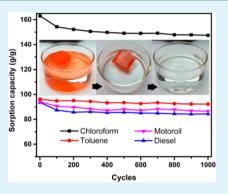# Superhydrophobic Silanized Melamine Sponges as High Efficiency Oil Absorbent Materials

Viet Hung Pham and James H. Dickerson*

Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States

S *Supporting Information*

ABSTRACT: Superhydrophobic sponges and sponge-like materials have attracted great attention recently as potential sorbent materials for oil spill cleanup due to their excellent sorption capacity and high selectivity. A major challenge to their broad use is the fabrication of superhydrophobic sponges with superior recyclability, good mechanical strength, low cost, and manufacture scalability. In this study, we demonstrate a facile, cost-effective, and scalable method to fabricate robust, superhydrophobic sponges through the silanization of commercial melamine sponges via a solution-immersion process. The silanization was achieved through secondary amine groups on the surface of the sponge skeletons with alkylsilane compounds, forming self-assembled monolayers on the surface of sponge skeletons. This resulted in our ability to tune the surface properties of the sponges from being hydrophilic to superhydrophobic with a water contact angle of 151.0°. The superhydrophobic silanized melamine sponge exhibited excellent sorption capacity for a wide range of organic solvents and oils, from 82 to 163 times its own weight, depending on the polarity and density of the employed organic solvents and oils, and high selectivity and outstanding recyclability with an absorption capacity retention greater than 90% after 1000 cycles. These findings offer an effective approach for oil spill containment and environmental remediation.

KEYWORDS: *superhydrophobicity, melamine sponge, oil absorbent, silanization, oil spill cleanup*

■ INTRODUCTION

With the growth of offshore oil exploration, production, and transportation, oil spills and other accidental pollution have become one of the most serious environmental and ecological problems.[1−3] The recent Deepwater Horizon oil spill comprised more than 200 million gallons of oil, which was released into the Gulf of Mexico, which affected a thousand miles of coastline near the oilfield.[4] Cleaning up oil spills and oil slicks from the surfaces of water and along the coastline, among other areas, is a challenging task. Several methods have been used to clean up such calamities, including in situ burning,[2,5] chemical dispersant,[3] skimming,[6,7] bioremediation[8,9] and using sorbents.[10−17] Skimming is the most common method for dealing with such situations, but its limitation involve time-consuming procedures for remediation, high expense, and poor segregation of oil and water.[7] The second most common method is using chemical dispersants to break up oil deposits into droplets, which are easily dissipated within a water column.[3] However, this method can cause additional damage to marine ecosystems due to the synergistic toxicity of the mixture of oil and the employed dispersants.[18] The use of oil sorbents has been considered one of the more effective approaches for oil spill cleaning due to its propensity for oil collection and separation from the present water.[11] Oil sorbents generally are able to concentrate and transform liquid oil into a semisolid or solid phase, which can then be removed from the spill area in a convenient manner.[10,11,14]

Properties of an ideal sorbent material for oil spill cleanup include hydrophobicity and oleophilicity, high oil sorption capacity, fast kinetics, no water sorption, buoyancy, good mechanical strength for easy recovery from the water surface, reusability, low cost, and broad availability.[11,14,19] Several conventional sorbents, such as modified organophilic clay, zeolite, silica aerogel, exfoliated graphite, cellulose-based materials, and propylene-based materials, exhibit some of these properties.[11] However, the primary limitations of these conventional sorbents are low oil sorption capacity (generally tens of grams of oil per gram of sorbent) and poor recyclability.

Recent studies of novel oil sorbents have focused on superhydrophobic sponges and sponge-like materials that exhibited superior oil sorption capacity.[13−16,20−31] Gui et al. reported the synthesis of CNT sponges by chemical vapor deposition in which nanotubes were self-assembled into a three-dimensionally interconnected framework.[13] The CNT sponges were very light (bulk density of 5−10 mg/cm³), highly porous (porosity > 99%), superhydrophobic in their pristine form (water contact angle of about 156°), and elastically and reversibly deformable into any shape, all of which were desired characteristics of ideal oil sorbent materials. The sponge absorbed a wide range of solvents and oils with excellent selectivity, and recyclability, with sorption capacities up to 180

times its own weight.[13] Zhao et al. prepared ultralight, nitrogen-doped graphene frameworks that mainly consisted of networks of only a few graphene layers.[16] These graphene frameworks had an ultralow density of 2.1 mg/cm³, one of the lowest densities for graphene framework architectures. These graphene frameworks exhibited excellent sorption capacity, with values as high as 200−600 times their own weight for common pollutants, organic solvents, and oils.[13] Although these graphene frameworks exhibited excellent oil sorption capacity, their recyclability was quite limited. To improve the oil sorption performance of the graphene frameworks, Sun et al. combined graphene and CNT to produce ultralight, superelastic aerogels with densities less than 1 mg/cm³ and porosities of approximately 99.9%.[21] The ultralight graphene−CNT aerogel possessed ultrahigh oil sorption capacity, 215−913 times its own weight depending on the oil density. In spite of exceptional oil sorption capacity, CNT, graphene, and graphene−CNT sponge-like materials are less practical in potential in oil spill cleanup application because of their high cost, their associated complex preparation processes, and existing challenges in scaling their fabrication.

Recently, the surface modification of commercial polymer sponges, such as polyurethane and melamine sponges, have tuned the surface properties of the sponges from hydrophilicity to superhyphobicity, which has attracted considerable attention.[15,24−30] Due to their low density, high porosity, three-dimensional skeleton structure, good elasticity, and flexibility, polymer sponges have exhibited excellent sorption of both water and oil, making them impractical for highly efficient and selective removal of oils from water.[15] However, the modification of sponges through coating hydrophobic materials on their surfaces can tune the surface property of a sponge from hydrophilicity to superhydrophobicity, resulting in great improvement of the sorption selectivity. Thus, far, several materials have been used to modify the surface properties of commercial sponges, such as hydrophobic polymers,[25,27] superhydrophobic activated carbon,[29] CNTs,[30] and graphene.[24,26] Zhu et al. modified polyurethane sponges by initially coating sponge skeletons with a film of copper via electroless deposition and subsequently modifying the skeletons with superhydrophobic and superoleophilic coatings through a solution-immersion process.[15] The obtained superhydrophobic sponges exhibited selective sorption of various oils up to 13 times their weight and sorption capacity retention of about 50−90% after nine cycles. In another study, Zhou et al. impregnated polyurethane sponges with ferric chloride and perfluorooctyltriethoxysilane (PTES) and subsequently vapor-phase-polymerized pyrrole to produce superhydrophobic coatings of PTES−polypyrrole.[25] The as-prepared sponge selectively absorbed oil from water with high uptake capacity, as much as 20 times its own weight and the sorption capacity retention of about 85% after 5 cycles. Wang and Lin recently reported a method to modify the surface properties of polyurethane sponges by repeatedly dip-coating them in a CNT/poly(dimethylsiloxane) (PDMS) solution, drying them, and finally curing them at 120 °C for 6 h.[30] The obtained superhydrophobic CNT−PDMS-coated sponges exhibited good oil sorption capacity, up to 25 times their own weight.

In a similar work, Nguyen et al. modified melamine sponges by using liquid-exfoliated graphene−PDMS coatings.[24] Melamine sponges were initially coated with graphene through a repeated dip-coating and drying technique, using a graphene suspension and a PDMS solution. This yielded thin PDMS

films that cemented the graphene nanosheets onto the sponge skeletons. The obtained graphene-based sponge exhibited sorption capacities ranging from 54 to 165 times its own weight for a variety of oils and solvents. However, squeezing the sponges extracted ∼20% of the absorbed oils, which greatly limited their potential for practical oil spill cleanup applications. The most effective modification of a sponge by using reduced graphene oxide (RGO) as a hydrophobic coating was reported by Liu et al.[26] Their polyurethane sponge first was dip-coated in an aqueous graphene oxide solution, followed by hydrazine reduction. The obtained RGO-coated sponge exhibited excellent oil sorption capacities (80−160 times its own weight) as well as recyclability (95% retention after 50 cycles). In general, surface modification of sponges by coating hydrophobic materials onto said sponge skeletons is an effective method to tune a sponge from hydrophilic to superhydrophobic. Almost all of the superhydrophobic sponges exhibit good oil sorption capacity and recyclability by distillation as the extraction method. However, their recyclability by squeezing (as the oil extraction method) remains quite poor. During the squeezing process, the hydrophobic coatings easily detach from the skeletons due to the weak adhesion between coatings and skeletons.[27] For large-scale oil spill cleanup, squeezing appears to be the only on-site, fast, and cost-effective extraction method to recover absorbed oil. Thus, the fabrication of robust superhydrophobic sponges that can withstand multiple cycles of sorption−squeezing continues to be a challenge.

In this work, we present a one-step, facile, cost-effective and scalable method to fabricate robust superhydrophobic sponges with excellent oil sorption capacity and exceptional recyclability. The superhydrophobic sponges were prepared by silanizing melamine sponges through secondary amine groups on the surface of the sponge skeletons with alkylsilane compounds, forming a self-assembled monolayer (SAM) on the surface of said sponge skeletons. The alkylsilane SAM covalently bonded onto the surface of the skeletons, turning the sponge from hydrophilic to superhydrophobic. Unlike previous superhydrophobic sponges in which hydrophobic coatings physically attached onto the sponge skeletons and easily detached during squeezing, the alkylsilane SAM covalently bonded on the skeletons, which remained unaffected by the squeezing process. The superhydrophobic melamine sponges absorbed a wide range of organic solvents and oils with sorption capacities of 82−163 times their own weight and exhibited outstanding recyclability with oil sorption retention of more than 90% after 1000 cycles of sorption−squeezing.

■ EXPERIMENTAL SECTION

Materials. Commercial melamine sponges were purchased from www.spongeoutlet.com. Octadecyltrichlorosilane and organic solvents (acetone, butanol, toluene, tetrahydrofuran (THF), dimethylformamide (DMF), and chloroform) were purchased from Sigma-Aldrich. Oils (motor oil, machine oil, and mineral oil) were obtained from McMaster-Carr. The diesel oil, also known as *On-Highway* diesel, a ultralow sulfur-grade diesel (15 ppm sulfur) was provided by Brookhaven National Laboratory. The biodiesel was provided by Hero BX (Hero BX 3000).

Silanization of Melamine Sponge. The silanization of the melamine sponges was performed by a simple solution-immersion process. The melamine sponges were cut into 2.5 × 2.5 × 3.0 cm³ pieces and were immersed in a solution of octadecyltrichlorosilane in toluene (0.5 wt %) for 5, 10, 20, and 30 min. Subsequently, the sponges were removed from the solution and were squeezed to extract
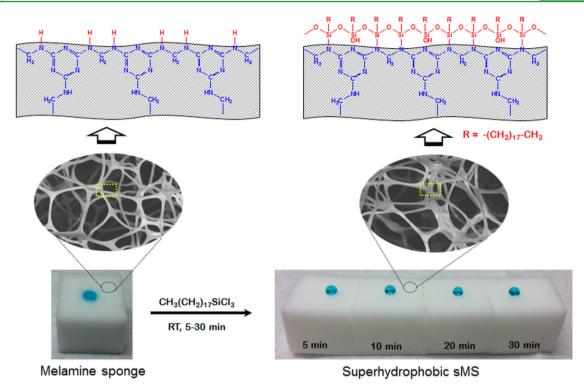
Figure 1. Schematic illustration of the silanization of a melamine sponge. The water droplet (colored with blue dye to facilitate observation) is completely absorbed by the untreated melamine sponge, whereas it is repelled from the sMS, indicating the hydrophobic characteristics of the sMS sponge.

the absorbed solution. Thereafter, they were repeatedly washed with fresh toluene by the sorption−squeezing process and were finally dried at 120 °C for 1 h. The resultant silanized melamine sponges were denoted as sMS-*x*, where *x* indicates the silanization time in minutes.

Characterizations. The sMS-*x* sponges were characterized by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR, Thermo Scientific). The elemental composition of the surface of the sponges was determined by X-ray photoelectron spectroscopy (XPS), conducted in an ultrahigh vacuum chamber equipped with an X-ray photoelectron spectrometer (SPECS Phoibos 100 MCD analyzer) and a nonmonochromatized Al Kα X-ray source (SPECS XR 50). The chamber was maintained at a base pressure of $\sim 2 \times 10^{-10}$ Torr. The morphologies of melamine sponges were observed by scanning electron microscopy (SEM, Hitachi S4800). Contact angle measurements were conducted using an OCA 15+ goniometer (DataPhysics). Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10 °C/min (PerkinElmer).

Oils Sorption and Recyclability of sMS. The absorption capacities of sMS for various oils and organic solvents were determined by dipping a piece of sMS into the target liquid (oil or organic solvent) until the sMS was saturated with said liquid and then taking it out for weight measurement. The gravimetric sorption capacity ($Q_{m/m}$), gravimetric/volumetric sorption capacity ($Q_{m/v}$), and volumetric sorption capacity ($Q_{v/v}$) were calculated according to the following equations:

$$Q_{m/m} = \frac{(m_{s,o} - m_s)}{m_s} \tag{1}$$

$$Q_{m/v} = Q_{m/m} d_s = \frac{(m_{s,o} - m_s)}{m_s} d_s \tag{2}$$

$$Q_{v/v} = \frac{Q_{m/v}}{d_o} = \frac{(m_{s,o} - m_s)}{m_s} \frac{d_s}{d_o} \tag{3}$$

where m_s and $m_{s,o}$ are the sponge's masses before and after sorption and d_s and d_o are the bulk density of the sponge and the density of organic liquid, respectively. The recyclability of sMS was evaluated by repeated sorption−squeezing processes. The sorption−squeezing was performed by immersing the sMS into oils, waiting until the sponge became saturated with the oils, and then manually squeezing the sponge using a clamp to extract at least 80% of absorbed oils (see Movie S1 of the Supporting Information).

■ RESULTS AND DISCUSSION

Melamine sponges are open-cell foam structures, consisting of formaldehyde-melamine-sodium bisulfite copolymer, which is widely used as an abrasive cleaner and as soundproofing material. Melamine sponges have low density (4−12 mg cm^{-3}), high porosity (>99%), and excellent elasticity, all of which are ideal characteristics for sorption materials. The melamine sponges used in this study have bulk density of 8.07 mg cm^{-3}, which accounts for a 99.49% porosity considering a specific density of 1.57 g cm^{-3} for melamine resin. The mechanism for the functionalization of the melamine sponges from hydrophilicity to superhydrophobicity is illustrated in Figure 1. The silanization was performed by dipping the melamine sponge into an octadecyltrichlorosilane solution at room temperature for 5−30 min, followed by a drying step at 120 °C for 1 h. Octadecyltrichlorosilane was first hydrolyzed by water that had absorbed onto the surface of the melamine sponge's skeleton (melamine sponges absorb ∼ 4.0 wt % H$_2$O at room temperature due to its high hydrophilicity) to form silanol compounds. Subsequently, two reactions simultaneously occurred: (i) direct hydrogen bonding between the silanol and the secondary amine groups on the of melamine sponge skeleton's surface and (ii) condensation of the Si−OH to form oligomers, which further interact with amine groups via hydrogen bonding. Finally during the drying step, dehydration

reactions occurred that resulted in the SAM covalently bonding onto the surface of the skeletons (Supporting Information Figure S1).[32]

The silanization efficiency was characterized by gravimetric measurements using an analytical balance with an accuracy of 0.01 mg. Table 1 shows that the alkylsilane loading on sMS was

Table 1. Properties of Melamine Sponge and sMS

	alkylsilane loading on sMS (wt %)	bulk density (mg/cm³)	porosity (%)
melamine sponge		8.07	99.49
sMS-5	0.338	8.10	99.48
sMS-10	0.507	8.11	99.48
sMS-20	0.572	8.11	99.48
sMS-30	0.588	8.12	99.48

very small, less than 0.6 wt %. The silanization occurred quickly during the first 10 min and approached saturation after 30 min. The bulk density of the sMS slightly increased as a function of silanization time, from 8.07 mg cm^{-3} for the untreated melamine sponge to 8.12 mg cm^{-3} for the sMS-30 sample. On the contrary, the porosities of the untreated melamine sponge and the sMSs were nearly identical.

The formation of the alkylsilane SAM on the sponge skeletons was characterized by ATR-FTIR, XPS, and TGA. Figure 2a shows the ATR-FTIR spectra of the untreated melamine sponge and the sMS as functions of silanization time. The spectrum of the melamine sponge displayed prominent peaks at 812, 1143, 1542, and 3394 cm^{-1} that were assigned to triazine ring bending, C−O stretching, C═N stretching, and

N−H (of the secondary amine) stretching, respectively. Peaks centered at 981, 1328, and 1467 cm^{-1} were indicative of C−H bending.[33] Moreover, two small peaks at 2827 and 2891 cm^{-1} were attributed to C−H stretching.[32] After silanization, the intensity of these peaks strengthened significantly and slightly red-shifted to 2850 and 2920 cm^{-1}, which were ascribed to C−H stretching in the -CH$_2$ and -CH$_3$ of the alkylsilane. In addition, the intensity of the peak centered at 990 cm^{-1} significantly increased due to the overlapping of the C−H bending peak (981 cm^{-1}) and a new Si−O−Si stretching peak (1004 cm^{-1}) that evolved due to the formation of alkylsilane SAM on the surface of sMS's skeleton.[34]

The XPS was employed further to confirm the silanization of the melamine sponges. The XPS survey spectrum in Figure 2b indicated five elements, including C, N, O, Na, and S. This was consistent with the composition of commercial foams containing the formaldehyde-melamine-sodium bisulfite co-polymer. Although no difference was observed in the binding energies of the element peaks after silanization, the intensity of C 1s significantly increased indicating the functionalization of alkylsilane on the surface of sMS's skeleton. The absence of a Si peak in the spectra of sMS might be explained by the low absolute concentration of Si within the system, below the detection limit.

Figure 2c shows TGA curves of melamine sponge and sMSs characterized in an argon atmosphere. The TGA curve of the melamine sponge can be divided into four temperature ranges through which the mass losses appeared: 30−100, 230−370, 370−405, and 405−600 °C. The ~4.0 wt % mass loss in the 30−100 °C range can be attributed to the evaporation of the
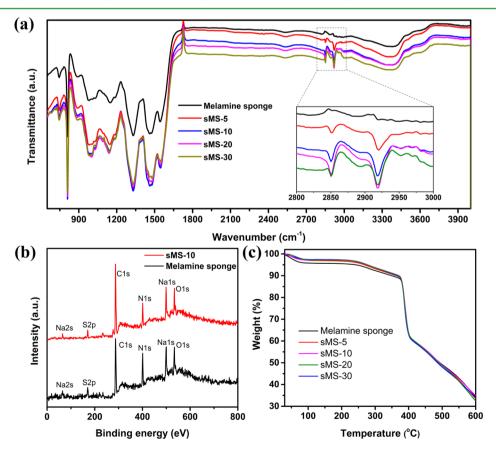

Figure 2. (a) ATR-FTIR, (b) XPS, and (c) TGA spectra of the untreated melamine sponge and the various sMS materials.

absorbed water on the hydrophilic surface of the sponge. The main mass loss of ~27.0 wt % that occurred in the temperature region of 370−405 °C can be ascribed to the breakdown of the methylene bridges. Mass losses at temperatures higher than 405 °C were attributed to the thermal decomposition of the triazine ring.[33] The TGA curves of sMSs were almost identical and were similar to the TGA curve of the untreated melamine sponge, though two small differences were evident: (i) the mass loss in the first temperature region was only ~2.5 wt % due to a smaller amount of water that had absorbed onto the hydrophobic surface of sMSs; (ii) the primary mass loss in the temperature range of 370−405 °C was slightly larger (~28.0 wt %) due to the thermal decomposition of the alkylsilane SAM.

The morphologies of the melamine sponges before and after silanization were examined by SEM, as shown in Figure 3. The
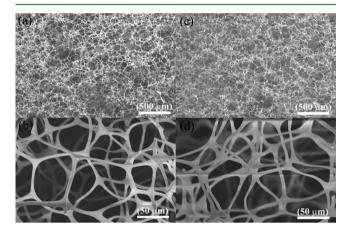

Figure 3. SEM images of (a, b) the untreated melamine sponge and (c, d) sMS-10.

melamine sponges comprised a three-dimensional, hierarchical, porous structure with pore sizes in the range of 100−150 μm and with smooth skeletons of average diameter ~10 μm. As expected, the sMS materials had the same porous structure and skeleton dimensions, reaffirming that the thickness of alkylsilane SAM (~3.0 nm) on the surface of the skeleton was well within the uncertainty of the skeleton's thickness (~10.0 μm).

The hydrophobicity of the sMS materials was characterized by water contact angle measurements. As shown in Figure 4a, the water contact angle of sMS notably increased as a function of silanization time, from 0° for the melamine sponge to 147.2 ± 1.5° after 5 min of silanization. After 10 min, the value reached 150.4 ± 1.2° and a maximum of 151.0 ± 1.1° after 30 min, indicating the superhydrophobic characteristics of the functionalized sponges. Figure 4b depicts a photograph of the superhydrophobic sMS-10 floated atop a water bath while the hydrophilic melamine sponge sank to the bottom. When immersing the superhydrophobic sMS-10 in water by applying an external force, an interface formed between entrapped air residing along the surface of the sponge and the surrounding water, giving rise to a mirror-like surface on the sMS-10; this phenomenon is due to the Cassie−Baxter nonwetting behavior.[23,25] After the external force was released, the sMS-10 immediately floated to the water surface without absorption of any of the surrounding water, indicating its excellent water repellency.
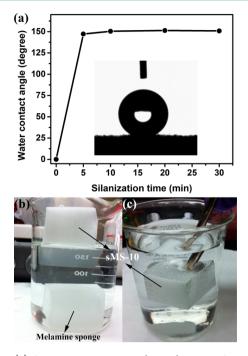

Figure 4. (a) Static water contact angle results on sMS materials as functions of silanization time. Inset: A representative optical photograph of a water droplet on sMS-10. Photographs of (b) the untreated melamine sponge and the sMS-10 being placed on the water meniscus and (c) sMS-10 being immersed in water by applying an external force.

Water repellency is a crucial property of sorption materials, particularly for oil spill remediation in aqueous environments. As shown in Figure 5, sMS-10 exhibited excellent selective sorption of oil on the surface of brackish water. By dipping the sMS-10 into a mixture of oil and water, the oil was quickly absorbed into the sponge in a few seconds. As seen in Figure 5, the oil-saturated sMS continued to float on the water surface;
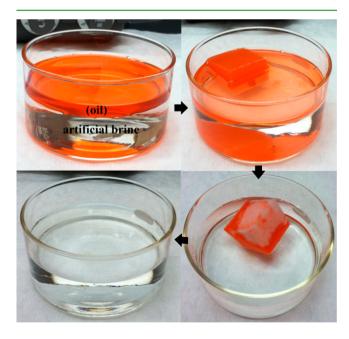

Figure 5. Photographs of the selective sorption of oil with the sMS-10 material. The oil was dyed with Sudan III to facilitate clear observation of the phenomenon.

removal of the oil, thus, involved removing the sMS-10 from the environment. The absorbed oil was easily recaptured by the aforementioned squeezing process. Then, the processed sMS-10 was reestablished at the oil−water interface to remove the remaining oil from the water surface, resulting in only clean water (see Figure 5 and Movie S2 of the Supporting Information).

To investigate the maximum sorption capacity, sorption tests were performed in the organic solvents and oils in the absence of water. Various organic solvents and oils with different polarities, densities, and viscosities were tested. The sorption uptake rate of the sMS strongly depended on the viscosity of the organic solvents and oils, ranging from a few seconds for low viscosity organic solvents, such as toluene, THF, DMF, and chloroform, to minutes for high viscosity oils, such as diesel, mineral oil, and machine oil. Table 2 shows the sorption

Figure 6. Sorption recyclability of sMS-10 for various kinds of organic solvents and oils.

Table 2. Sorption Capacities and Sorption Capacity Retentions after 100 Cycles of Sorption−Squeezing of sMS-10 for Various Organic Solvents and Oils

	density (g/cm^3)	sorption capacity (g/g)	sorption capacity retention after 100 cycles (%)
acetone	0.79	83.6	96.1
butanol	0.81	82.0	97.4
toluene	0.87	96.2	98.6
THF	0.89	91.1	96.1
DMF	0.94	97.4	98.7
chloroform	1.48	163.0	94.6
diesel	0.83	93.6	93.4
motor oil	0.86	94.0	95.5
machine oil	0.86	99.8	96.4
biodiesel	0.88	98.2	94.0
mineral oil	0.88	100.7	96.9

capacities and their retentions after 100 cycles of sorption−squeezing of sMS-10 for various kinds of organic solvents and oils. The sMS-10 exhibited very high sorption capacity, from 82 to 163 times its own weight, depending on the polarity and density of the employed organic solvents and oils. More interestingly, the sMS-10 also showed excellent recyclability with sorption capacity retention after 100 cycles of sorption−squeezing of more than 93% for all kinds of organic solvents and oils. For further analysis of the recyclability of sMS-10, four kinds of organic solvents and oils, including toluene, chloroform, diesel, and motor oil, were chosen to be tested up to 1000 cycles of sorption−squeezing at a strain compression of 80%. As shown in Figure 6, the sorption capacity retention of sMS-10 for all of the chosen organic solvents and oils remained higher than 90%, indicating the outstanding recyclability of sMS-10. To the best of our knowledge, sMS-10 is the first sponge or sponge-like sorbent material that possesses a demonstrated sorption−squeezing recyclability capacity greater than 90% for cycling up to 1000 cycles for a variety of organic solvents and oils.

For the majority of those studies of oil absorbent materials, the gravimetric sorption capacity was used to evaluate the overall absorption ability of said materials. The gravimetric sorption capacity density greatly depends on the bulk density, much more than on the porosity of the sorbent material. Therefore, the sorbent materials that have low or ultralow bulk densities typically exhibit very high gravimetric sorption capacities. However, their volumetric sorption capacity some-
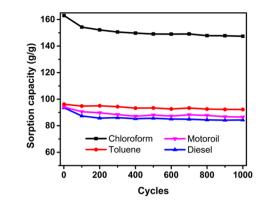
times can be lower than that of other sorbent materials that have low gravimetric sorption capacity. For example, as shown in Table 3, graphene−CNT aerogel has a gravimetric sorption capacity for chloroform of up to 568 g/g and a volumetric sorption capacity of only 0.537 m^3/m^3, which is significantly lower than that of marshmallow-like macroporous gel (gravimetric sorption capacity = 14 g/g). For practical applications, use of the volumetric sorption capacity and the gravimetric/volumetric sorption capacity, instead of the gravimetric sorption capacity, are notably more reasonable and are more appropriate figures-of-merit. For example, although the marshmallow-like macroporous gel reference reports a gravimetric sorption capacity of 14 g/g, the study's data subsequently led to a volumetric sorption capacity of 1.135 m^3/m^3, which is unphysical. In other words, the report suggests that this macroporous gel can retain a larger volume of chloroform than the volume that is encapsulated by the exterior surface of the gel itself (by a factor of 1.135). Table 3 juxtaposes the properties of sMS with other sponge and sponge-like sorbent materials. Not only do the sMS materials possess high sorption capacities that are comparable to the best sorbent materials, the sMS also exhibits markedly enhanced recyclability by the sorption−squeezing process, compared with the other sorbent materials. Moreover, the fabrication of sMS is very fast, simple, cost-effective, and easily scalable. More significantly, the sMS materials provide comparable, if not superior, oil sorption characteristics, making them very promising materials for oil spill remediation applications.

■ CONCLUSION

In summary, a one-step, facile, and cost-effective method was reported for the fabrication of robust, superhydrophobic sponges by silanization of commercial melamine sponges via a solution-immersion process. The silanization occurred through secondary amine groups attached to the surface of sponge skeletons with alkylsilane compounds, forming a SAM on their surface. This resulted in our ability to tune the surface characteristics of the sponges from hydrophilicity to super-hydrophobicity. The novel superhydrophobic sponges possessed many of the crucial properties of an ideal sorbent material for oil spill cleanup, such as excellent sorption capacities up to 163 times its own weight, high oil selective sorption, outstanding recyclability with sorption capacity retention of more than 90% after 1000 cycles of sorption−squeezing process, being inexpensive, and wide availability. We

Table 3. Comparison of Sponge and Sponge-like Sorbent Materials

sorbent materials	solvent/oil	sorption capacity (g/g)	sorption capacity (kg/m^3)	sorption capacity (m^3/m^3)	recyclability by sorption-squeezing process	cost	ref
marshmallow-like macroporous gel	chloroform	14	1680	1.135	not reported	medium	17
	mineral oil	8	960	1.090			
carbon fiber aerogel	chloroform	115	1380	0.932	fair	quite low	23
	olive oil	85	1020	1.133			
CNT sponge	chloroform	176	1038	0.701	excellent	high	13
	diesel	144	849	0.998			
graphene framework	chloroform	490	1029	0.695	poor	high	16
	olive oil	480	1008	1.095			
graphene-CNT aerogel	chloroform	568	795	0.537	excellent	high	21
	motor oil	341	477	0.542			
graphene coated melamine sponge	chloroform	165	1864	1.259	poor	medium	24
	pump oil	92	1040	1.155			
reduced graphene oxide coated polyurethane sponge	chloroform	160	1408	0.951	good	medium	26
	pump oil	100	880	0.978			
mercapto-functionalized polydopamine coated melamine sponge	chloroform	195		0.90	outstanding	medium	31
	pump oil	100		0.80			
sMS	chloroform	163	1337	0.903	outstanding	low	present work
	mineral oil	101	862	0.938			

assert that such sponges are promising sorbent materials for oil spill containment and environmental remediation.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Figures showing mechanism of silanization of melamine sponge and a photograph of sMS after 1000 cycles of sorption—squeezing for different organic solvents and oils, and movies showing oil absorption and recyclability and oil selective absorption. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: jdickerson@bnl.gov.

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

ABBREVIATIONS
CNT, carbon nanotube
PTES, perfluorooctyltriethoxysilane
PDMS, poly(dimethylsiloxane)
RGO, reduced graphene oxide
SAM, self-assembled monolayer
THF, tetrahydrofuran
DMF, dimethylformamide
sMS-x, silanized melamine sponge where x indicates the silanization time in minutes
ATR-FTIR, attenuated total reflection-Fourier transform infrared spectroscopy
XPS, X-ray photoelectron spectroscopy
SEM, scanning electron microscopy
TGA, thermogravimetric analysis

REFERENCES
(1) Peterson, C. H.; Rice, S. D.; Short, J. W.; Esler, D.; Bodkin, J. L.; Ballachey, B. E.; Irons, D. B. Long-term Ecosystem Response to the Exxon Valdez Oil Spill. *Science* **2003**, *302*, 2082−2086.
(2) Schaum, J.; Cohen, M.; Perry, S.; Artz, R.; Draxler, R.; Frithsen, J. B.; Heist, D.; Lorber, M.; Phillips, L. Screening Level Assessment of Risks Due to Dioxin Emissions from Burning Oil from the BP Deepwater Horizon Gulf of Mexico Spill. *Environ. Sci. Technol.* **2010**, *44*, 9383−9389.
(3) Kujawinski, E. B.; Kido Soule, M. C.; Valentine, D. C. L.; Boysen, A. K.; Longnecker, K.; Redmond, M. C. Fate of Dispersants Associated with the Deepwater Horizon Oil Spill. *Environ. Sci. Technol.* **2011**, *45*, 1298−1306.
(4) Allan, S. E.; Smith, B. W.; Anderson, K. A. Impact of the Deepwater Horizon Oil Spill on Bioavailable Polycyclic Aromatic Hydrocarbons in Gulf of Mexico Coastal Waters. *Environ. Sci. Technol.* **2012**, *46*, 2033−2039.
(5) Aurell, J.; Gullett, B. K. Aerostat Sampling of PCDD/PCDF Emissions from the Gulf Oil Spill in situ Burns. *Environ. Sci. Technol.* **2010**, *44*, 9431−9437.
(6) Broje, V.; Keller, A. A. Improved Mechanical Oil Spill Recovery Using an Optimized Geometry for the Skimmer Surface. *Environ. Sci. Technol.* **2006**, *40*, 7914−7918.
(7) Broje, V.; Keller, A. A. Effect of Operational Parameters on the Recovery Rate of an Oleophilic Drum Skimmer. *J. Hazard. Mater.* **2007**, *148*, 136−143.

(8) Zahed, M. A.; Aziz, H. A.; Isa, M. H.; Mohajeri, L.; Mohajeri, S. Optimal Conditions for Bioremediation of Oily Seawater. *Bioresour. Technol.* **2010**, *101*, 9455−9460.

(9) Boopathy, R.; Shield, S.; Nunna, S. Biodegradation of Crude Oil from the BP Oil Spill in the Marsh Sediments of Southeast Louisiana, USA. *Appl. Biochem. Biotechnol.* **2012**, *167*, 1560−1568.

(10) Choi, H.-M.; Cloud, R. M. Natural Sorbents in Oil Spill Cleanup. *Environ. Sci. Technol.* **1992**, *26*, 772−776.

(11) Adebajo, M. O.; Frost, R. L.; Kloprogge, J. T.; Carmody, O.; Kokot, S. J. Porous Materials for Oil Spill Cleanup: A Review of Synthesis and Absorbing Properties. *J. Porous Mater.* **2003**, *10*, 159−170.

(12) Wei, Q. F.; Mather, R. R.; Fotheringham, A. F.; Yang, R. D. Evaluation of Nonwoven Polypropylene Oil Sorbents in Marine Oil-Spill Recovery. *Mar. Pollut. Bull.* **2003**, *46*, 780−783.

(13) Gui, X.; Wei, J.; Wang, K.; Cao, A.; Zhu, H.; Jia, Y.; Shu, Q.; Wu, D. Carbon Nanotube Sponge. *Adv. Mater.* **2010**, *22*, 617−621.

(14) Zhu, H.; Qiu, S.; Jiang, W.; Wu, D.; Zhang, C. Evaluation of Electrospun Polyvinyl Chloride/Polystyrene Fibers As Sorbent Materials for Oil Spill Cleanup. *Environ. Sci. Technol.* **2011**, *45*, 4527−4531.

(15) Zhu, Q.; Pan, Q.; Liu, F. Facile Removal and Collection of Oils from Water Surfaces through Superhydrophobic and Superoleophilic Sponges. *J. Phys. Chem. C* **2011**, *115*, 17464−17470.

(16) Zhao, Y.; Hu, C.; Hu, Y.; Cheng, H.; Shi, G.; Qu, L. A Versatile, Ultralight, Nitrogen-Doped Graphene Framework. *Angew. Chem., Int. Ed.* **2012**, *51*, 11371−11375.

(17) Hayase, G.; Kanamori, K.; Fukuchi, M.; Kaji, H.; Nakanishi, K. Facile Synthesis of Marshmallow-like Macroporous Gels Usable under Harsh Condition for the Separation of Oil and Water. *Angew. Chem., Int. Ed.* **2013**, *52*, 1986−1989.

(18) Rico-Martínez, R.; Snell, T. W.; Shearer, T. L. Synergistic Toxicity of Macondo Crude Oil and Dispersant Corexit 9500A® to the *Brachionus plicatilis* Species Complex (Rotifera). *Environ. Polutt.* **2013**, *173*, 5−10.

(19) Yuan, X.; Chung, T. C. M. Novel Solution to Oil Spill Recovery: Using Thermodegradable Polyolefin Oil Superabsorbent Polymer (Oil−SAP). *Energy Fuels* **2012**, *26*, 4896−4902.

(20) Gui, X.; Li, H.; Wang, K.; Wei, J.; Jia, Y.; Li, Z.; Fan, L.; Cao, A.; Zhu, H.; Wu, D. Recyclable Carbon Nanotube Sponges for Oil Absorption. *Acta Mater.* **2011**, *59*, 4798−4804.

(21) Sun, H.; Xu, Z.; Gao, C. Multifunctional, Ultra-flyweight, Synergistically Assembled Carbon Aerogels. *Adv. Mater.* **2013**, *25*, 2554−2560.

(22) Wu, Z.-Y.; Li, C.; Liang, H.-w.; Chen, J.-F.; Yu, S.-H. Ultralight, Flexible, and Fire-Resistant Carbon Nanofiber Aerogels from Bacterial Cellulose. *Angew. Chem., Int. Ed.* **2013**, *52*, 2925−2929.

(23) Bi, H.; Yin, Z.; Cao, X.; Xie, X.; Tan, C.; Huang, X.; Chen, B.; Chen, F.; Yang, Q.; Bu, X.; Lu, x.; Sun, L.; Zhang, H. Carbon Fiber Aerogel Made from Raw Cotton: A Novel, Efficient and Recyclable Sorbent for Oils and Organic Solvents. *Adv. Mater.* **2013**, *25*, 5916−5921.

(24) Nguyen, D. D.; Tai, N.-H.; Lee, S.-B.; Kuo, W.-S. Super-hydrophobic and Superoleophilic Properties of Graphene-based Sponges Fabricated Using a Facile Dip Coating Method. *Energy Environ. Sci.* **2012**, *5*, 7908−7912.

(25) Zhou, X.; Zhang, Z.; Xu, X.; Men, X.; Zhu, X. Facile Fabrication of Superhydrophobic Sponge with Selective Absorption and Collection of Oil from Water. *Ind. Eng. Chem. Res.* **2013**, *52*, 9411−9416.

(26) Liu, Y.; Ma, J.; Wu, T.; Wang, X.; Huang, G.; Liu, Y.; Qiu, H.; Li, Y.; Wang, W.; Gao, J. Cost-Effective Reduced Graphene Oxide-Coated Polyurethane Sponge as a Highly Efficient and Reusable Oil-Absorbent. *ACS Appl. Mater. Interfaces* **2013**, *5*, 10018−10026.

(27) Zhu, Q.; Chu, Y.; Wang, Z.; Chen, N.; Lin, L.; Liu, F.; Pan, Q. Robust Superhydrophobic Polyurethane Sponge as a Highly Reusable Oil-Absorption Material. *J. Mater. Chem. A* **2013**, *1*, 5386−5393.

(28) Chen, N.; Pan, Q. Versatile Fabrication of Ultralight Magnetic Foams and Application for oil Water Separation. *ACS Nano* **2013**, *7*, 6875−6883.

(29) Sun, H.; Li, A.; Zhu, Z.; Liang, W.; Zhao, X.; La, P.; Deng, W. Superhydrophobic Activated Carbon-Coated Sponges for Separation and Absorption. *ChemSusChem.* **2013**, *6*, 1057−1062.

(30) Wang, C.-F.; Lin, S.-J. Robust Superhydrophobic/Super-oleophilic Sponge for Effective Continuous Absorption and Expulsion of Oil Pollutants from Water. *ACS Appl. Mater. Interfaces* **2013**, *5*, 8861−8864.

(31) Ruan, C.; Ai, K.; Li, X.; Lu, L. A Superhydrophobic Sponge with Excellent Absorbency and Flame Retardancy. *Angew. Chem., Int. Ed.* **2014**, *53*, 1−6.

(32) Arkles, B. Tailoring Surfaces with Silanes. *CHEMTECH* **1977**, *7*, 766−778.

(33) Merline, D. J.; Vukusic, S.; Abdala, A. A. Melamine Formaldehyde: Curing Studies and Reaction Mechanism. *Polym. J.* **2013**, *45*, 413−419.

(34) Kulkarni, S. A.; Ogale, S. B.; Vijayamohanan, K. P. Tuning the Hydrophobic Properties of Silica Particles by Surface Silanization Using Mixed Self-Assembled Monolayers. *J. Colloid Interface Sci.* **2008**, *318*, 372−379.