Extremely Efficient and Recyclable Absorbents for Oily Pollutants Enabled by Ultrathin-Layered Functionalization

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S *Supporting Information*

ABSTRACT: Oils and organic solvents that leak into water bodies must be promptly removed to avoid ecological disasters, for example, by selective absorption using oleophilic absorbents. However, it remains a challenge for the low-cost synthesis of efficient and recyclable absorbents for oily pollutants. By surface functionalization to inexpensive polyurethane (PU) foams, we synthesize oil absorbents exhibiting the highest absorption capacity and the best recyclability among all polymeric absorbents. The synthesis is enabled by atomic layer deposition of $\sim$5 nm-thick Al_2O_3 transition layer onto the skeleton surface of PU foams, followed by coupling a single-molecule layer of silanes to the Al_2O_3 layer. The sub-10 nm functionalization layer provides the PU foam an outstanding water-repelling and oil-absorbing functionality without compromising its high porosity and elasticity. The functionalized foam is able to quickly absorb oily pollutants spread on water surfaces or precipitated in water with a capacity more than 100 times its own weight. This ultrathin-layer-functionalization method is also applicable to renewable porous biomaterials, providing a sustainable solution for oil spills. Moreover, we propose devices than can continuously operate to efficiently collect oil spills from water surfaces based on the functionalized PU foam developed in this work.

KEYWORDS: atomic layer deposition, silanization, absorption, polyurethane foam, oleophilicity, oil spill
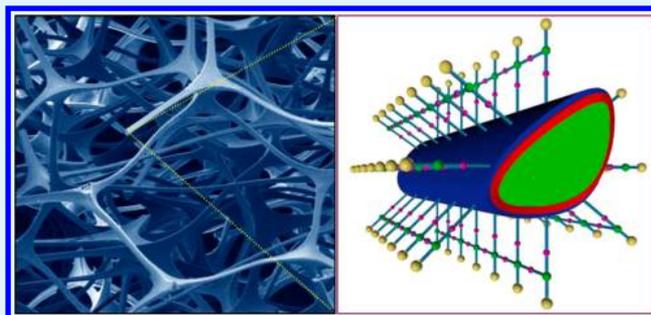
INTRODUCTION

The effective cleanup of oil spills and other organic contaminants from oceans, rivers, and lakes becomes increasingly important as oil and chemical leakages occur frequently and such accidents may lead to disastrous environmental and ecological consequences.[1–4] Such oily contaminants are typically removed by skimming[5] or burning.[6] However, these methods are inefficient or incapable of thoroughly removing the oily contaminants from water bodies. Moreover, burning causes secondary contamination, and the spilled oil cannot be recovered in a usable fashion. A more efficient and economic approach is to use oleophilic and hydrophobic porous media to selectively absorb oily liquids from water. The absorption process is usually fast, and in ideal cases, the absorbed oils can be recovered from the absorbents.[7–12]

Hydrophobic, porous, carbonaceous and polymeric materials have extensively been used as oil absorbents. For example, activated carbons and graphite have long been used to absorb spilled oils.[12] However, these conventional porous carbons exhibit very limited absorption capacities, typically less than 10 times their own weights. Very recently, delicate foam-like structures constructed from carbon nanomaterials, including carbon nanotubes[7–10] and graphene,[13–16] have proven capable of absorbing oils with capacities of up to several hundred times their own weights. Such high absorption capacities are

attributed to the ultralight weights and the high porosities of carbon foams. Unfortunately, the high cost and the sophisticated fabrication process for carbon foams severely limit their mass production and their practical applications at a large scale. Moreover, the regeneration of the used carbon foams and the recovery of the absorbed oils from carbon foams remain considerable challenges. Hydrophobic porous polymers, either naturally existed or artificially synthesized, are also used to absorb oils.[17–19] However, they usually exhibit poor water/oil selectivity and/or a relatively low absorption capacity (typically less than 10 times their own weights).

Therefore, low-cost and recyclable oil absorbents that have high oil/water selectivity, a large absorption capacity, and a fast absorption rate are highly desirable. In this study, we prepare highly efficient and recyclable oil absorbents using commercially available polyurethane (PU) foams as inexpensive sources of the substrate materials. As depicted in Scheme 1, we first deposited a thin layer of Al_2O_3 by atomic layer deposition (ALD) with a thickness of a few nanometres on the surface of the PU foam. Subsequently, a low-cost silanization agent, γ-methacryloxypropyl trimethoxysilane (KH570), was coupled to

Scheme 1. Schematic Process of the Surface Functionalization on PU Foams[a]
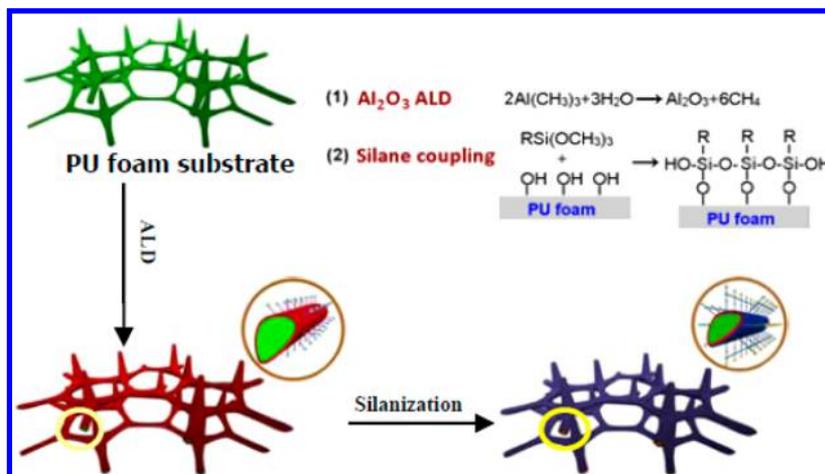
[a]The process includes atomic layer deposition of Al_2O_3 and silane coupling. The equations of the involved chemical reactions are provided in the inset (R: $CH_2=C(CH_3)COOC_3H_6$).

the PU surface via the hydroxyl groups on the Al_2O_3, making the PU foam highly water-repelling and oil-absorbing. Thus-functionalized PU foams exhibit absorption capacity and recyclability both remarkably better than other polymeric oil absorbents. We should note that absorbents including the functionalized PU foams reported in this work are suitable to selectively remove "free oil" floating on the water surface or precipitated under water but not suitable for oil/water emulsions.

MATERIALS AND METHODS

Materials. The PU foams with apparent densities of 7.12 mg/cm³, 9.01 mg/cm³, and 11.89 mg/cm³ as well as dried loofah were purchased from local markets and used as substrates to prepare oil absorbents. As the bulk density of polyurethane resin is 1.2 g/cm³, we can estimate that the porosities of the three PU foam are 99.4%, 99.3%, and 99.0%, respectively, by comparing their bulk densities and apparent densities. Trimethylaluminum (TMA, 99.99%, Nanjing University) and deionized water (Conductivity: 8−20 μs/cm, Wahaha Co.) were used as the metal precursor and the oxidant source, respectively, for the ALD deposition of Al_2O_3. The γ-methacryloxypropyl trimethoxysilane (KH570, 98%) used as the coupling agent was purchased from Meryer Co. Ltd., Shanghai. Oils involved in this work such as vegetable oil, diesel oil, lubricating oil, and methyl silicone oil were all obtained from local suppliers. Organic solvents including chloroform, cyclohexane, and ethanol were of analytical grade and commercially acquired and used as received. The oil-soluble dye, Oil Blue 35, used to mark the oleic liquids was purchased from Daxing Dye Chemicals Co. Ltd., Shenzhen was a purity of 99.5%.

ALD of Al_2O_3. Al_2O_3 deposition was carried out by atomic layer deposition (Savannah S100, Cambridge NanoTech) using TMA and deionized water as precursors. We used nitrogen as the carrier and purging gas. Pulse and exposure time for both precursors were 0.015 and 10 s, respectively. Nitrogen purging time was set as 30 s and the N_2 flow rate 1.2×10^{-4} m³/h (20 sccm). The ALD of Al_2O_3 on PU foams were operated at 80 °C. The ALD chamber with PU foams inside was heated to the deposition temperature and pumped to reach a pressure <1 Torr. The chamber was kept pumping at the deposition temperature for at least 30 min before the commencement of the ALD process.

Silanization. After Al_2O_3 deposition, pieces of PU sponges with a dimension of $1.5 \times 1.5 \times 1.5$ cm³ were immersed in the ethanol solution of KH570 with a concentration of 0.5 wt %. The solution was moderately stirred for 3−7 h at room temperature to guarantee a

sufficient coupling. Then, the foams were taken out, rinsed with ethanol for three times, and dried at 70 °C.

Characterizations. The surface morphologies of the samples were observed using a field emission scanning electron microscope (FESEM, Hitachi S4800) operated at 5 kV. Prior to SEM examination, the samples were sputter-coated with a thin layer of platinum/palladium alloy to enhance their conductivity. An EDS detector (Oxford INCA 350) equipped to the SEM was used to analyze the elemental composition of the samples. Thermogravimetric (TG) analysis was performed on a NETZSCH TG209F1 thermal analyzer in nitrogen with a heating rate of 10 °C/min from room temperature to 1200 °C. A contact angle goniometer (DropMeter A100, MAIST Vision) was used to measure the water contact angles of the functionalized PU foam. Five different sites on the sample were measured and the mean value was reported. The surface compositions of PU samples at different functionalization steps were analyzed with X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD) with a transmit energy of 160 eV and step length 1 eV.

Absorption Tests. The PU foam was first dipped into a specific oil or organic solvent for 5 min. Then, it was carefully removed, hung in air for 30 s to drain the excess oil/solvent off the surface, and finally, it was weighed. The absorption capacity of the foam was defined as the weight of oils or organic solvents absorbed per the unit weight of the foam, namely the weight ratio of the absorbed oil/solvent to the foam.

We placed PU foams into the oils or organic solvents and measured the amount of the absorbed oil/solvent over different periods of time up to 30 min. The absorption capacity (Q_t) at time t can be determined using the following equation:

$$Q_t = (m_t - m_0)/m_0 \tag{1}$$

where m_0 is the initial weight of the PU foam and m_t is the weight of foam containing the absorbed oil in the period of time t. When Q_t does not change with time, it indicates that the foam had reached the saturation of absorption. For each absorption experiment, at least three samples were tested and the average values were reported.

Regeneration of the Absorbed PU Foams. The oil-absorbed foams were compressed with a pair of tweezers several times until no more oil could be extracted from the foam; this process regenerated the foams and recovered the absorbed oil. The regenerated foam was then used again for oil absorption. To test the recyclability, the PU foams functionalized by 30 and 200 ALD cycles were used to repeatedly absorb diesel oil and then regenerated by compressing. The absorption capacity of the foam after every regeneration was recorded and correlated with the times of reuse.

Water/Oil Separation. Vegetable oil and chloroform were used as the representative of the oils lighter than water and solvents heavier

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than water, respectively, to test the separation of oleic liquids from water by the selective absorption of the functionalized foams. To obtain a stronger contrast with water both vegetable oil and chloroform were dyed blue with an oil-soluble dye (Oil Blue 35). Vegetable oil and chloroform were dropped into water, forming the mixture of water/oil with oil spread on the water surface, and the mixture of water/chloroform with chloroform precipitated in the bottom of water, respectively. We then used a pair of tweezers to force the functionalized foam contact vegetable oil or chloroform and recorded the selective absorption process with a digital camera (Cannon G10).

RESULTS AND DISCUSSION

The as-received, pristine PU foams show similarly good absorption for water and oil, and consequently, they do not have a noticeable selectivity between oil and water. However, in contrast, the PU foam functionalized by the ALD coating of Al_2O_3 and silanization displayed a highly water-repelling and oil-absorbing function with a water contact angle of 137.7°. We used vegetable oil as the model oil to examine the ability of the functionalized PU foam to selectively absorb oils/organic solvents from mixtures with water. Upon addition to water, vegetable oil (dyed blue) spread on the water surface as an immiscible thin layer (Figure 1a). We placed the functionalized
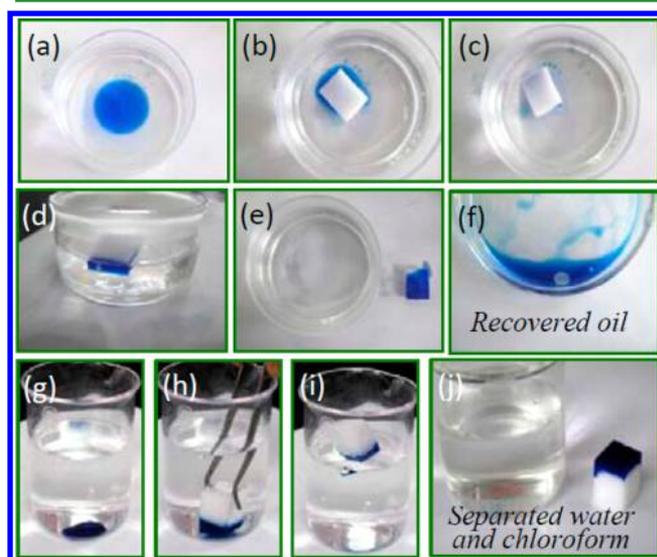

Figure 1. Selective absorption of oils/organic solvents from water of the functionalized PU foams. Photographs show the process of the functionalized PU foam selectively absorbing vegetable oil (dyed blue) spread on a water surface and the recovery of the absorbed oil (a–f) and the underwater absorption of chloroform (dyed blue) by the functionalized PU foam (g–j).

PU foam on the water surface, and once the foam came into contact with the oil layer, it "stuck" to the oil layer and automatically absorbed oil (Figure 1b). The area of the oil layer decreased quickly (Figure 1c) until it was completely absorbed by the foam (Figure 1d). After oil absorption, the foam remained floating on the water surface, allowing it to be easily removed from the water for regeneration. As shown in Figure 1e, the water surface became free of oil because the foam completely absorbed the oil layer. Additionally, the oil absorbed in the PU foam can be recovered simply by compressing the foam using a pair of tweezers, and the foam is therefore regenerated and ready for reuse (Figure 1f). A video recording the selective absorption of oil spread on the water surface by

the functionalized PU foam is given in Supporting Information Movie S1.

Some water-immiscible organics, for example, halogenated hydrocarbons, have a density higher than that of water. When leaked into water, they will sink to the bottom of water bodies and are even more difficult to remove. We found that the functionalized PU foam can also be used to selectively absorb heavy organics that sink to the bottom of water. We used chloroform (d = 1.484) as the model heavy organic liquid. As shown in Figure 1g, chloroform (dyed blue) sank to the bottom of the beaker when dropped onto the water surface. We pressed the functionalized foam into the bottom of the beaker to make contact with and absorb chloroform (Figure 1h). It took several seconds for the foam to completely absorb chloroform. The chloroform-containing foam automatically floated up to the water surface when we released it (Figure 1i), and the foam with its absorbed chloroform can be removed from water to be recovered (Figure 1j). Note that no water was incorporated into the functionalized PU foam during the underwater absorption process. A video recording of the selective absorption of organics under water can be found in Supporting Information Movie S2.

The functionalized PU foam is able to selectively absorb diverse types of oils and organic solvents with very high absorption capacities (Q). For example, the functionalized PU foam showed a saturated absorption capacity of 110, 101.4, 116.8, 105.5, and 97.8 for vegetable oil, diesel oil, silicone oil, lubricating oil, and cyclohexane, respectively. Compared to oil absorbents reported in the literature, for example, gold nanoparticle-poly(dimethylsiloxane) nanocomposite foam (Q = 2−14),[17] perfluorooctyltriethoxysilane (PTES) and polypyrrole (PPy) modified PU foams (Q = 17−31),[11] graphene-based foams (Q = 8−20),[15] and nanocellulose aerogels (Q = 20−40),[18] the functionalized PU foam prepared in this work possesses the highest absorption capacity among all polymeric oil absorbents, and its absorption capacity is typically 5−50 times higher than the values for other absorbents. The absorption capacity of the functionalized PU foam varies for different oils and organics because of the changing density, polarity, and viscosity of these liquids. Furthermore, it is found that the apparent density of the pristine PU foams determines the absorption capacity for the same oil of the corresponding functionalized foams. Larger apparent densities imply smaller porosities and consequently less space to accommodate absorbed organics. Figure 2a displays the absorption capacities for different organics of functionalized PU foams with three different original apparent densities but the same functionalization treatment. For every type of organic liquid, the absorption capacity increases with the decreasing apparent density of the PU foam. For instance, the Q values for vegetable oil and lubricating oil of the heaviest foam used in this work, with an apparent density of 11.89 mg/cm^3, are 93 and 86, respectively, whereas the Q values for the two oils of the lightest PU foam, which has an apparent density of 7.12 mg/cm^3, increased remarkably to 140 and 130, respectively. We then investigated the rate of absorption of vegetable and diesel oil by the functionalized PU foam. As shown in Figure 2b, the functionalized foam shows a similar kinetics profile when it absorbs vegetable and mineral oils. The amount of the absorbed oil increases very rapidly in the initial stage and then stabilizes when it reaches the saturated value. It takes ~10 s and ~30 s for the functionalized PU foam to reach saturation for the absorption of diesel oil and vegetable oil, respectively. The
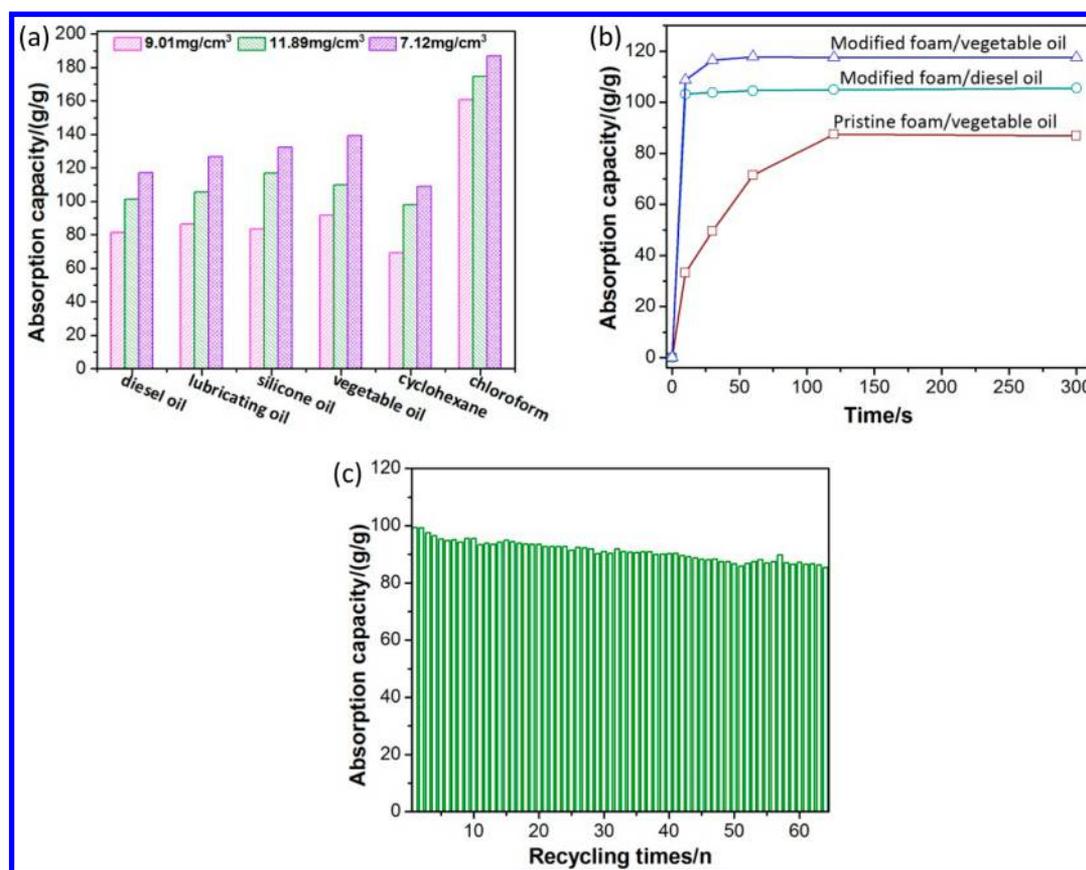
Figure 2. (a) Saturated absorption capacity of the functionalized PU foams with three different apparent densities for various types of organics; (b) the change of the amount of absorbed vegetable oil or diesel oil for the pristine and the functionalized PU foam according to the absorption time; (c) the absorption capacity of the functionalized PU foam for diesel oil after being recycled for different times.

absorption rate is mainly determined by the viscosity of the oil, as thicker oils, such as vegetable oil, take a longer time to be absorbed into the porosity of the PU foam. In contrast, the pristine PU foam requires a much longer time (~120 s) to reach saturated absorption for vegetable oil, and the absorption capacity of the pristine PU foam is ~30% lower than that of the functionalized one. Therefore, the surface functionalization significantly enhances both the capacity and the rate of the PU foam in the absorption of oils.

After absorption, the oil-containing absorbents are generally further treated either by burning or by rinsing with other solvents in the case that the absorbents are produced from incompressible stiff materials. Such treatments may cause secondary pollution and serious waste of resources. In contrast, for compressible absorbents made from elastic materials, absorbed oils can be extracted by mechanical compressing, which allows the absorbents to be regenerated. We investigated the recyclability of the functionalized PU foams. Figure 2c shows the absorption capacity for diesel oil for the functionalized PU foam during recycling up to 64 times. The freshly prepared functionalized PU foam exhibits an absorption capacity of ~100, and the absorption capacity only slightly decreases when the foam is continuously reused tens of times. After absorption and regeneration 64 times, the foam still has an absorption capacity of 87.7, which is only a 12.3% reduction compared to the initial capacity of the functionalized foam and is still much higher than that for other polymeric absorbents that are freshly prepared. The recyclability of the PU foam functionalized in this work is strikingly better than that of all

other compressible absorbents. For example, the absorption capacity of foams made from carbon nanotubes suffers from a reduction of 82.6% after reuse for only 10 times,[10] the absorption capacity of carbonized wood fibers show a reduction of 26.3% after reuse for 8 times,[19] and the absorption capacity of PU foams functionalized by PPy-PTES have a reduction of 14.8% after reuse for only 5 times.[11] Such an outstanding recyclability by compression of the functionalized PU foams should also be attributed to the strong adhesion of Al_2O_3 on the PU substrate ensured by the subsurface infiltration of precursors following the mechanism of sequential infiltration synthesis during the ALD process.[20]

Our functionalization strategy includes two main steps, deposition of Al_2O_3 by ALD and silanization, both of which are based on surface reactions producing ultrathin coating layers. Silanes are well-known to react with hydroxyl groups on the surface of various substrates, forming single-molecule layers with strong hydrophobicity. There are a large number of silanes commercially available at reasonably low prices. However, silanes cannot be directly coupled to the surface of PU foams because of the absence of hydroxyl groups.[21] We must establish a hydroxyl-group-carrying transition layer on the PU surface before we perform the silanization. ALD is used in this work for its outstanding capability in producing ultrathin and conformal oxide layers along the pore walls of porous substrates.[22,23] For the sake of high porosity, the ALD cycle number should be as low as possible to obtain the thinnest achievable deposition layer. However, at a very low cycle number, the surface of the PU foam may not be completely covered by either Al_2O_3 or the
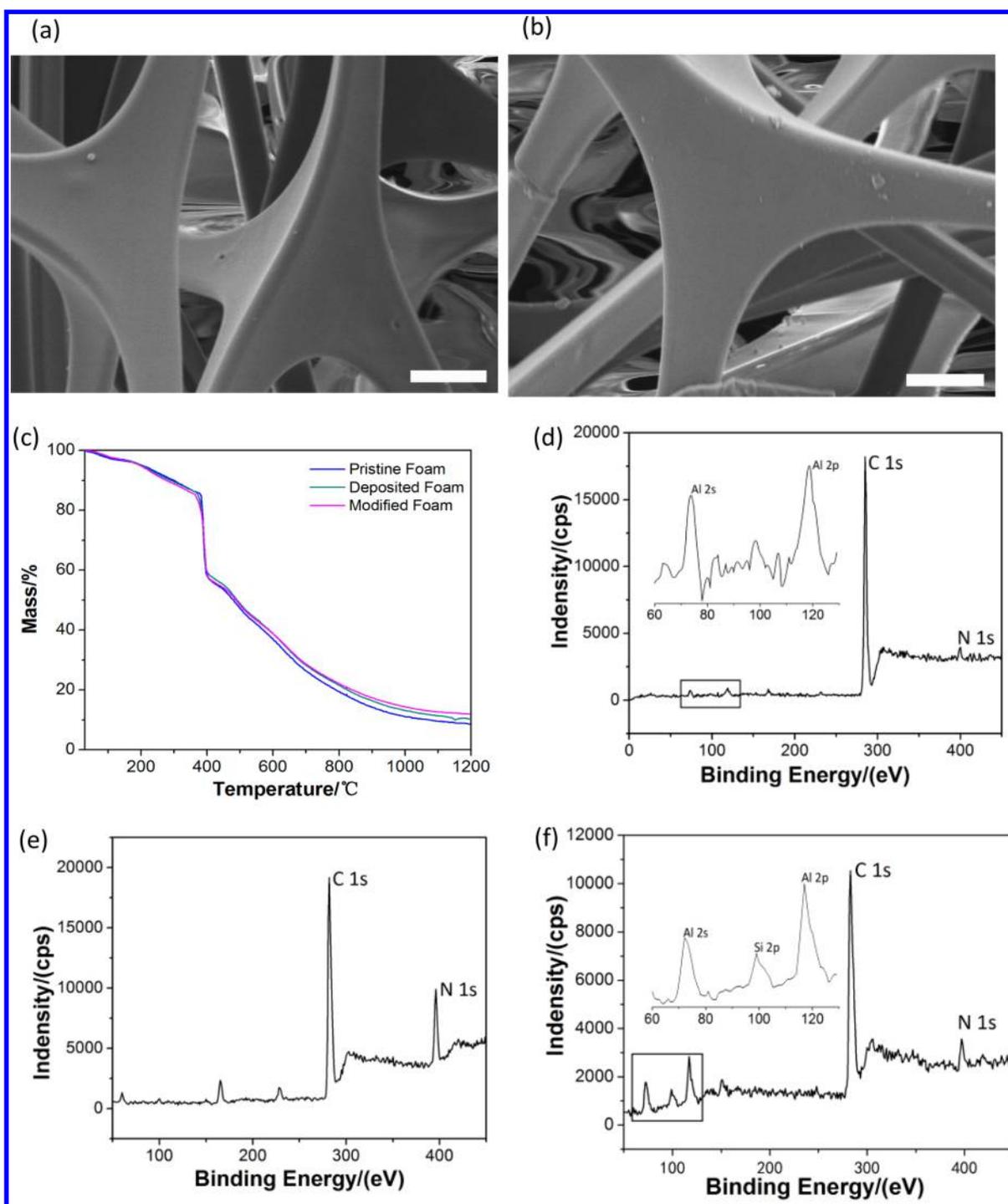
Figure 3. SEM micrograph of the PU foam with an apparent density of 9.01 mg/cm³ before (a) and after (b) the ALD and silanization functionalization, the TG curves of PU foams subjected to different treatment (c), and XPS spectra of the pristine PU foam (d), the aluminum-oxide-deposited PU foam (e), and the aluminum-oxide-deposited and KH570-coupled PU foam (f). The scale bars in a and b correspond to 10 μm.

KH570 molecules in the subsequent silanization step. Therefore, there exists a critical cycle number that can produce the thinnest functionalization layer that completely covers the PU foam. We deposited Al_2O_3 onto PU foams using various numbers of ALD cycles up to 200 and then performed silanization on these foams. The pristine PU foam will sink into water within 1−2 s upon placement on the water surface because of its strong affinity to water. In contrast, the foams functionalized with even a few ALD cycles take a much longer time to sink into water due to the enhanced hydrophobicity

resulting from the KH570 coupled to the deposited Al_2O_3. The functionalized PU foams with 5 and 20 ALD cycles take approximately 2 min and 6 h to fully absorb water, corresponding to a moderately and a strongly enhanced hydrophobicity, respectively. We ultimately determined that 25 ALD cycles were the critical value for the functionalized PU foam as this functionalized foam can permanently float on a water surface, exhibiting a complete water repulsion property. Therefore, we predominantly deposited the PU foams with 30 cycles, which is slightly higher than the critical value in the

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preparation of oil-absorbing foams. Additional cycles beyond the critical value do not provide better absorption performance; instead, they reduce the absorption capacity and the recyclability of the functionalized PU foam. This is because the thicker Al_2O_3 layer non-negligibly reduces the porosity of the foam and is easily detached from the PU substrate by repeated use. As shown in Supporting Information Figure S1, there is a general trend of a slight reduction in the absorption capacity for vegetable oil for the functionalized PU foams with an increase in the number of ALD cycles. For example, the absorption capacity of the functionalized foam after 200 ALD cycles is reduced to 105 compared to 110 for the foam after 30 ALD cycles. Even worse, the absorption capacity of a PU foam functionalized by 200 ALD cycles degrades at a higher rate with repeated use (Supporting Information Figure S2), compared to the one functionalized with only 30 ALD cycles (Figure 2c). For instance, the reductions in absorption capacity after being used 64 times are 33.7% and 12.3%, respectively, for the PU foams treated with 200 and 30 ALD cycles.

As we described above, the functionalized PU foams prepared in this work are distinguished from other oil absorbents by a much higher absorption capacity, a faster absorption rate, excellent recyclability, and low cost. All of these advantages result from the ultrathin nature of the functionalization layer on the highly porous and elastic PU foams. Here, we used different characterization approaches to discuss the ultrathin nature of the functionalization layer on the PU foam. We used PU foams with three different apparent densities (7.12, 9.01, and 11.89 mg/cm^3), all of which had a very high porosity larger than 99%. As revealed by scanning electron microscopy, these PU foams are composed of a structure consisting of a three-dimensionally interconnected skeleton. The skeleton has a width in the range of approximately 5−20 μm, and pores varying from 50 to 200 μm are defined by the skeleton. After the Al_2O_3 ALD and silanization, there is no noticeable change in the microstructure of the skeleton, which maintains a smooth surface after the functionalization (Figure 3a and b). Such a well-maintained microstructure implies that the hydrophobilization process occurred only on the surface of the PU skeleton and produced a very thin functionalization layer. We further used energy-dispersive spectroscopy (EDS) to analyze the functionalized PU foam but failed to detect Al and Si despite the fact that they should be present in the functionalized foam that has Al_2O_3 and Si-containing KH570. The reason is that the concentration of Al and Si in the functionalized PU is lower than the detection limit of the EDS detector. The functionalized PU foam is subjected to an Al_2O_3 coating for 30 ALD cycles. As the typical growth rate of Al_2O_3 on polymeric substrates with nitrogen-containing active groups (e.g., nylon and polyvinylpyridine) using TMA and water as the precursors is 0.15−0.2 nm per cycle within the first 100 cycles,[24] the thickness of the Al_2O_3 deposited on PU foam can be estimated to be approximately 5 nm. On the other hand, according to the mechanism of the reaction between the silanes and the hydroxyl-terminated substrate surface, one single molecular layer of silanes will be coupled to the surface of the Al_2O_3 layer. As the chain length of KH570 is approximately 0.99 nm,[25] the total thickness of the functionalization layer, including the oxide layer and the silane layer, is approximately 6 nm. We purposely increased the number of cycles of Al_2O_3 ALD and found that signals from Al and Si can be detected from the functionalized PU foam only after 200 or more cycles (Supporting Information Figure S3).

We performed TG analysis on PU foams at different functionalization steps. As shown in Figure 3c, all of the samples reach a nearly constant weight after being heated to 1200 °C in nitrogen. The remaining weight of the pristine PU foam, the ALD-treated PU foam, and the PU foam subjected to Al_2O_3 deposition and KH 570 coupling is 8.57%, 10.27%, and 11.93%, respectively. The TG results reveal that there is only 1.6−1.7% weight gain both in the step of Al_2O_3 ALD for 30 cycles and in the step of slianization. As the porosity of the pristine PU foam is known to be 99.3% the porosity of both the deposited and silanized PU foam can be calculated to be still larger than 99.0%.[26] Therefore, the high porosity of the PU foam remains after the two-stepped functionalization process, confirming again the ultrathin nature of the functionalization layer. We further used XPS, which is more sensitive to surface composition than EDS, to analyze the functionalized PU foam with 30 ALD cycles. By comparing Figure 3d and e, we found that new peaks assigned to Al 2S and Al 2P appear in the XPS spectrum of the ALD-treated PU foam, indicating the successful deposition of Al_2O_3 on the foam. Moreover, as shown in Figure 3f, peaks attributed to both Al and Si are present in the XPS spectrum of the deposited and silanized PU foam, once again confirming the occurrence of Al_2O_3 deposition as well as the silanization. The very weak intensity of these peaks indicates the very limited concentration of Al and Si because of the few-nanometer-thick functionalization layer.

The ultrathin functionalization layer contributes in several ways to the overall excellent oil-absorbing performance of the functionalized PU foams. First, considering the micrometer-scaled pore size of the pristine PU foam, the few-nanometer-thick functionalization layer does not noticeably reduce the porosity of the PU foam, and consequently, all of the free space in the PU foam can be used to incorporate absorbed oil, ensuring a high absorption capacity. Second, the ultrathin inorganic layer does not appear to change the high elasticity and compressibility of the PU foam, allowing an outstanding recyclability of the functionalized PU foam for repeated absorption and regeneration by compressing. Third, the very thin nature of the functionalization layer results in shorter periods of time and a lowered consumption of reagents for the functionalization, making the functionalization process more cost efficient.

Considering the high capacity and the fast rate of the functionalized PU foams for absorbing oil as well as their excellent recyclability, we outline plans for a device that is able to continuously recover oily pollutants from water surfaces. This device is designed to be attached to boats and is suitable for use in the cleanup of large-area oil spills on oceans and other water bodies. As shown by the schematic depiction in Figure 4, functionalized PU foams are fixed onto a conveyor belt and driven by the belt. The lower part of the belt with the foam is immersed into the oil layer spread on the water surface. This part of the foam makes contact with and quickly absorbs oil and is then transferred by the moving belt to the upper position, at which a roll compresses the foam to extract the oil from the foam. When the foam passes the roll, the foam is regenerated and is transferred back to the water surface to absorb oil again. The extracted oil drains to the collecting tray fixed under the belt through leaking pores on the belt, and the oil collected in the tray can be pumped into the oil tank on the boat. Such an absorption and extraction process repeats, and therefore, oil spills are removed from the surface of the water
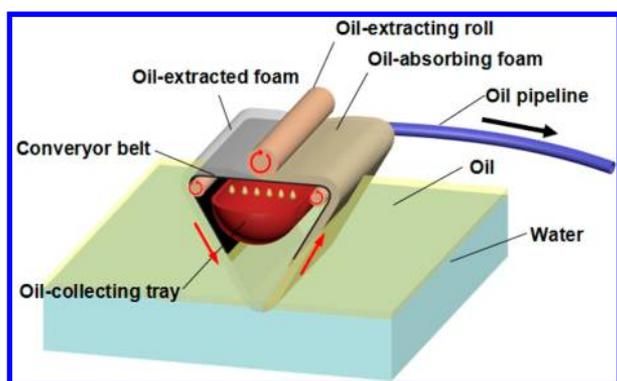
Figure 4. Schematic depiction of a continuous oil-absorbing and extracting device.

and are collected continuously with high efficiency (Supporting Information Movie S3).

Moreover, we demonstrate that the ultrathin-layer-enabled surface functionalization strategy can also be applied to other porous materials, for example, natural loofah foams. Dried loofah possesses a foam-like structure with a high porosity and is composed of multilevel pores ranging from the millimeter to the nanometre scale (Figure 5a and b). A pristine loofah is
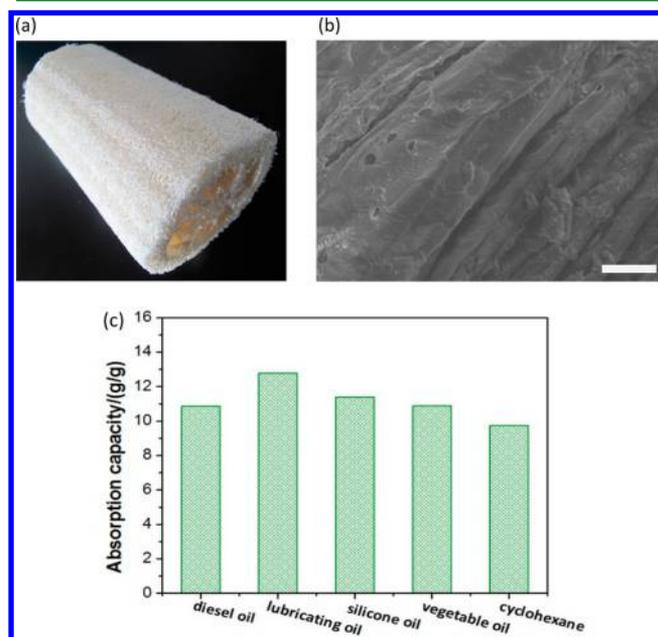

Figure 5. Oil absorbents based on porous biomaterials. Oil absorbents based on porous biomaterials. (a) Photograph of a dried loofah, (b) an SEM micrograph of the loofah, showing the presence of nanoscale pores on it, and (c) the absorption capacity of the functionalized loofah for a variety of oils and solvents. The scale bar in b corresponds to 10 μm.

hydrophilic and does not absorb oils. However, after a surface modification by ALD of Al_2O_3 and coupling of KH570, the loofah becomes highly hydrophobic and capable of selectively absorbing oil from a water surface. As shown in Figure 5c, the modified loofah shows moderate absorption capacities to different oils and solvents, typically in the range from 10 to 12 times of its own weight. Compared to the PU foams modified with the same protocol, the absorption capacity of the modified loofah is much smaller, which may be attributed to the

much larger apparent density of loofah. However, its absorption capacity is still comparable to many other oil absorbents prepared from expensive materials and agents using complicated methods. The loofah-based oil absorbents provide a sustainable and efficient approach for the cleanup of oil spills. We believe such a modification method is also applicable to other porous materials for the generation of highly efficient, water-repelling, and oil-absorptive thin layers on their surfaces.

CONCLUSIONS

We report the production of superb absorbents for oily contaminants with exceptional absorption performances and recyclability by coating ultrathin functionalization layers onto inexpensive, commercially available polyurethane foams. We first deposited an Al_2O_3 transition layer, with a thickness of ca. 5 nm, by atomic layer deposition onto the surface of the PU foam, and we subsequently coupled a single-molecule layer with a thickness <1 nm of silanes to the foam via the hydroxyl groups on the surface of the Al_2O_3 layer. The PU foams consequently obtained outstanding water-repelling ability and oil-affinity without compromising their high porosity and elasticity. Moreover, the ultrathin functionalization layer significantly enhances both the absorption capacity and the absorption rate of PU foams. The functionalized PU foams quickly absorb oils and organic solvents spread on a water surface or precipitated in water. Their highest absorption capacities for diesel oil and vegetable oil reach 120 and 140 times their own weights, values that are typically 5−50 times higher than those for other previously reported polymeric oil absorbents. Moreover, the functionalized PU foams can be recycled more than 60 times with only a slight reduction in the absorption capacity, which is the best recyclability among all reported oil absorbents. Based on the high absorption capacity, the fast absorption rate, and the superior recyclability of the functionalized PU foam, we proposed a device that can be continuously operated to efficiently collect oil spills from a water surface.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional characterization results on oil absorbents prepared at different conditions and the morphology and absorbing properties of functionalized loofah, and movies recording the functionalized PU foam absorbing oil and chloroform and the proposed device continuously absorbing and extracting oil from a water surface. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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