investigate the oil/water separation performance of the superhydrophobic sponge. Once the superhydrophobic sponge is dropped on the oil/water surface, it immediately absorbs the dyed oil (1-octadecene dyed with oil red) and becomes red (Figure 4c). The process is fast: all the oil was absorbed by the sponge within a few minutes. Such fast absorption kinetics of the sponge is attributed to the combination of its high porosity, oleophilic nature, and capillary action. As a consequence of its superhydrophobicity and low density, the sponge still floats on the water surface after absorbing all the oil, and is therefore easy to collect. Subsequently, the absorbed oil can be recycled easily through mechanical squeezing. The sponge retains its original morphology and size after the absorbed solvent is squeezed out, and only a small amount of residual oil is present on the surface of a used sponge. Chloroform, in contrast, sinks to the bottom of water (stained with oil red) but can also be removed and recycled efficiently using the superhydrophobic MF sponge (Figure 4d). A control experiment on cotton demonstrated its poor separation efficiency (see Figure S16 in the Supporting Information). As a next step, the practical application of the superhydrophobic MF sponge for crude oil removal was investigated. Once the sponge is dropped on a crude oil/water surface, it immediately absorbs the black oil, thereby causing the saturated portion to turn black (Figure 5a). Within a few minutes, all the oil is taken up by the sponge, leaving a fresh water surface. Subsequently, the sponge is taken out to collect the crude oil by manual squeezing. As the crude oil is viscous, some residual oil will stick to the sponge after the oil is recycled by squeezing. Therefore, solvent extraction was applied for further regeneration of the sponge and recovery of the oil. As expected, all the residual oil sticking to the sponge can be easily washed out by cyclohexane without sacrificing the superhydrophobicity of the sponge (see Figure S17 in the Supporting Information). Furthermore, the sponge recovers its original size and morphology because of its robust stability, thus indicating the recovery of the initial absorption efficiency.

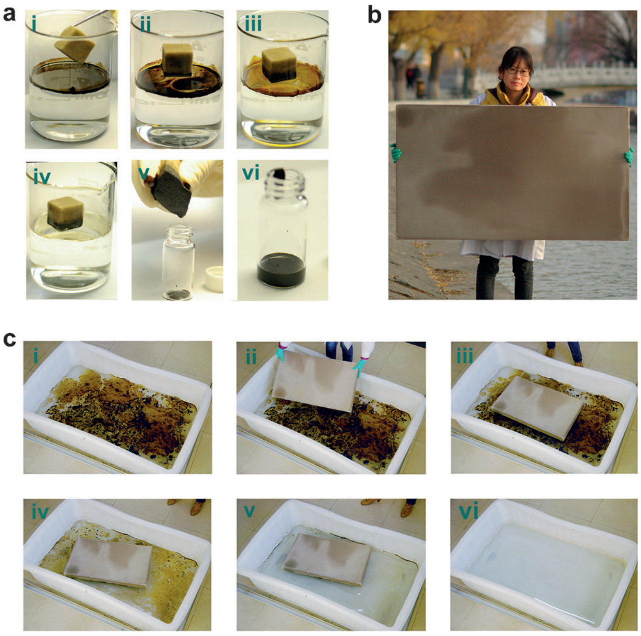

Figure 5. a) The absorption and recycling process of crude oil. b) The scalable manufacture of the superhydrophobic MF sponge (size: 120 cm × 70 cm × 5 cm). c) Removal of crude oil from water using the superhydrophobic MF sponge (size of sponge: 70 cm × 40 cm × 5 cm).

For practical applications, it is essential to scale up production. Our approach is not complicated nor does it use sophisticated equipment. Therefore, it is quite easy to realize large-scale synthesis of the superhydrophobic MF sponge by simply enlarging the size of the raw sponge and the reaction container. As a proof of concept, a typical sample with a size of 120 cm × 70 cm × 5 cm was prepared (Figure 5b). To more realistically model the clean-up of an oil spill, an oil separation experiment was scaled up and performed in a large container (140 cm × 90 cm). The as-prepared sponge could successfully remove all the oil floating on the water surface within a few minutes, leaving a fresh water surface (Figure 5c). We believe that the large-scale production, combined with easy preparation will significantly increase the feasibility of practical application.

In summary, a superior superhydrophobic sponge with excellent absorption performance (including high capacity, good selectivity, extraordinary recyclability, and simple and versatile recycling routes), improved flame retardancy, and robust stability (against various organic solvents, heating, and freezing) was prepared through a straightforward two-step strategy. Moreover, the fabrication of this sponge is easy to scale up, since it does not use a complicated process or sophisticated equipment. Therefore, this superior sponge offers great technological promise in the field of water remediation, clean-up of large-area oil spills, and oil recovery.

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