Superhydrophobic Melamine Sponge Coated with Striped Polydimethylsiloxane by Thiol–Ene Click Reaction for Efficient Oil/Water Separation

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Supporting Information

ABSTRACT: Superhydrophobic and oleophilic sponges have been demonstrated as promising candidates for oil/water separation. However, there are still challenges in large-scale fabrication of superhydrophobic sponges with low cost and feasible method for industrial applications. Herein, we report a superhydrophobic and oleophilic melamine sponge functionalized by a uniform polydimethylsiloxane (PDMS) film that can be easily coated onto the sponge skeleton through UV-assisted thiol–ene click reactions. The PDMS films are characterized by a hierarchically striped microstructure with an average distance less than 2 μm. Because of the striped microstructure and the hydrophobic property of silicone, a high contact angle of 156.2° was achieved. Importantly, the interconnected open-cell structure of the melamine sponge was preserved by adapting the thickness of the PDMS film. The PDMS-coated melamine sponge exhibited a desirable absorption capacity of 103–179 times its own weight with oils and organic solvents. The excellent mechanical properties of melamine and the flexibility of PDMS enable the PDMS-coated melamine sponges to be squeezed repeatedly without collapsing. This study offers a robust and effective approach in large-scale preparation of a superhydrophobic sponge for large-scale oil spill containment and environmental remediation by the inexpensive commercial polymethylvinylsilicone and facile dip-coating/UV-curing method.

INTRODUCTION

Oil spills and industrial organic pollutants have resulted in severe water pollution that threatens every species in the ecological system from low-grade algae to higher mammals, including human beings. For example, 4.9 million barrels of crude oil was released in the Gulf of Mexico, resulting in catastrophic damage to marine and aquatic ecosystems. Concurrently, oily water in inland water has significant impacts on public health. Therefore, efficiently separating the oil from the water is a trending environmental concern. Traditional methods of oil separation include physical methods, chemical methods, and biological methods for recovering spilled oil on water. However, these traditional methods such as skimming systems, in situ burning, dispersants, and sorbents can have limitations. High cost, oily water collection, and less than ideal marine climate often limit the use of these traditional methods. Fortunately, the rapid development of interface science has offered brand-new solutions for separating oil/water mixtures including simple oil/water layered mixture and oil/water emulsion. Superhydrophobic and porous interfaces, including two-dimensional meshes and three-dimensional sponges, can efficiently achieve the remediation of water system polluted by oil. However, two-dimensional membranes and meshes need to collect the oily water prior to disposal, resulting in energy consumption and lack of efficiency. Three-dimensional superhydrophobic porous materials offer a promising solution with low energy. Until now, graphene and graphene oxide sponges, silicone sponges, porous nanocellulose aerogels, carbon nanofiber aerogels, cotton fabric, Janus polymers, and carbon soot sponges have been developed for oil absorption without energy consumption. Accordingly, superhydrophobic three-dimensional materials are typically fabricated using one of the two strategies: the first is to construct porous sponges with superhydrophobic materials and the second is to modify chemicals with low surface energy on a porous sponge frame. The second method is simpler and cheaper in application. On the other hand, some sophisticated hierarchical surface topologies with superhydrophobicity have been fabricated following the biomimetic principles. Two key factors that dominate the wettability of the surface are

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Lotus leaves have superhydrophobic properties because of their micropapillae nanostructure, and lotus leaf-inspired materials have been prepared as superhydrophobic coatings for different applications. However, previous processes for fabrication of biomimetic superhydrophobic surface are complex and restricting their scale preparation and industrial applications. A powerful strategy for modern materials science called click chemistry, coined by Sharpless and colleagues in 2001, describes organic reactions with highly selective, simple orthogonal reactions and exhibits high efficiency under a variety of mild conditions. Several processes, such as the nucleophilic ring-opening reactions, the non-aldol carbonyl chemistry, the additions to carbon–carbon multiple bonds, and the cycloaddition reactions, were identified. The radical-mediated thiol–ene reaction proceeds rapidly to a high yield with high efficiency; this is typical for a click reaction. Furthermore, the thiol–ene reaction is photoinitiated for functional polymers. As a second-order reaction, the conversion of thiol groups increases rapidly during the initial stage of UV-curing. Therefore, the thiol–ene click chemistry has been used in numerous applications, such as optical components, adhesives, and high-impact energy-absorbing materials. In addition, thiol–ene chemistry is also a popular surface modification reaction by “grafting-from” and “grafting-onto” approaches. Typically, thiopropionic acid and thiol alkanes were attached to polymethylvinylsilicone by thiol–ene reactions to adjust the surface wetting property. Advincula fabricated a highly efficient mesh with superhydrophobic coating by thiol–ene reaction. When compared with tetravinylcyclotetrasiloxane, polymethylvinylsilicone is seemingly an idyllic choice for preparation of superhydrophobic surfaces by the click reaction method. First, the polysilicone backbone exhibits a low surface tension value of around 21 mN/m, which is suitable for water repellency. Second, the rich vinyl group pendant from the backbone can be cured by multithiol cross-links. The UV-induced curing process and commercial polysilicone provide a unique opportunity to scale the preparation of extremely hydrophobic surfaces in an eco-friendly and economically friendly fashion.
Here, we report a simplistic and inexpensive two-step procedure to produce polysilicone-coated melamine sponges, which involves dip-coating of polymethylvinylsilicone (PMVS) with a multithiol cross-linker onto the melamine sponge, followed by UV-curing. The efficient click chemistry of the thiol–ene reaction results in a polydimethylsiloxane (PDMS)-coated melamine sponge with superhydrophobicity for oil/water separation. Surface topography, oil/water separation efficiency, and thermal stability were studied.

**RESULTS AND DISCUSSION**

The overall fabrication process of PDMS-coated melamine sponges consisted of two main steps. First, the linear PMVS and the cross-linker pentaerythritol tetras(2-mercaptoacetate) (PETMP) were coated onto the melamine skeleton by the dip-coating method. The thiol–ene cross-linking reaction was then performed under UV light. The click reactions between rich vinyl groups and multithiol PETMP resulted in the cross-linked PDMS network uniformly covering the melamine skeleton (Figure 1a). The PMVS concentration was well-controlled in order to adjust the thickness of the coated PDMS film. The successful fabrication of the PDMS-coated melamine sponge was evident from X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectrometry (EDS), thermogravimetric analysis (TGA), Fourier transform infrared (FTIR), Raman spectra, and scanning electron microscopy (SEM) photographs. Figure 1a shows the photoinitiated thiol–ene click reaction leading to cross-linked PDMS. The successful coating of cross-linked PDMS onto the sponge frame was confirmed by XPS, FTIR, TGA, EDS, and Raman spectra. Figure 1b shows the typical XPS survey spectra of pristine melamine sponge and PDMS-modified melamine sponge. Both samples exhibit a C 1s peak at 284.8 eV and an O 1s peak at 531.7 eV. Si 2s and Si 2p peaks were found at 151.8 and 102.1 eV, respectively. This evidences that PDMS was successfully attached to the sponge frame during the dipping-coating process. The N 1s peak located at 397.7 eV was detected on the pristine melamine sponge surface, and disappeared in the PDMS-modified sponge (Figure S1), which are attributed to the Si–O–Si, Si–CHx, and CHx vibration, respectively. XPS, FTIR, TGA, EDS, and Raman spectra results confirmed the successful coating of PDMS on the sponge framework.

**Morphology of Sponges.** SEM, as shown in Figure 2, examined the morphologies of the pristine melamine sponge and PDMS-coated melamine sponges. The pristine melamine sponge comprised a three-dimensional porous structure with concave triangular fibers. The skeletons of the melamine sponge are smooth with an average diameter of ~7.6 μm. Compared to the pristine melamine sponge, the PDMS-coated melamine sponges have unique morphologies. First, a thin, uniform layer of PDMS film was coated onto the sponge skeleton. Each melamine skeleton was covered continuously with PDMS without defect. PMVS and multithiol cross-linker solution can be adsorbed evenly on the melamine skeleton because of the amphiphilic property of melamine. Second, interesting regularly arranged resembling strips were observed throughout the whole sponge skeleton. Curing-induced shrinkage and migration of silicone result in undulating wrinkles with an average distance between these strips less than 2 μm, and the width of these strips is about 0.8 μm. Finally, the average diameter of the sponge skeleton fibers was increased to 8.4, 9.4, and 9.9 μm with the increase of the PMVS concentration as 1, 5, and 10 wt %, respectively. Importantly, small amounts of closed cells appeared (Figure 2g, inset) when the PMVS concentration increased to 10 wt %, which would be hazardous to the absorption capacity of the modified sponges. There were nearly no closed cells when the concentration of PMVS is less than 5% by mass. These results indicated that PMVS solution can be adhered to the surface of the sponge skeleton fibers uniformly and thiol–ene click reaction completes rapidly under UV light.
and the PDMS-coated sponge was oleophilic (Figure 3a). The pristine melamine sponge exhibits amphiphilic properties, behavior of water drops and oil drops on the sponge surface. The properties of the sponges were explored by analyzing the concentrations (1% for c, d; 5% for e, d and 10% for g, h). Inset: framework. SEM images of sponges. pristine melamine sponge (a, b); and PVMS modified melamine sponges with different PVMS concentrations (1% for c, d; 5% for e, d and 10% for g, h). Inset: closed cell formed due to the high concentration of PMVS.

**Superwetting of PDMS-Coated Sponges.** Wetting properties of the sponges were explored by analyzing the behavior of water drops and oil drops on the sponge surface. The pristine melamine sponge exhibits amphiphilic properties, and the PDMS-coated sponge was oleophilic (Figure 3a). The difference in the PDMS-coated sponge is reflected in its wetting property, when in contact with water (Figure 3b). The PDMS-coated sponge samples show a superhydrophobic character with contact angles more than 150° (Figure 3f). The surface chemical composition and surface topography are the main factors that determine the wetting property of the surface. It is known that a high surface roughness brings a significant change in the wetting property of the surface. Figure 3c depicts the large magnifications of the PDMS-coated melamine sponge skeleton, and regular undulating wrinkles are visible. Thereby, polysilicone ensures the low surface energy of the sponge skeleton, and surface roughness enhances the surface hydrophobicity. Compared with a smooth surface, water drops on the surface with high roughness tend to reflect the Cassie model, which corresponds to the lowest energy state in the open-air regime (Figure 3c, d). The roughness makes water drops have more than one metastable position of equilibrium, and water drops can transfer from one metastable equilibrium to the other, resulting in superhydrophobic property. Because of the stability of the silicone material, the PDMS-coated sponge also shows superhydrophobic property against acid, alkali, and NaCl solutions (Figure S2). The water sliding angle on the PDMS-coated sponges was tested to be about 8°. As we know, a superhydrophobic surface with a sliding angle lower than 10° often indicates that this surface owns self-cleaning property. The self-cleaning property was also confirmed by antifouling test. The antifouling test showed that the PDMS-coated sponge remained very clean against dyed water (Figure S3).

**Oil/Water Separation.** The superhydrophobic surface property and a large amount of open cells make the PDMS-coated melamine sponge a viable material for the rapid removal of various oils and organic solvents from water. Selective sorption is a crucial property of oil/water separation materials, particularly for oil spill remediation in aqueous environments. As shown in Figure 4, both oil-red dyed float hexane and sink chloroform were removed quickly and completely when the PDMS-coated melamine sponge was in contact with the oils, and clean water was left in only a few seconds. The PDMS-coated melamine sponge has different sorption performances with different oils and organic solvents. Figure 5a shows the maximum sorption capacity for oils and solvents in the absence of water. The mass-based sorption capacity for oils was 103–179 times the weight of the individual sponge. The excellent oil/solvent sorption capacity is attributed to the highly porous structure as well as the oleophilic properties. Because of the excellent mechanical strength of the commercial melamine sponge, the shape integrity and porous structure of the sponges can be well kept even after 10 sorption/squeezing cycles (Figure 5b). The hydrophobic property was sustained because of the flexibility of PDMS.

**CONCLUSIONS**

In summary, this study put forth a facile approach for fabricating superhydrophobic and oleophilic PDMS-coated melamine sponges by dip-coating and thiol–ene click reaction. The interconnected open-cell structure was sustained by adjusting the PMVS concentration of the coating solution. The regularly arranged resembling strips made the PDMS-coated melamine sponge superhydrophobic and oleophilic. The high mass absorption capacities toward different oils and organic solvents demonstrate the new opportunities for fast oil/water separation. Importantly, not only does our study highlight a convenient method toward engineering superhydrophobic three-dimensional sponges, but it also provides hopes to industrial large-scale production in the near future.

**EXPERIMENTAL SECTION**

**Materials.** PMVS (viscosity ≈ 3000 mPa·s) with a vinyl content of 10 mol % was obtained from Shin-Etsu Chemical Co. PETMP was purchased from J&K Scientific Ltd. (Beijing, China). Melamine sponges were purchased from a commercial store (7.90×10⁻³ g/cm³). The solvents and oils used in the absorption experiments were used as received without further purification.

**Preparation of the Superhydrophobic Melamine Sponge by Thiol–Ene Click Reaction.** The silanization of the melamine sponges was performed by the dip-coating process and photocuring. The PMVS sample (2.56 g, 0.40 mmol C=C groups) and PETMP (1 equiv, 0.10 mmol) were...
dissolved in CH$_2$Cl$_2$ (1, 2, 3, 5, and 10 wt %). The melamine sponges were cut into 3 × 2.2 × 1.8 cm$^3$ pieces and were immersed in a solution of PMVS and PETMP in CH$_2$Cl$_2$ (1, 2, 3, 5, and 10 wt %) for 5 min. Subsequently, the sponges were removed from the solution, then squeezed to extract the absorbed solution, and finally irradiated at room temperature with a WFH-204B lamp at 365 nm with a light intensity of 10$^7$ mW·cm$^{-2}$ for 10 min. They were then repeatedly washed with CH$_2$Cl$_2$ using the sorption/squeezing process for the removal of any unreacted starting materials. Finally, they were dried in air for 6 h. The resultant silanized melamine sponges were denoted as 1, 2, 3, 5, and 10% PDMS-coated.

**Characterization.** TGA was conducted on a TG Q500 thermogravimetric analyzer under a heating rate of 10 °C/min. ATR–FTIR spectra were recorded on a Thermo Nexus 470 FT-IR spectrophotometer with a universal ATR sampling accessory.

Figure 3. Superwetting of PDMS-coated sponges. (a) Amphiphilic property of pristine melamine sponge. (b) Superhydrophobic and oleophilic property of PDMS-coated melamine sponge. (c) Undulating wrinkles on the PDMS-coated melamine sponge skeleton. The inset shows a large magnification of undulating wrinkles. (d,e) Scheme of different hydrophobic states. (f) Contact angles of 1, 2, 5, and 10% PDMS-coated melamine sponges.

Figure 4. Photographs of the selective sorption of oil with the PDMS-coated melamine sponge. The oil was dyed with Sudan III to facilitate clear observation of the phenomenon.
accessory. Surface analysis was performed by an X-ray photoelectron spectrometer with ESCALAB 250Xi apparatus equipped with monochromator Al Kα as the X-ray source. An energy-dispersive X-ray spectrometer fitted to the scanning electron microscope was used for chemical elemental identification. The micromorphologies were observed by SEM with an S-4800 field emission electron microscope at an accelerating voltage of 5 kV. The wetting properties of the PDMS-coated sponge were investigated by static contact angle measurements at room temperature using a CA 20 contact angle goniometer with a droplet volume of 5 μL.

**Oil Absorption Experiments.** The absorption capacities of the PDMS-coated sponge for various oils and organic solvents were determined by dipping a piece of PDMS-coated sponge into the liquid (oil or organic solvent) until the PDMS-coated sponge was saturated with the liquid and left to drip for 30 s for weight measurement. Repeated sorption/squeezing processes were used to evaluate the recyclability of the PDMS-coated sponge.

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