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Letter

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Robust Superhydrophobic/Superoleophilic Sponge for Effective Continuous Absorption and Expulsion of Oil Pollutants from Water

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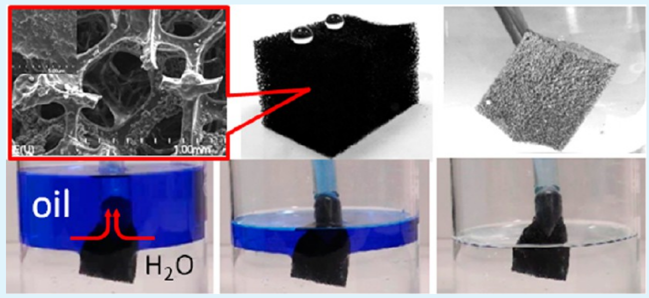
S Supporting Information

ABSTRACT: With the growth of oil production and transportation, there is greater potential for accidental oil spills. Here we fabricated a robust superhydrophobic and superoleophilic carbon nanotube/poly(dimethylsiloxane)-coated polyurethane sponge for the continuous absorption and expulsion of oils and organic solvents from water surfaces. When applied in conjunction with a vacuum system, this sponge could separate great amounts of oils—up to 35000 times its own weight—from water in a one-step process and could also separate surfactant-free water-in-oil emulsions with high efficiency (oil purity: >99.97 wt %), making it a promising candidate material for use in oil-spill cleanups.



KEYWORDS: *superhydrophobic, superoleophilic, continuous separation, emulsion separation, carbon nanotube, sponge*

■ INTRODUCTION

With the expansion of oil production and transportation, there is increasing potential for oil spills from industrial accidents or the sinking of oil tankers or ships. In 2010, the explosion of BP's Deepwater Horizon oil rig resulted in 210 million gallons of oil being released into the Gulf of Mexico. As a result, there is a need to develop new materials for the collection and separation of large amounts of organic pollutants from water surfaces.[1−3] Recently, materials possessing both superhydrophobic and superoleophilic properties—particularly meshes, films, and membranes—have attracted broad attention because of their capacity for the efficient separation of oils, organic pollutants, and other hydrophobic organic solvents from water.[4−9] Although these previously developed materials can be effective for oil/water separation, they cannot be applied to the oil spills because they require the polluted water to be accumulated first and then filtered.

In previous reports, superhydrophobic/superoleophilic three-dimensional (3D) porous materials have been suggested for the absorption and removal of various kinds of oils and organic solvents from water surfaces, as a facile approach for the cleanup of oil spills.[10−17] Calcagnile et al. described magnetically driven floating foams possessing superhydrophobicity and superoleophilicity for the efficient separation of oil from water.[10] Li and co-workers developed superhydrophobic and superoleophilic conjugated microporous polymers that can efficiently absorb a broad range of organic solvents and oils with high levels of selectivity.[11] More recently, superhydrophobic graphene-based materials have been prepared and used for the successful separation and adsorption of oils or organic solvents.[13,14] The oils or organic pollutants absorbed by such superhydrophobic 3D porous materials are usually removed using mechanical squeezing procedures,[15] burning processes,[12] or solvent-washing methods,[14] all of which require long production times for the separation of large amounts of oil pollutants from water surfaces, thereby limiting their practical applicability. Therefore, the need remains to develop novel materials for the continuous absorption and removal of oil pollutants from water with high separation capacity.

In this paper, we present a simple and inexpensive dip-coating method for the fabrication of a superhydrophobic and superoleophilic carbon nanotube (CNT)/poly(dimethylsiloxane) (PDMS)-coated polyurethane (PU) sponge. PU sponges are commercially available 3D porous materials having the ability to absorb both water and oils or organic solvents. We anchored the hydrophobic CNT/PDMS coatings onto the frame of the sponge to change its wettability from hydrophilic to superhydrophobic. The as-prepared CNT/PDMS-coated PU sponge absorbed a broad variety of oils and organic solvents with high selectivity and good absorption capacities. Because of its robust superhydrophobicity and superoleophilicity, this CNT/PDMS-coated PU sponge could be used in conjunction with a vacuum system for the continuous absorption and removal of oil pollutants from water surfaces. Interestingly, this modified sponge could also effectively separate micrometer-sized surfactant-free water-in-oil emulsions, with high separation efficiency (oil purity in filtrate after separation: >99.97 wt %). The specific wettability of this CNT/PDMS-coated PU sponge suggests its potential applicability in oil/water separations and oil-spill cleanups.

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■ RESULTS AND DISCUSSION

After spin-coating PDMS onto glass slides and then curing the samples at 120 °C for 1 h, we obtained smooth PDMS films. We prepared the PDMS-coated PU sponge by dipping the PU sponge into a PDMS solution and then curing as indicated above. The water contact angles of the PDMS coating and the PDMS-coated PU sponge were 104 ± 2° and 140 ± 3°, respectively; although hydrophobic, these values are too low for the materials to be classified as superhydrophobic.

Generally, the wettability of a solid surface depends on two factors: its topographical microstructure and its surface chemical composition.[18−20] Combining hydrophobic CNT/PDMS nanocomposites with the microscale roughness of the surface of a PU sponge provided us with a superhydrophobic sponge. We used a dip-coating method to deposit the CNT/PDMS suspension (Figure S1 in the Supporting Information, SI) onto the PU sponge and then cured the sample in an oven. The as-prepared CNT/PDMS-coated PU sponge in Figure 1a possessed superhydrophobicity (water contact angle: 162 ± 2°) and superoleophilicity (contact angles of *n*-hexane, *n*-hexadecane, and gasoline: all close to 0°). On this superhydrophobic surface, water droplets possessed near-spherical shapes and rolled off with ease. We used scanning electron microscopy (SEM) to study the morphologies of the sponge before (Figure 1b) and after (Figure 1c) modification with CNT/PDMS coatings. We observed that the smooth skeletons of the original sponge were covered with CNT/PDMS nanocomposites after dip-coating. Figure 1d provides a higher-magnification image of the CNT/PDMS nanocomposites; it reveals hierarchical structures that existed in the form of crater-like nanostructures. Such a structure dramatically increased the surface roughness and led to a composite interface in which air became trapped within the grooves beneath the liquid, thereby inducing superhydrophobicity (the so-called Cassie−Baxter model).[21] Figure 1e reveals the change in the appearance of the as-prepared superhydrophobic sponge after immersion in water. The surface of the superhydrophobic PU sponge appeared like that of a silver mirror when immersed in water under an external force, suggesting that this sponge featured Cassie−Baxter surfaces. Figure S2 in the SI displays the approach, contact, and departure of a 4-μL water droplet, suspended on a syringe, for the CNT/PDMS-coated PU sponge immersed in *n*-hexane. The water droplet readily and completely departed from the surface, indicating that the sponge maintained its superhydrophobicity even in the presence of an organic solvent. Next we tested the organic pollutant/water separation and absorption capacities of the CNT/PDMS-coated PU sponge to evaluate how it would respond as an effective absorbent. Figure S3 in the SI presents the result of an *n*-hexane/water separation test performed using the CNT/PDMS-coated PU sponge. A droplet of *n*-hexane labeled with a blue dye was placed on a water surface, and then a piece of CNT/PDMS-coated PU sponge was forced into contact with the *n*-hexane droplet; the *n*-hexane droplet was adsorbed as soon as it made contact with the CNT/PDMS-coated PU sponge. We employed the absorption capacity (k) as a measure of how much oil or organic solvent the CNT/PDMS-coated PU sponge could capture. Figure 1f reveals that the absorption capacities of the CNT/PDMS-coated PU sponge for oils and organic solvents were 15−25 times its own weight, depending on the density and viscosity of the oils and solvents.

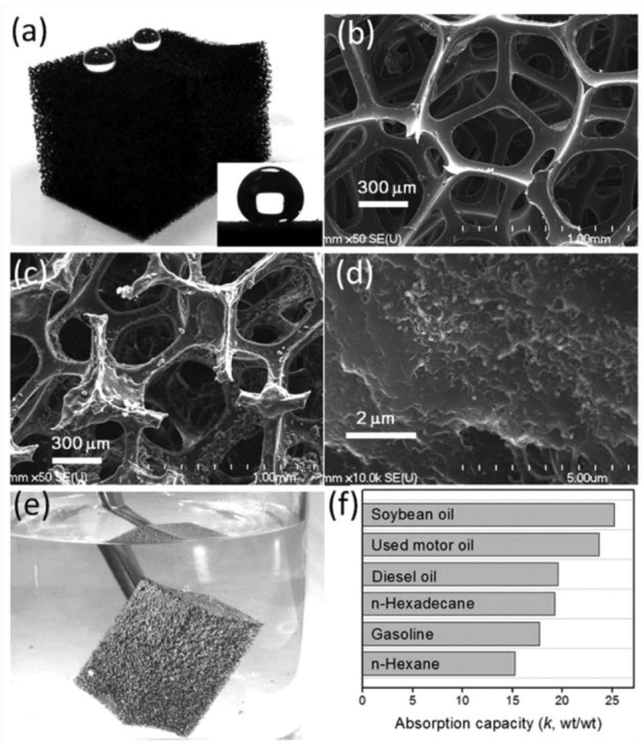

Figure 1. (a) Photograph of the CNT/PDMS-coated PU sponge. Inset: optical image of a water droplet on the as-prepared sponge. SEM images of (b) the unmodified PU sponge and (c) the CNT/PDMS-coated PU sponge. (d) Enlarged view of the microstructure in part c. (e) Images of the CNT/PDMS-coated PU sponge immersed in a water bath under an external force. (f) Absorption capacities of the CNT/PDMS-coated PU sponge toward oil and organic solvent.

Most interestingly, we found that the CNT/PDMS-coated PU sponge could be used in conjunction with a vacuum system for the continuous absorption and removal of organic pollutants from water surfaces (Figure 2). We connected a CNT/PDMS-coated PU sponge to a tube and used it as a filter that we dipped into a mixture of oil (*n*-hexane, labeled with a blue dye) and water, placing it at the oil−water interface (Figure 2a). As indicated in Figure 2b, the CNT/PDMS-coated PU sponge quickly filled with the oil, repelling the water completely because of its superoleophilicity and under-oil superhydrophobicity. Subsequently, we employed the vacuum system to remove the oil from the water surface in a continuous manner. Ultimately, the oil was removed completely from the water surface, resulting in only transparent, clean water remaining in the beaker. In addition, no water droplets were visible to the naked eye in the collected filtrate oil (Figure 2c). We also performed these continuous oil/water separation experiments with other water/oil (such as *n*-hexadecane and gasoline) mixtures; all of these mixtures were separated completely (Figures S4 and S5 in the SI). The fluxes of *n*-hexane, gasoline, and *n*-hexadecane through soaking through the CNT/PDMS-coated PU sponge (as calculated from the valid area of the tube under the pressure difference of ~0.027 MPa) are 2.93×10^6, 1.04×10^6, and 6.86×10^5 L m^{-2} h^{-1} bar^{-1}, respectively, depending on the viscosities of the oils and solvents. To the best of our knowledge, we are unaware of any previously reported studies of the use of spongelike materials with superhydrophobicity and superoleophilicity for the continuous absorption and expulsion of oil from water surfaces.

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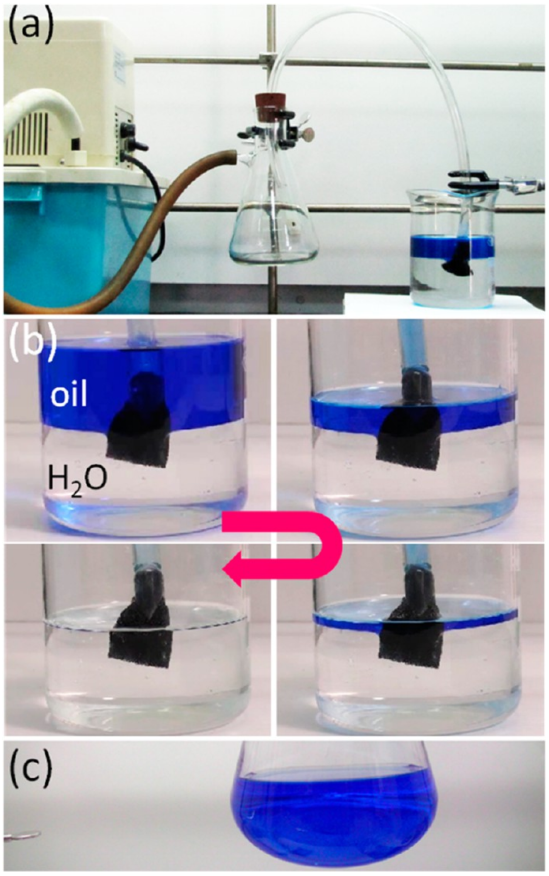

Figure 2. Photographs of (a) the continuous oil/water separation system, (b) the progress of the continuous absorption and removal of an organic solvent from the water surface, and (c) the oil collected in part b.

In addition, we found that a small piece of our CNT/PDMS-coated PU sponge (2.0 × 2.0 × 3.0 cm^3, ca. 0.42 g) could be used for the continuous removal of at least 20.0 L of oils (*n*-hexane, *n*-hexadecane, or gasoline) from water surfaces with high separation efficiency. In other words, the CNT/PDMS-coated PU sponge could be used to separate great amounts of oils—up to 35000 times its own weight—from water surfaces when using this one-step process. This approach for removing oils appears to be very suitable for the separation of large amounts of oil pollutants from water surfaces—much more so than any of the previously reported methods.[12,14,15] Because of its specific wettabilities, this CNT/PDMS-coated PU sponge has great potential applicability for use in oil-spill cleanups.

To our surprise, this CNT/PDMS-coated PU sponge also possessed high efficiency when separating emulsified oil/water mixtures. To test the separation ability, we prepared a series of surfactant-free water-in-oil emulsions, which we then separated through the CNT/PDMS-coated PU sponge with the aid of a vacuum system. The oils instantly absorbed and permeated through the sponge, causing emulsion droplets to demulsify and leaving behind the water, similar to previous reports.[7,22] All of the emulsified oil/water mixtures were well-separated and collected through a single step. We then used a Karl Fischer analyzer to investigate the water contents of the collected oils by measuring their water weight percentages. Figure 3a reveals that the purities of oils collected from the *n*-hexane, *n*-hexadecane, and gasoline emulsions were 99.99, 99.99, and 99.97%, respectively, suggesting excessively high levels of separation efficiency. To further examine the separation efficiency, we used an optical microscope to record images of the droplets in the original emulsions and in the corresponding collected filtrate. Figure 3b presents optical microscopy images of the water-in-*n*-hexadecane emulsion as an example. No droplets are evident in the collected filtrate in this photograph, confirming the high purity of the collected oils and the effectiveness of the CNT/PDMS-coated PU sponge for separation of water-in-oil emulsions.

CONCLUSION

We have reported a facile, inexpensive method for the fabrication of a CNT/PDMS-coated PU sponge displaying superhydrophobicity and superoleophilicity; this material has practical use in the continuous absorption and expulsion of oils or organic solvents from water surfaces. When combined with a vacuum system, this unique PU sponge could separate large amounts of oils—up to 35000 times its own weight—from water surfaces in a one-step process. Moreover, this CNT/PDMS-coated PU sponge also allowed the effective separation of surfactant-free water-in-oil emulsions with high separation efficiency (oil purity: >99.97%). We believe that this kind of sponge is a promising candidate for use in the large-scale removal of oils and organic pollutants from water.

ASSOCIATED CONTENT

Supporting Information

Experimental details, water droplet images in *n*-hexane of the CNT/PDMS-coated PU sponge, snapshots of the removal process of *n*-hexane, photographs of the continuous removal of *n*-hexadecane or gasoline from the water surface, and a video clip showing the continuous oil expulsion process. This material is available free of charge via the Internet at http://pubs.acs.org.

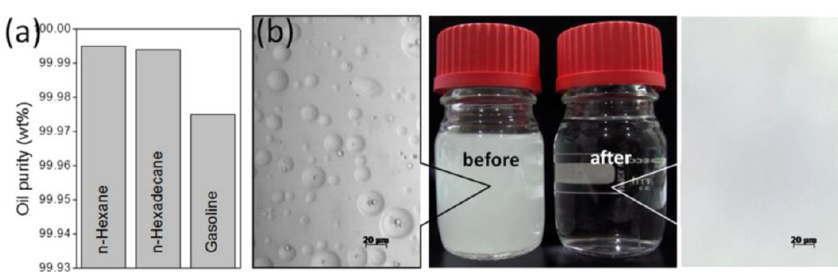

Figure 3. Using the CNT/PDMS-coated PU sponge in the demulsification and separation of surfactant-free water-in-oil emulsions. (a) Oil purities of three kinds of filtrates collected from their emulsion. (b) Photographs of the surfactant-free water-in-*n*-hexadecane emulsion before and after separation.

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Notes

The authors declare no competing financial interest.

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