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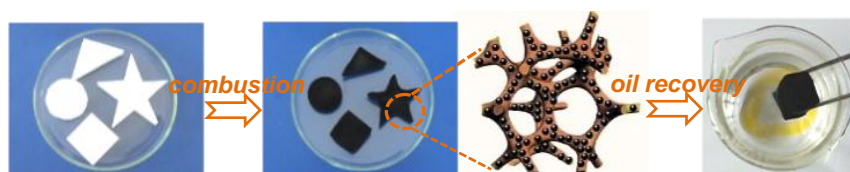
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An ultralight, superhydrophobic, compressible, self-cleaning, and fire-resistant sponge is achieved by a simple combusted-assisted in-situ carbon deposition method basing on commercially available melamine sponge.

Multifunctional, robust sponges by a simple adsorption-combustion method

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Three-dimensional porous materials with superior hydrophobic/oleophilic property hold considerable promise as absorbents for oil/water separation. However, it is still a challenge to produce high-efficiency oil absorbents on a large scale. A mild, broadly applicable, cost-effective method to yield absorbents with excellent absorption performance is desired. Herein we report for the first time a facile and inexpensive combust-assisted in-situ carbon deposition method to fabricate effective absorbents using a commercially available sponge as a porous substrate. This prototype offers large-scale preparation of the target product. The obtained sponge exhibits excellent hydrophobicity, fire-resistance, compressibility, and self-cleaning properties, and can effectively separate oils from water even under harsh conditions. More importantly, the obtained sponge is demonstrated with excellent oil recoverability and absorbent regenerability, being one of the most comprehensive oil absorbents. Moreover, this method is suitable for different types of porous substrates and will find widespread applications for the separation of oils from water.

Introduction

Three-dimensional (3D) porous materials have shown great application potentials in artificial muscles, electrodes, gas sensors, catalyst supports, and absorbents for water purification, by incorporating with some specific functionalities like biocompatibility, electrochemical property, gas sensitivity, catalysis, and metal ion-chelating ability.^[1] Recently, endowing the porous materials with hydrophobicity and oleophilicity has become increasingly important as the functional architectures obtained can be served as efficient absorbents to address the removal of spilled oils or leakage chemicals from water. Much effort has been devoted to develop advanced 3D porous materials with desirable wettability, most of which have been demonstrated significantly improved absorption performance towards various oils and organic solvents.^[2] For example, Yu et al. have prepared ultralight, flexible, and fire-resistant carbon nanofiber aerogels by pyrolyzing the bacterial cellulose.^[2e] The resultant carbon-based framework could absorb a wide range of organic solvents and maintain excellent recyclability and selectivity. Gao et al. have fabricated a compressible graphene-based aerogels with a superhydrophobic structure which was constructed with cell walls of giant graphene sheets and carbon nanotube ribs.^[2f] This kind of oil absorbents was demonstrated with extremely high absorption capacities for organic liquids as their ultralow density (as low as 0.16 mg cm⁻³). Zhang et al. have used raw cotton-derived hydrophobic aerogels to separate oils or organic solvents from water. This way had

comprehensive recyclability and provided a remarkable impact on oil/water separation.^[2g] Yet, with respect to the industrial production requirements, the possibility of large-scale production is a key criterion for their wide use in the practical applications.

Commercially available polymeric sponges, such as polyurethane (PU) and poly(melamine-formaldehyde) (PMF) sponges have been proved to be desirable templates for fabricating ultralight porous functionalized materials on a large scale.^[3] Owing to their easy operation of hydrophobic modification, a number of efficient polymeric sponge-derived oil absorbents were developed and most of them showed the possibility of large-scale production.^[4] The noteworthy achievements, like ultralight magnetic foams by pyrolyzing PU sponges grafted with metal acrylate,^[4b] elastic carbon foam via direct carbonizing PMF sponges at 1800 °C,^[4e] and fire-retardant sponges prepared by two-step modification of dopamine and mercapto-functionalized hydrophobic molecules based on PMF sponges,^[4f] offer great technological promise in the cleanup of oil-spills and provide enlightened inspiration to realize the massive production of oil absorbents. Nevertheless, certain drawbacks involve in current strategies such as overmuch cost of energy and time, the requirement of a complicated process or sophisticated equipment, and the large use of chemicals and nonaqueous solvents during the modification, which restrict their industrialization. A challenge, therefore, still facing practical applications is the large-scale production of porous materials with effective oily water

purification performance in a time-saving and cost-effective approach.

Herein, we report a new, efficient route for preparing ultralight, high-hydrophobic, fire-resistant sponges (UHF sponges) by a simply combust-assisted in-situ carbon deposition method based on commercially available PMF sponges without using any extra modification reagents or complicated processes for the first time. Compared with other polymeric sponges like PU sponges, the PMF sponges consist of a high content of nitrogen with the C:N weight ratio of about 1:9 (Table S1), endowing them and their derivatives with excellent flame-retardance.^[4e,f] The obtained UHF sponges have a micro-nanoscale hierarchical porous structure with vast carbon nanoparticles immobilized on the skeleton surface. The unique multiscale structure endows this 3D architecture with excellent oil absorption performance, including excellent absorption selectivity due to the hydrophobicity, high absorption capacity traced from the ultralow density, extraordinary recyclability resulted from the excellent fire-resistance and compressibility, and high oil keeping efficiency from the robust skeleton. In addition, the UHF sponges possess the remarkable self-cleaning property, which has a positive effect on avoiding the influence of solid impurities and enhances the durability of the surface wettability. More importantly, this simply combust-assisted in-situ carbon deposition strategy to realize the hydrophobization is much more convenient, economical, and time/energy-saving than conventional approaches for surface wettability modification, which included eliminating hydrophilic groups (like pyrolysis and chemical reduction),^[2c,5a] introducing groups of low surface tension (like fluoride groups),^[4b,f] using hydrophobic nanomaterials as the 3D building block (like chemical vapor deposition method),^[5b] and roughening the surface with multiscale structure like that of lotus leaf (nano-corrosion et al.).^[3d,4c] The excellent absorption performance, the self-cleaning property and the ability of easily large-scale production make this combust-assisted in-situ carbon deposition method an ideal strategy to fabricate oil absorbents with great potential applications in oil/water separation.

Experimental Section

Materials

PMF foams were provided by Guangzhou GreenCARE Co. Ltd., China. Nickel foams were achieved from Wuzhou Sanhe New Mater Co., Ltd., China. PU foams were purchased from local supermarket. Toluene was obtained from Guangdong Guangzhou Chemical Factory Co. Ltd., China. Hydrophobic SiO₂ nanoparticles and hydrophilic SiO₂ nanoparticles were kindly donated from Wacker Chemie (Burghausen) whose primary particles are approximately spherical of diameter between 5 and 30 nm.

Fabrication of UHF sponges

In a typical experiment, a piece of PMF sponge of 3 × 2 × 2 cm in size was washed with alcohol and distilled water three times, and then was dried in an oven at 80 °C. Toluene of 0.6 mL was added to the sponge, and then the toluene-absorbed sponge was under a compress-release cycle process for at least 5 times until the toluene was homogeneous distributing in the sponge. After that, the UHF sponge was achieved by lighting the toluene-absorbed sponge in a fuming cupboard.

Fabrication of hydrophobic nickel foams

The nickel foam was cleaned by washed with alcohol three times and dried in an oven at 80 °C. Then, the foam was wetted by toluene and lighted in a fuming cupboard for three times, and the hydrophobic nickel foam was obtained.

Fabrication of hydrophobic magnetic UHF sponges

A piece of PMF sponge of 3 × 2 × 2 cm in size was washed with alcohol and distilled water three times, and then was dried in an oven at 80 °C. 0.6 mL of oleic acid-modified Fe₃O₄ nanoparticle toluene suspension (0.5 wt %) was added to the sponge, and then the toluene-absorbed sponge was under compress-release cycle process for at least 5 times until the toluene and Fe₃O₄ nanoparticles were homogeneous distributing in the sponge. After that, the hydrophobic magnetic UHF sponge was achieved by lighting the toluene-absorbed sponge in a fuming cupboard.

Oil removal test

First, we measured the absorption capacity of the UHF sponges for various organic solvents and oils. The oil or organic solvent was poured in a beaker. UHF sponges were forced into the organic liquids for about 1 minute and then picked out for measurements. In order to avoid evaporation of absorbed organic liquids, weight measurements were performed quickly. The UHF sponge weights before and after absorption were recorded for calculating the values of weight gain.

Regeneration of UHF sponges and recoverability of oils

The regeneration of oil-adsorbed UHF sponges and recoverability of oils include absorption/distillation, absorption/combustion, and absorption/squeezing methods. First, in absorption/distillation cycles, the oil-adsorbed UHF sponges were regenerated by heat treatment at a selected temperature around the boiling point of the oil, and then the dried UHF sponges were used in a further cycle. For absorption/combustion cycles, the oil-adsorbed UHF sponges were applied for direct combustion in air, and then the no-oil UHF sponges were used in the next cycle. In absorption/squeezing cycles, the oil-adsorbed UHF sponges were employed for direct squeezing to recover the oil, and then the no-oil UHF sponges were used in the next cycle. The weights of UHF sponges were recorded before and after each cycle to determine the absorption capacity.

Characterization

The sample structure was observed by Scanning electron microscopy (SEM) images which were taken with a Zeiss EVO 18 scanning electron microscope equipped with a field emission electron gun and the contents of C, N and O were determined by energy-dispersive spectrometer (EDS) at an acceleration voltage of 5 kV. TGA was performed using a NETZSCH TG 209 instrument under an air atmosphere with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from 30 to $800\text{ }^{\circ}\text{C}$. The wetting properties of different samples were evaluated through contact angle tests, which were performed by the CAST 2.0 contact angle analysis system at room temperature (OCA20LHT-TEC700-HTFC1500, Dataphysics, Germany). The sonication treatment of the UHF sponge was conducted by a KQ 218 ultrasonic cleaner (Kunshan Ultrasonic Instruments CO.LTD, with a power of 100 W and a frequency of 40 KHz).

Results and Discussion

To reduce its hydrophilicity, as shown in Fig. 1a, the PMF sponge was homogeneously wetted by toluene via an absorb-compress-release cycle process with 50 mg cm^{-3} of sponge (Fig. S1). Then, the toluene-wetted sponge was lighted and directly burned in air resulting in UHF sponges. The size and shape of the UHF sponges can be finely tuned by changing the shape of the pristine PMF sponges (Fig. 1b,c), and it is feasible to fabricate a series of complex shapes of UHF sponges suited for different applications. Furthermore, scale-up production can be easily achieved by simply enlarging the size of the raw sponge, and a typical sample of $70 \times 70 \times 5\text{ cm}$ in size was prepared (Fig. 1d). Meanwhile, the combustion treatment is affectless to the general 3D interconnected porous structure of the sponges, while the morphology of the skeleton surface changes dramatically (Fig. S2 and Fig. 1e,f). Large amount of carbon nanoparticles of $\sim 100\text{ nm}$ densely and homogeneously cover the surface of the sponge, endowing the sponge with a highly rough structure at nanometer and micrometer scale simultaneously. This can be ascribed to the incomplete combustion process which generates abundant carbon nanoparticles and the flame source provides high temperature environment to heat the sponge for enhancing the deposition and immobilization of the carbon nanoparticles on the sponge surface. Other carbon sources like xylene which possess a higher temperature during the combustion process cannot achieve similar structures due to their intense thermal action which is too harsh for the generation and deposition of carbon nanoparticles (Fig. S3). Although some carbon sources with lower temperature in the combustion like benzene can achieve similar structure as that of toluene case, they are not suitable for the practical applications due to the high toxicity (Fig. S4). Moreover, it was found that increasing the toluene amounts do not have obvious influence on the sponge structure and properties (Fig. S5). Therefore, the optimal prospectus should be fixed at using toluene as carbon source with a dosage of 50 mg cm^{-3} . In addition, the carbon nanoparticles exhibit robust immobilization with a resistance sonication in ethanol

for 2 min with significant amount of carbon nanoparticles still anchoring on the sponge surface (Fig. S6).

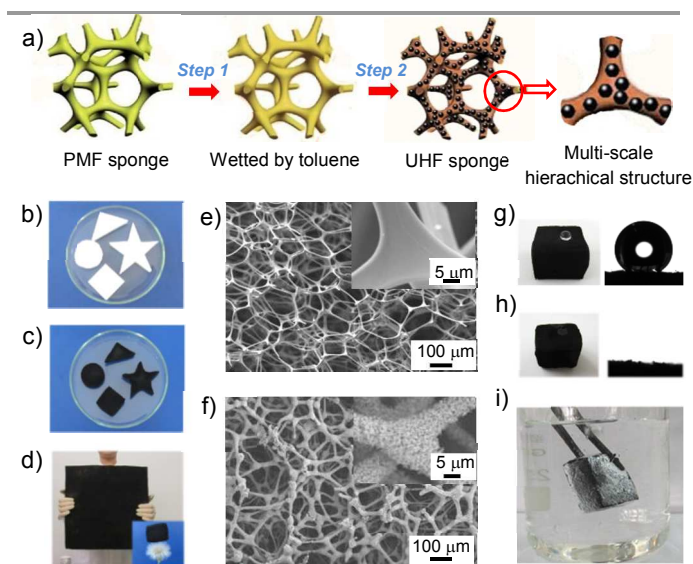


Fig. 1. Formation and morphology of the UHF sponges. **a)** Schematic illustration of the synthetic steps: Step 1, wetting the PMF via an absorb-compress-release cycle process; Step 2, combust-treating the wetted sponge by lighting it up. **b,c)** show the morphologies of the original and the obtained UHF sponges. **d)** Photograph of a piece of UHF sponge with a size of $70 \times 70 \times 5\text{ cm}$, and the inset picture exhibits that a piece of UHF sponge effortlessly stands on a dandelion effortlessly. **e,f)** SEM images of the original and obtained UHF sponges, respectively. The insets are their corresponding magnified images. **g,h)** Photographs and contact angles of water droplet and oil droplet, respectively. **i)** A piece of UHF sponge was immersed in water.

The obtained UHF sponge inherits the ultralight property of the pristine sponge, which has a density of $9\text{--}13\text{ mg cm}^{-3}$. This explains why a piece of UHF sponge could effortlessly stand on a dandelion (inset image in Fig. 1d). The sponge also exhibits high-hydrophobicity with a water contact angle of 149° (Fig. 1g and Fig. S7). The water droplet maintains typical spherical shape on the UHF sponge surface, while the oil droplet was rapidly absorbed by the sponges, giving a contact angle of 0° . A control experiment was conducted by blacken a glass slide via a toluene burner, with a water contact angle of 65.4° (Fig. S8). This indicated that the surface coating itself was not the sole contributor to the hydrophobicity of the UHF sponge. According to Cassie Equation in Electronic Supplementary Information,^[6] 89.9 % of the contact area between the water droplet and the sponge surface is occupied by air, which is accordance with the high porosity of the sponge (87.5 %). It was macroscopically verified by immersing the sponge in water by an external force, and the UHF sponge surface acted like a silver mirror when viewed at a glancing angle due to the refraction between water and the air which was captured in the sponge inner space (Fig. 1i). The great water repellence ascribed from carbon nanoparticles and the air trapped on the surface endows the obtained sponge with potential applications in oil/water separation.

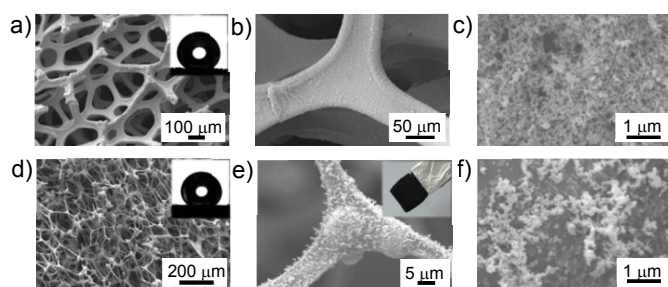


Fig. 2. SEM images the modified nickel foam (a,b,c) and the magnetic UHF sponge (d,e,f). The inset pictures in a and d show the corresponding water contact angles. The inset in e shows that a piece of magnetic UHF sponge could be manipulated by a magnet bar.

The versatility of the present strategy was demonstrated by using different types of porous substrates, and the functionalization of the obtained materials also could be easily achieved. Carbon nanoparticles were effectively immobilized on the nickel foam with a more homogeneous and denser coverage, and the resultant foam showed hydrophobic properties as expected (Fig. 2a-c and Fig. S9). Furthermore, the combust-assisted in-situ carbon deposition method is easy to fabricate hydrophobic materials with some special properties. For example, hydrophobic magnetic UHF sponges were successfully prepared via combustion treatment, of which the carbon source is hydrophobic Fe_3O_4 nanoparticle toluene suspension (Fig. 2d-f and Fig. S10). Carbon and Fe_2O_3 nanoparticles were evenly anchored on the sponge skeleton and the obtained sponge exhibited excellent magnetism and water-repellency simultaneously. For its hydrophobicity, the sponge could separate oils from water. Furthermore, the magnetic sponge could be easily driven to the polluted region by an applied magnetic field, providing a facile method to collect oils from a polluted water area (Fig. S10).^{3f,10a}

Besides their superior water-repellency, UHF sponges possess similar characteristic with lotus leaf, showing a quite low adhesion to water and being one of the best materials with self-cleaning property.^[3d,7] As reflected in Fig. 3, all the powdered dirt, including hydrophobic nanoparticles, hydrophilic nanoparticles, and microparticles with size of about 300 nm, can be easily removed from the surface of sponge owing to the rolling motion of water on the surface (Movie S1). It can be ascribed to their micro/nano-scale hierarchical structure: micro-scale structure prevents the capillary permeability of the water; the nano-scale structure can effectively reduce the close contact between the solid and liquid and influence the shape, length, and continuity of the triple-phase contact line. Thus, the rolling angle is substantially reduced, endowing the UHF sponges with excellent self-cleaning property. This property was investigated by dropping water droplets on an aclinic or inclined sponge surface, respectively (Fig. 3b-d, and Fig. S11). When the droplet was falling on the aclinic surface, it bounced immediately without any delay. In the case of inclined surface, the water droplet rolled off the surface quite quickly within a very short time.

The sliding speeds varied from 25 to 45 mm/s, depending on the inclined angle and the pH of the water (Fig. 3e,f). In the practical oil/water separation process, the nano-or-macro solid impurities in the oil/water mixture affect the wettability of the absorbent surface, having a negative effect on the separation efficiency. Thus, incorporating self-cleaning property into the hydrophobic absorbent is an inspiring strategy to enhance the durability of the surface hydrophobicity.

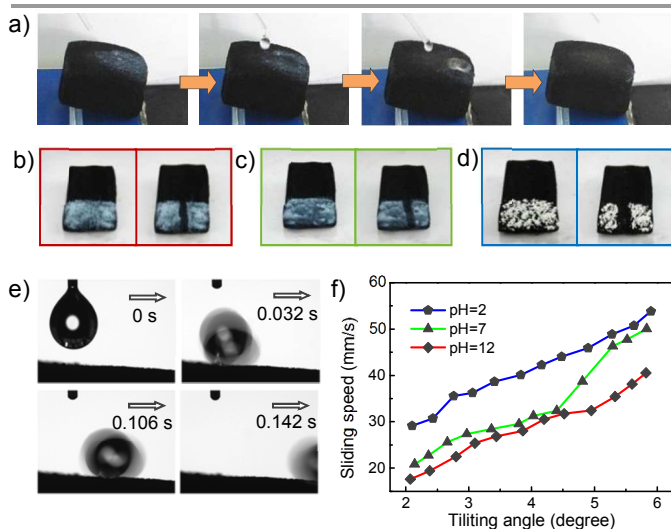


Fig. 3. Self-cleaning properties of the UHF sponges. a) The snapshots of self-cleaning process of UHF sponge surface with a layer of hydrophobic SiO_2 particles. Self-cleaning performance of UHF sponges for different particles on the surface: b) Hydrophilic SiO_2 nanoparticles with a diameter of 10-30 nm; c) Hydrophobic SiO_2 nanoparticles with a diameter of 10-30 nm; d) Hydrophilic SiO_2 microparticle with a diameter of ca. 300 nm. e) A water droplet (8 μL) can easily slide off a UHF sponge surface with sliding angle of 3°. f) Variation of sliding speed with tilting angle on the UHF sponge surface (8 μL of water droplet).

It has already been confirmed that fire-resistance and compressibility are beneficial to diversify the oil and absorbent recycle ways.^[8] Encouragingly, the UHF sponges inherited both characteristics from the pristine PMF sponges commendably. To investigate the fire-resistance of the UHF sponge, procedures of exposing sponges to the flame of an alcohol burner, direct combustion of alcohol-absorbed sponges, and thermal gravity analysis (TGA) at air atmosphere were conducted. As comparison, superhydrophobic PU sponges modified by chlorotrimethylsilane were also performed. It showed that the PU-based sponges were lighted with the assistance of alcohol burner, while the UHF sponges exhibited without any burning (Fig. 4a,b). The direct combustion experiment (Fig. 4c,d) also revealed that the UHF sponges were fire-resistant enough to maintain their original morphology, while the PU-based sponges ruinously burned thoroughly without any residue. The TGA which was conducted in air atmosphere quantitatively demonstrated that the UHF sponges possessed high thermostability as their lost little weight even under 500 °C in air (Fig. S12). In general, the outstanding fire-resistance of the PMF sponge-based materials make them much better than other polymeric sponge derivatives as oil absorbents for flammable oils and organic compounds.^[4b,c] Furthermore,

compression experiments of the UHF sponges showed a nearly complete recovery after 40-80 % compression (Fig. 4e,f and Fig. S13). In the first cycle, the loading curve shows 3 regions: i) a nearly linear region from 0 to 20%, which is caused by the bending and buckling of sponge skeleton; ii) a successive linear region with a gentle slope, which is owing to the partially irreversible fracture of the sponge skeleton; iii) in the densification region of strain > 45%, the stress rises steeply with compression, because the skeleton impinge upon each other. From the second cycle, the loading curves were nearly overlapped with each other and each of them showed two regions: a nearly linear region and another one with a steeper slope. The stress-strain curve of the 1000th cycle was identical to that of the second cycle, with the exception that the compressive stress decreased slightly to 78.2 % of the original value (Fig. 4f). Meanwhile, the inner structure of UHF sponges still maintained well-defined 3D porous structure with just some of the skeleton broken off (Fig. S14), demonstrating the outstanding compressibility of the sponge.

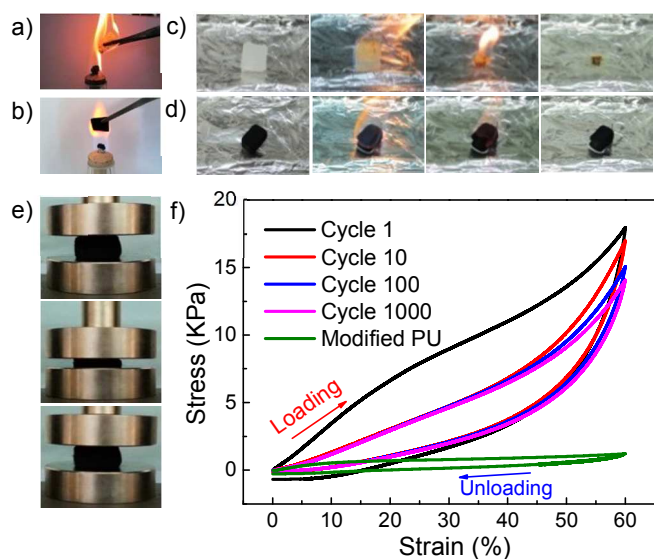


Fig. 4. Fire-resistance and compressibility of the UHF sponges. Photographs of modified PU sponge (a) and UHF sponge (b) in a hot flame of an alcohol burner. The combustion process of alcohol-absorbed modified PU sponge (c) and alcohol-absorbed UHF sponge (d). The contact angle and sliding angle of alcohol-absorbed UHF sponge after fire-resistance test was turned out to be 150.6° and 2.2° . e) Sequential photographs of the UHF sponge during the compression process (60 % strain). f) The compressive stress-strain curves of the modified PU sponge and the UHF sponge for different cycles.

Because of their high porosity, great water repellence, self-cleaning property, mechanical stability, and open-cell structure, the UHF sponge is desirable oil absorbent for effective separation of oils from water even under harsh conditions. To simulate the removal of the spilled oils, a piece of USF sponge was forced to the n-hexane layer on a water surface, and the oil was completely absorbed in a few seconds (Fig. 5a and Movie S2). The sponge also could quickly absorb dichloromethane which sunk at the bottom of water (Fig. S15). In addition, the large-scale separation was successfully realized with a

complete absorption by simply magnifying the corresponding parameters (Fig. 5b). On the other hand, in practical application, the oil/water separation may face varies harsh conditions. For example, in the offshore area or inland river basins, nano/macro-scale solid impurities containing in the oil/water mixture destroy the wettability of a material surface, greatly reducing the separation efficiency of the absorbents. Benefit to the self-cleaning property, UHF sponges maintained excellent selective absorption ability even there are vast hydrophilic (and/or hydrophobic) particles in the water (and/or oil) phase (Fig. 5c). Meanwhile, the absorption capacity of UHF sponges for varies of oils and organic solvents were investigated. The UHF sponges exhibited a superior absorption capacity in the range 58 to 143 times of its own weight depending on the density, viscosity, and surface tension of the absorbed liquids (Fig. 5f). Additionally, the volume absorption capacities of the present sponges for oils ranged from 68 % to 90 % (Fig. S16), being one of absorbents with the highest space-utilizations for oil-storage.[9] Moreover, the UHF sponge was demonstrated possessing remarkable oil keeping efficiency compared with the modified PU sponge (Fig. S17 and Fig. S18), owing to its much more robust skeleton and smaller pore size. The oil-water separation was also successfully conducted by using the UHF sponge as oil filter materials as shown in Fig. S19.

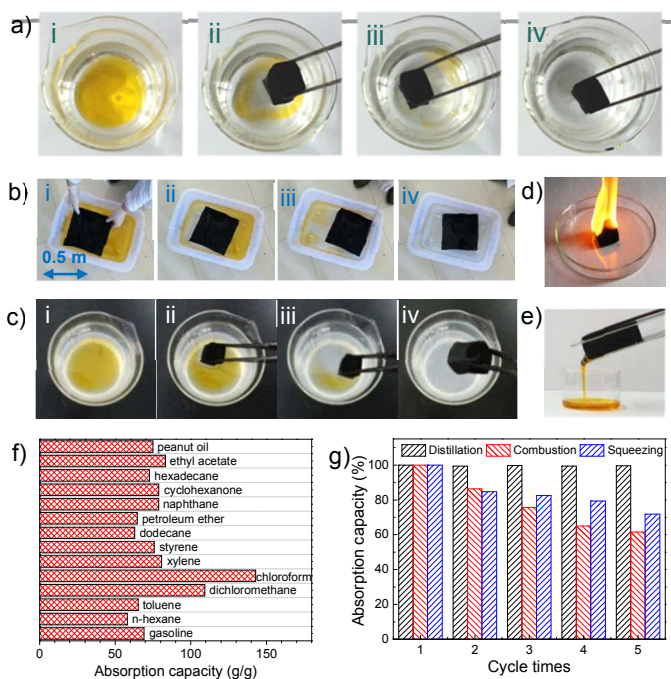


Fig. 5. Oil/water separation performance of the UHF sponges. Snapshots of removal process of n-hexane (dyed with Sudan I) floating on water using the USF sponge: a) size of $2\text{ cm} \times 1\text{ cm} \times 1\text{ cm}$, b) size $40\text{ cm} \times 40\text{ cm} \times 5\text{ cm}$; c) hydrophobic SiO_2 nanoparticle dispersing in oil phase and hydrophilic SiO_2 nanoparticle dispersing in water phase. The oil-absorbed UHF sponge can be regenerated by d) combustion and e) squeezing methods. f) Sorption efficiency of UHF sponges for various organic liquids. Weight gain here is defined as the weight ratio of the absorbate to the dried UHF sponge. g) The absorption capacity of the UHF sponges recycled via distillation, combustion, and squeezing methods.

Moreover, the absorbed oils can be recovered and the UHF sponges can be regenerated by distillation, combustion, squeezing, or a combination of them, depending on different types of oils. Firstly, to deal with oils with low boiling points like hexane, the absorption/distillation cycle method is employed. The sample was heated at the boiling point to release the absorbed liquid, and then we collected the vapor of the liquid for recycling (Fig. S20). If the spill oils have a high boiling point like dodecane, which could not be recovered by distillation, they could be directly combusted after being absorbed by the UHF sponges (Fig. 5d). It was desirable to find that the UHF sponge maintained 61.5 % of the original absorption capacity value after 5 cycles due to its excellent fire-resistance (Fig. 5g and Fig. S21). For precious or nonflammable pollutants with high boiling points, like gasoline, dibutyl phthalate, or decalin, squeezing is an attractive alternative method. For example, the gasoline could be easily recovered by simply squeezing because of the good compressibility of the UHF sponge (Fig. 5e, Fig. S22, and Movie S3). In the recycling process, the hydrophobicity of the UHF sponges was successfully maintained (Fig. S23). Comparing with other reported materials, the comprehensive performance of the present UHF sponge is impressive.^[10] The UHF sponge consists of enough hydrophobicity, high absorption capacity, various recycling methods depending on different requirements, and low cost of large-scale industrial production, showing a great promise as an ideal absorbent for the removal of oils from water.

Conclusions

In summary, we have developed a simple and general combustion-assisted in-situ carbon deposition method to prepare novel ultralight sponges with high hydrophobicity, fire-resistance, compressibility, and self-cleaning properties. The fabrication of this sponge is easy to be scaled up and functionalized, and this method can be extendable for different substrates. The sponges obtained can effectively separate oils from water even under harsh conditions, with maximum absorption capacities up to 145 times of its own weight. More importantly, excellent recyclability, outstanding oil recoverability, and good oil keeping efficiency make the sponge being versatile and comprehensive absorbents to satisfy various practical separation requirements. We believe this simply and general method could be applied to fabricate far more excellent oil absorbents to settle the severe water pollution caused by the growing number of oil spill accidents and chemical leakages.

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: Characterization and oil removal performance of sponges. See DOI: 10.1039/b000000x/

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