Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Journal of
Materials Chemistry A

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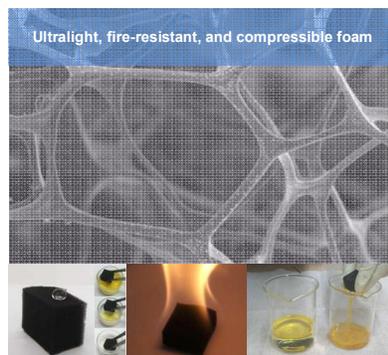
Ultralight, fire-resistant, and compressible foams as recyclable oil absorbents are facilely prepared from cheap melamine resins.

Journal of Materials Chemistry A

ARTICLE

Multifunctional foams derived from poly(melamine formaldehyde) as recyclable oil absorbents

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Owing to the severe environmental and ecological issues arising from oil spill and toxic chemical leakage, the separation of oil from water presents a worldwide challenge to save the endangered environment. A versatile absorbent which can deal with different types of oil contaminants is in high demanded for this issue. In this work, we obtain an ultralight, fire-resistant, and compressible foam (UFC foam) by pyrolysis and post hydrophobic-modified treatment using commercially available poly(melamine formaldehyde) foams as precursors. The present UFC foam not only effectively separates oils from water as expected, but also possesses a much higher absorption capacity for the removal of oils from water up to 158 times its own weight. More importantly, due to its fire-resistance and compressibility, distillation, combustion and squeezing, or a combination of them can be applied for recycling the foams dependent on the type of pollutants, making them being a versatile and comprehensive absorbent to satisfy various practical separation requirements.

Introduction

With the increase of the oil transport and marine petroleum exploitation, oil spill accident is of common occurrence, such as oil spill in Gulf of Mexico, which had caused extensive permanent damage to local marine and coastal ecosystems. More and more similar accidents would occur with the development of the industry. Therefore, materials that can effectively absorb, remove, and transfer spilled oils or organic contaminants from water are in urgently needed.

It has already been confirmed that physical sorption by porous materials is considered to be the most effective and promising technique for spill-oiled remove.[1-12] In this respect, porous materials with interconnected structure and hydrophobic surface, such as superwetting monolithic SiO_2,[13] macroporous Fe/C nanocomposites,[14] magnetic carbon nanotube (CNT) sponges,[15] hydrophobic nanocellulose aerogels,[16] and superhydrophobic conjugated microporous polymers,[17] were successfully employed into the separation of oil from water. With hydrophobic surface, the materials can only be wetted by oils; and the open-cell structure provides efficient channel and space for organic liquids diffusion and enrichment. Until now, however, most of the previous absorbents were not widely used in many situations because of certain drawbacks such as low absorption capacity, poor oil recoverability and poor absorbent recyclability.[13-17] The absorbed oil can only be recovered by distillation by the previous means in particular. But in the case of recovering high boiling point or low volatile solvents, distillation recycling method loses its practical significance. To improve the recycling performance, fire-resistant property is

incorporated into the hydrophobic porous materials.[18-22] Thus, the low boiling point oils are recovered by distillation as before, whilst the low volatile solvent-absorbed absorbents can be directly burned for recycling use as the excellent fire-resistant properties of the absorbents. Plenty of the corresponding materials have been introduced to recover the oils, including graphene/α-FeOOH aerogel,[19] robust carbonaceous nanofiber aerogels,[20] and carbon nanofiber aerogels from bacterial cellulose.[21] They all showed excellent fire-resistance for the combustion recycle applications. However, directly burning would not be an appropriate way when the spilled chemical reagents may have other further use. To further enhance the recyclability of the oils and the absorbents, the strategy of utilizing compressible absorbents under absorption/squeezing recycle way is a vital candidate.[23-27] The compressible porous materials, such as CNT spongs,[23] hydrophobic polyurethane foams,[24] graphene aerogels,[25] and flexible silicane aerogels,[26] can be regenerated by simply squeezing in the separation process without any complex operation. Unfortunately, some viscous oils face challenge in this simple squeezing recycling process, but it can be recycled by the absorption/combustion way. In a word, different oils can be recovered by the corresponding functional absorbents. Therefore, a versatile spilled oil recovered material would be a multifunctional comprehensive porous material integrating hydrophobility, fire-resistance and flexibility, possessing of distillation, combustion and squeezing regenerate ways for different types of spilled oil. Very recently, Yu's and Zhang's groups reported the twisted carbon fiber aerogels with good selective sorption of organic

liquids by carbonizing bacterial cellulose and raw cotton, more importantly, these aerogels can be regenerated by distillation, combustion, or squeezing depending on the type of the oils as expected.[21,28] The steps of science should not stop here, similar and even more excellent materials are in high demanded. Great effort should be devoted to exploring a more facile and straightforward strategy to prepare lighter and more robust fire-resistant, compressible oil absorbents, especially aiming at enhancing the possibility of large-scare industrial production.

Herein, we obtain an ultralight, fire-resistant, and compressible foam (UFC foam) by using a facile and easily scalable fabrication technique based on commercially available poly(melamine formaldehyde) (PMF) foams. In addition to having the compressibility of the other amino resin foams like polyurethane (PU) foams which were used in previous researches,[29-32] the PMF foam contains high content of nitrogen (ca. 54%, Fig. S1). As we know, the nitrogen compound is a novel and high efficiency flame retardant for the low toxicity of itself and its decomposer, so the PMF-derived foams would possess additional fire-resistance as resulted. Generally, these UFC foams were demonstrated as absorbents with highly efficient oil/water separation capability with a maximum sorption capacity up to 158 times the weight of the original UFC foam. Moreover, the UFC foam also exhibits the excellent recyclability, and maintains a high sorption capacity even after five cycles through distillation, burning or squeezing. We believe that such commercially PMF foam-derived novel hydrophobic foam with good performance will have great potential for industrial applications and oil spill treatments.

Experimental Section

Materials

PMF foams from Clean Wrap Company were achieved from the local supermarket. Chlorotrimethylsilane and n-hexane were obtained from J&K Chemical and used as received.

Preparation of UFC foams

PMF foam was cut into piece of 5.0×4.0×3.0 cm in size, and then was washed with alcohol and distilled water for three times. After dried in oven at 80 $^{\circ}$C, the melamine foam was pyrolyzed at 400 $^{\circ}$C for 1h under nitrogen atmosphere. The obtained nitrogen-rich carbon foams were dipped in a hexane solution of 2% (v/v) chlorotrimethylsilane for 0.5 h and then dried at 50 $^{\circ}$C for 1 h to give rise to UFC foam.

Oil removal test

First, we measured the absorption capacity of the UFC foam for various organic solvents and oils. The oil or organic solvent was poured in a beaker. UFC foams 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 should be done quickly. The UFC foams weights before and after absorption were recorded for calculating the values of weight gain.

Regeneration of UFC foams

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

Materials 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 amounts of elements 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 $^{\circ}$C min^{-1} from 30 to 800 $^{\circ}$C. The wetting properties of different samples were evaluated through contact angle tests, which were performed by the CAST2.0 contact angle analysis system at room temperature (OCA20LHT-TEC700-HTFC1500, Dataphysics, Germany).

Results and discussion

As shown in **Fig. 1**a, the volume of the obtained UFC foam is ca. 60% of the original PMF foam. Meanwhile, the density decreases from 12 mg cm^{-3} for PMF foams to 8-9.5 mg cm^{-3} for UFC foams, owing to the thermal degradation of organic compounds, being one of the lightest hydrophobic materials even reported. Furthermore, increasing the pyrolysis temperature would lead to a decrease of the compressibility of the obtained foams. For example, the foams fabricated by 1000 $^{\circ}$C pyrolysis treatment are brittle without any compressibility. So the samples based on 400 $^{\circ}$C treatment were chosen. As a result, a piece of ultralight foams can effortlessly stand on a grass (Fig. 1d). SEM images show that the UFC foam possesses an interconnected porous framework with skeleton of diameter of ca. 5 μm (Fig. 1b,c). Including the ultralight property, the UFC foam also has outstanding surface wettability. In contrast to the superhydrophilic orginal and pyrolyzed PMF foams (with water contact angle of 0°, Fig. S2), the chlorotrimethylsilane-modified UFC foam shows great water repellency with water contact angle of 145.4°. It is highlighted in Fig. 1e: The water droplets exhibit typical spherical shapes on the UFC foam surface; and when immersed into water by an external force, the UFC foam surface acts like a sliver mirror when viewed at a glancing angle. Moreover, elemental analysis reveals that the obtained UFC foams consist of 37.8 wt% C, 5.3 wt% O, 3.2 wt%

H, and 41.1 wt% N. The high content of nitrogen endows the UFC foams with excellent fire-resistance.
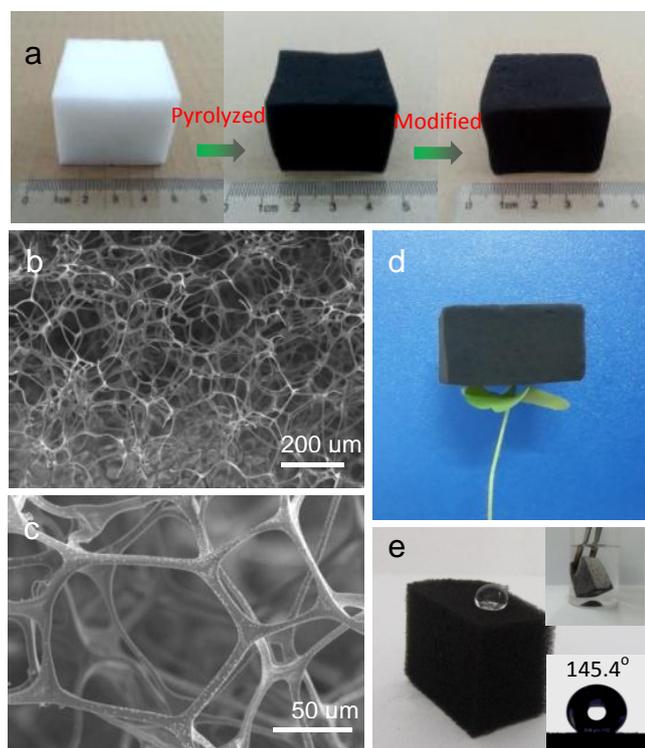
Fig. 1. (a) The fabrication of the UFC foams based on PMF foams by pyrolysis and modification. (b,c) SEM images of the UFC foam on different magnification. (d) A 15 cm³ UFC cuboid foam standing on a piece of marsilea quadrifolia grass. (e) Water droplet exhibits spherical shape on the surface of the UFC foams. Mirror-like phenomenon can be observed on the UFC foam submerged in water from the inset picture on the upper right. The inset image on the bottom right shows the water contact angle on the surface of the UFC foam.

Fig. 2a shows the TGA curve of the UFC foam performed at air atmosphere. The UFC foam reveals to consist of outstanding thermostability as they lost little weight even under 450 °C at air atmosphere, and it exhibits excellent fire-resistant property when exposed to the flame of the alcohol burner without any burning. Furthermore, the open-cell structure and the inherent flexibility of the skeleton endow good mechanical performance to the UFC foam. Fig. 2b shows the stress-strain curves of the UFC foams at maximum strain ε of 40%, 60% and 80%. The loading process shows three distinct regions, including the elastic region during which the stress increases linearly with the strain where $\varepsilon<10\%$, the plateau region at $10\%<\varepsilon<60\%$ from which most of the absorbed energy dissipated, the densification region at $\varepsilon>60\%$ marked by the rapid increase of stress due to the continuously decreasing pore volume. Hysteresis loops appear indicating dissipation of mechanical energy due to friction between flowing air and the foam skeleton. After 10 cycles of compression testing with $\varepsilon=60\%$, the porous 3D interconnected structure is almost remained just with some of the skeleton broken off (Fig. 2c,d). However, the UFC foam still keeps its original macroscopic

appearance (inset of Fig. 2b) and maintains good flexibility with compressive stress decreased slight of 90.1% of the original value (Fig. 2b). The compressive durability immensely expands the practical application of UFC foams.
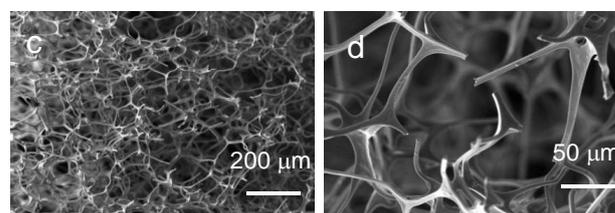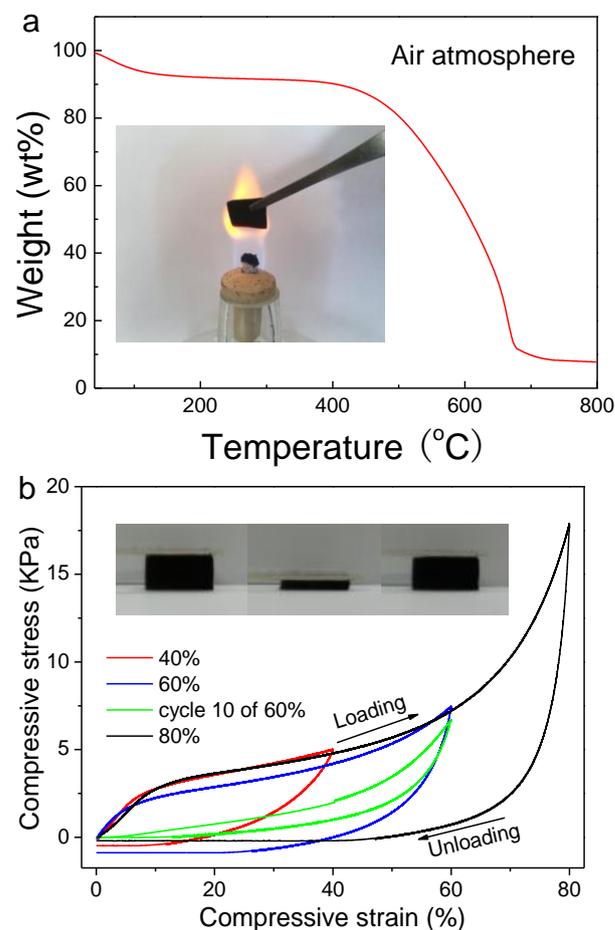

Fig. 2. (a) TGA curve of the UFC foam. TGA was performed under an air atmosphere and a heating rate of 10 °C min⁻¹ from 30 to 800 °C. The inset in (a) is a photograph of UFC foam in a hot flame of an alcohol burner. (b) Compressive stress-strain curves of UFC foams at different set strain ε of 40, 60, and 80%. The inset in (b) shows the sequential photographs of the UFC foam during the compressive process (in the middle, the compressed form is shown). (c,d) SEM images of the UFC foam after 10 cycles compression testing with $\varepsilon=60\%$ in different magnification.

The superhydrophobicity and porous open-cell structure make the UFC foams being ideal absorbents for highly efficient separation of oil contaminants from water. The strong selective sorption capability of UFC foams is demonstrated in **Fig. 3**a, 3b,

and Movie S1, S2. After forcing the UFC foam to n-hexane (dyed with Sudan I) on a water surface, the oil layer was quickly absorbed by the foam within a few seconds (Fi. 3a and Movie S1). In addition, the UFC foam was also applied for quickly absorbing dichloromethane (dyed with Sudan I) which sank at the bottom of water due to its larger density than water's (Fig. 3b and Movie S2). The quickly separation indicates the great potential use of the UFC foams for the facile removal of oil spillage and chemical leakage. In order to investigate the absorption efficiency, the UFC foam was forced to absorb various kinds of organic liquids, such as hexane, sunflower oil, toluene and gasoline, which are the common oily pollutants in daily life or industry. It is revealed that the UFC foam exhibit excellent absorption capacity of ranging 71-158 times of its own weight depending on density, viscosity, and

Fig. 3. Sorption of organic liquids by UFC foams. Snapshots of removal process of (a) n-hexane (dyed with Sudan I) floating on water and (b) dichloromethane (dyed with Sudan I) sinking below water using the hydrophobic foam. (c) Sorption efficiency of UFC foams for various organic liquids. Weight gain here is defined as the weight ratio of the absorbate to the dried UFC foam.

surface tension of the absorbed liquids (Fig. 3c). The oil-absorption capacities are much higher than other reported porous materials such as polymethylsilsesquioxane aerogel (6-14 times),[26] Fe/C nanocomposites (4.8-9.4 times),[14] macroporous carbon nanotubes (49-56 times),[15] nanocellulose

aerogels (20-40 times),[16] ultralight magnetic foams (61.8-102.6 times),[29] robust carbonaceous nanofiber aerogels (40-115 times),[20] porous poly(dimethylsiloxane) (40-34 times),[34] and spongy graphene (20-86.1 times),[6] indicating that the UFC foam exhibits one of absorbents possessing the highest absorption capacity.
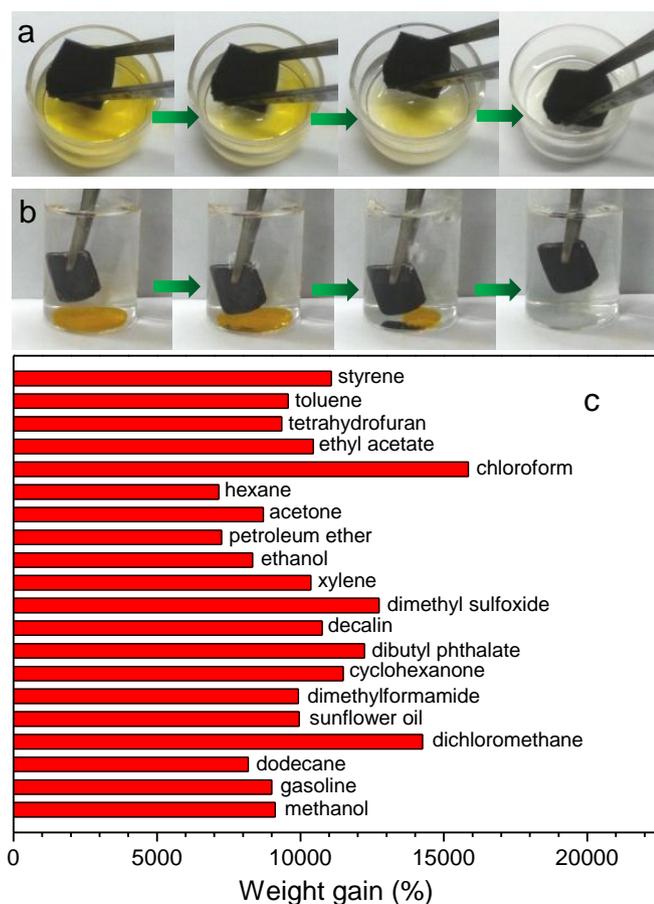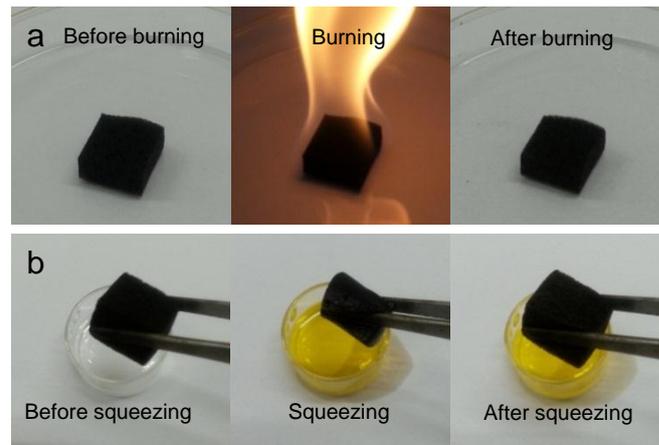

Fig. 4. The regeneration of the UFC foams via (a) combustion and (b) squeezing.
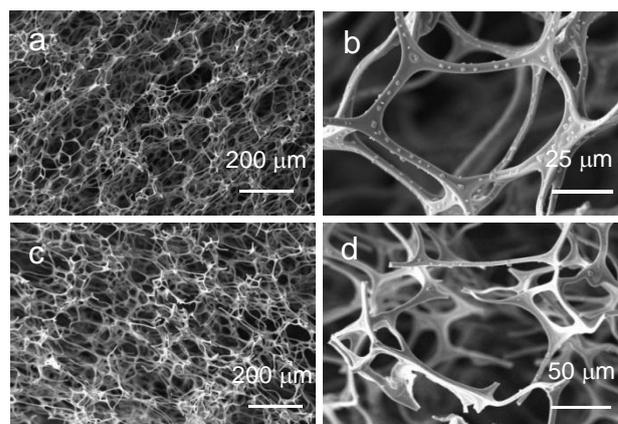

Fig. 5. SEM images of the UFC foams after 5 cycles of (a,b) absorption/combustion and (c,d) absorption/squeezing in different magnification.

As a comprehensive sorbent, not only should it effective separate oil from water, but also possesses excellent recyclability and recoverability of the absorbed organic liquids simultaneously. The present UFC foam, demonstrated with excellent fire-resistance and good compressibility, consists of three common methods to recover spill oils depending on different practical requirements (**Fig. 4-6**). Firstly, to deal with the oils with low boiling points like hexane, toluene, or dichloromethane, absorption/distillation cycle way is employed. The sample was heated at the boiling point to release the absorbed liquid, and then we collected the vapour of the liquid for recycling. The corresponding cyclic test in Fig. 6a,d shows

that no obvious change in absorption capacity was found after 5 absorption/distillation cycles. Moreover, if the spill oils having a high boiling point like dodecane, hexadecane, pump oil, or sunflower oil, which cannot be recovered by distillation, it can be directly combusted after being absorbed by the UFC foams (Fig. 4a, Movie S3). It is desirable to find that the UFC foam maintains 59.7% absorption capacity of the original value due to its excellent fire-resistance (Fig. 6b,d). And the SEM test confirms that of the combust-treated foam still remains a similar structure of UFC foam (Fig. 5a,b). Furthermore, for precious or nonflammable pollutants with high boiling points, like gasoline, dibutyl phthalate, or decalin, squeezing is an attractive alternative method. The recycling process of the UFC foam is illustrated in Fig. 4b and Movie S4. For example, with simply squeezing the gasoline-absorbed UFC foam, the gasoline can be easily recovered for the good compressibility of the UFC foam. Even after 5 cycles, the 3D structure of the foam was kept only with some of the skeleton broken off (Fig. 5c,d), while the absorption capacity still possesses 69.2 % of the original value (Fig. 6c,d). Therefore, benefiting from its good thermal stability and excellent mechanical properties, any of the three common methods mentioned above, i.e., distillation, combustion and squeezing, or a combination of them can be applied for recycling UFC foams dependent on the type of pollutants. Compared the present UFC foam with other reported materials,[35-46] a single property may not be the best, but the comprehensive performance is the most excellent. The UFC foam consists of enough hydrophobicity, highly absorption capacity, various recycle means depending on different requirements and low-cost for large-scare industrial production, exhibiting as an ideal absorbent for the removal of oil from water.

Conclusions

In summary, an excellent oil/water separation material derived from commercially available PMF foam has been developed by a cost-effective, facile and scalable method via hydrophobic functionalization between the pyrolyzed PMF foam and chlorotrimethylsilane. The resultant UFC foam simultaneously possesses of great water repellent (with water contact angle of $145.4°$), ultralight (with density of 8-9.5 mg cm^{-3}), excellent fire-resistant and good compressible properties. Compared with other absorbents, the present UFC foam not only effectively separates oils from water as expected, but also possesses a much higher absorption capacity for the removal of oils and organic liquids from water with maximum absorption capacities up to 158 times its own weight. More importantly, due to its fire-resistance and compressibility, distillation, combustion and squeezing, or a combination of them can be applied for recycling the foams dependent on the type of pollutants, making them being a versatile and comprehensive absorbent to satisfy various practical separation requirements. These promising results demonstrate such a relatively easy-synthesis, low-cost, easily scalable produced, and performance-comprehensive materials have great potential in the spill oil recovery applications and environmental protections.

Acknowledgements

Notes and references

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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.

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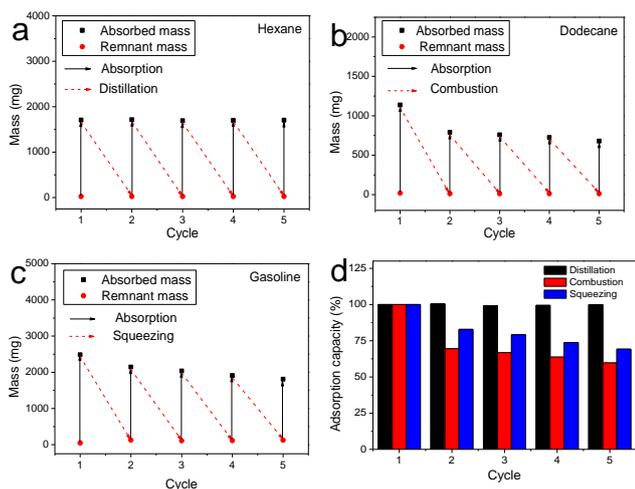
Fig. 6. The properties of (a) the hexane-absorbed UFC foams recycled by distillation, (b) the dodecane-absorbed UFC foams recycled by combustion, and (c) the gasoline-absorbed UFC foams recycled by squeezing. (d) The absorption capacity of the UFC foams recycled via distillation, combustion, and squeezing methods.

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