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Published in:
Langmuir

DOI:
[10.1021/acs.langmuir.0c02755](https://doi.org/10.1021/acs.langmuir.0c02755)

Published: 01/01/2021

Document Version
Peer reviewed version

Please cite the original version:
Wang, B., Ma, Y., Ge, H., Luo, J., Peng, B., & Deng, Z. (2021). Design and Synthesis of Self-Healable Superhydrophobic Coatings for Oil/Water Separation. *Langmuir*, 36(50), 15309-15318.
<https://doi.org/10.1021/acs.langmuir.0c02755>

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Design and Synthesis of Self-healable Superhydrophobic Coatings for Oil/water Separation

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ABSTRACT: The introduction of self-healing function into superhydrophobic surfaces has recently raised increasing attentions because it can renew the feature of the surface iteratively, to a large extent extend the service lifespan of the surface in practical applications. However, it still faces a great challenge on how to achieve this unique surface with tunable self-healing function via an easy and effective way. Here, we propose a general, yet easily implemented strategy to endow a diversity of commercial substrates with self-healable superhydrophobic surfaces mainly relying on the collective use the polydopamine (PDA) chemistry with a hydrophobic silane-octadecyltrimethoxysilane (ODTMS). Upon applying ultrasonication for 30 min to an alkaline aqueous solution comprising dopamine hydrochloride (DA) and ODTMS, ODTMS disperses into aqueous phase as the micro-droplets, while DA polymerizes into polydopamine exclusively onto the micro-sized oil droplets, forming capsules with nano-roughness. In the presence of substrates, PDA also anchor these composite capsules onto substrates, resulting in hierarchical surfaces. ODTMS is detected abundant on the hierarchical surfaces, leading to superhydrophobic surfaces. Remarkably, this superhydrophobicity is self-restorable at room temperature (e.g., days) once it is deteriorated by the air plasma or extremely acid/alkali treatment, and this self-restoration can be significantly accelerated via the heating (2 h) or rubbing (5 min) treatment. Generally, heating and rubbing are the valid ways to induce the self-healing, which is speculated to accelerate the migration of hidden ODTMS from the capsules to the surfaces because of the minimization of the global surface free energy. Benefiting from the self-healing superhydrophobicity, we devise oil/water separation using various surface-modified commercial fabrics, which exhibit prolonged lifespan in applications, may further facilitate other usage in environmental remediation and water purification.

KEYWORDS: self-healing, superhydrophobicity, polydopamine, ultrasonication, oil/water separation.

INTRODUCTION

Superhydrophobic surfaces, a special group of water-repellent surfaces defined with both a water contact angle (WCA) higher than 150° and a sliding angle smaller than 10° , have attracted considerable interest not only because of their elusive fundamental science but also due to their great potential applications in industry and engineering, for instance, self-cleaning,¹⁻³ antifouling,⁴ anticorrosion,⁵ antifogging,⁶ water collection,⁷ and oil-water separation.⁸⁻¹³ Generally, it is widely agreed that both the hierarchical micro/nano-surface morphologies and the low-surface-energy chemical composites are crucially important elements to the artificially produced superhydrophobic surfaces.¹⁴⁻¹⁶ Based on this principle, a great number of superhydrophobic surfaces have been developed for various purposes. However, applying these artificial superhydrophobic surfaces into practical applications remains a great challenge and is hindered thanks to their poor durability. The excessive reliance on the hierarchical surface morphologies and surface chemical composites of the artificial superhydrophobic surfaces increases vulnerability of the superhydrophobic surfaces to practical damages (such as physical crush, sunlight irradiation, and organic contamination) in applications, which would lead to the decline or even the complete loss of the superhydrophobicity of the surfaces with irreversible structural and/or composite damages.¹⁷

Recently, the addition of self-healing functionality to superhydrophobic surfaces offers a novel solution to restore the damaged surface morphology and/or surface chemistry, which, in turn, proposes a plausible way to improve the durability in application so as to extend the practical service lifespan of the superhydrophobic surfaces.¹⁸⁻²⁹ In general, various strategies relying on the recovering of either the low-surface-energy surface or the hierarchical surface morphologies, have been proposed to restore the superhydrophobic surfaces. The former strategy relies on the reservoir

of the low-surface-energy chemicals inside the superhydrophobic surfaces. Physical damage to the superhydrophobic surfaces enables to trigger the release of the low-surface-energy chemicals stored in the materials diffusing towards the damaged sites, accomplishing the self-healing process.^{18-19, 23} Following this scenario, Li et al. reported a multi-step approach to synthesize self-healable superhydrophobic coatings by layer-by-layer methods, in which the healing agent: fluoroalkylsilane was stored in their porous polymer matrix. By breaking the matrix, the preserved low-surface-energy fluoroalkylsilane was released and migrated to the damaged surface. Self-healing occurred.¹⁸ Since then, diverse porous materials including microcapsules,³⁰⁻³⁵ mesoporous silica particles,³⁶⁻³⁸ nanoporous aluminum,³⁹ and etc. were employed as the reservoirs in the construction of self-healable superhydrophobic surfaces. In contrast, the latter strategy is dependent on the regeneration of hierarchically micro-/nanoscaled surface topology on water-unfavorable surfaces. Currently, both shape memory materials and special chemical reactions that can regenerate the hierarchical surface structures, have been developed to recovery the superhydrophobic surfaces.^{20-22, 40-41} In spite of great success of these strategies in the development of self-healable superhydrophobic surfaces, the challenges involving time-consuming, operational complexity, limited applicable scopes, durable self-healing capability, and environmentally unfriendly processes still remain. Thus, in turn, it is highly desirable to develop a time-effective, facile, universal, robust self-healing capability, and green strategy to synthesize the self-healable superhydrophobic surfaces, which would sustain a prolonged service lifespan in practical applications.

Here, we develop a straightforward, yet versatile to endow diverse commercial substrates with robust, self-healable superhydrophobic surfaces based on coupling the usage of polydopamine (PDA) chemistry and a hydrophobic silane octadecyltrimethoxysilane (ODTMS) in

the presence of ultrasonication. In this general approach, ODTMS is dispersed into the aqueous phase in the format of emulsion droplets under ultrasonication. Dopamine self-polymerizes into PDA, which preferably first coat on the ODTMS droplets forming core-shell composite particles prior to the addition of substrates, then anchor these composite particles to the substrates after the addition of the substrates, resulting in hierarchical surfaces. These surfaces are abundant with ODTMS molecules, exhibiting superhydrophobicity. Interestingly, this superhydrophobicity is self-healable by heating or rubbing when the superhydrophobicity is diminished by air plasma or acid/alkali treatments. This self-healing capability is ascribed to the migration of the ODTMS molecules from the interior of the composite particles to the surfaces, which is essentially assumed imputed due to the minimization of overall surface free energy. The self-healable superhydrophobic fabrics are promising materials for oil/water separation with a considerably prolonged service lifespan.

EXPERIMENTAL SECTION

Materials. The fabrics, i.e., cotton, silk, fiberglass and nylon fabrics, were purchased from Shanghai Textile Industry. Octadecyltrimethoxysilane (ODTMS) was supplied by J&K Scientific Ltd. Dopamine hydrochloride (denoted as DA, 98%) was purchased from Sigma-Aldrich. Aqueous ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28 wt%), hydrochloric acid (HCl, 36 wt%), sodium hydroxide (NaOH, 96%), rhodamine B and organic solvents, were purchased from Sinopharm Chemical Reagent Co., Ltd.

Preparation of superhydrophobic surfaces. The general synthetic route to allow fabric substrates with superhydrophobic surfaces was illustrated in Scheme 1. Typically, first, octadecyltrimethoxysilane (ODTMS, 100 μL) was dispersed in ultrapure water (100 mL) to form an oil-in-water emulsion under ultrasonication for 1 min. Subsequently, dopamine hydrochloride

(DA, 0.3 g) and aqueous ammonia (50 μ L) was added to ODTMS aqueous emulsion. This mixture was ultrasonicated at an acoustic power of 80 W for 30 min. Next, a piece of clean fabric substrate was immersed into this mixture. The reaction was complete in 24 h, and the fabric was retreated and washed with deionized water, and eventually dried in an oven at 80 $^{\circ}$ C for 1 h.

Characterization. The surface microstructures of the fabrics were investigated with a field emission scanning electron microscope (SEM, Hitachi SU8020). The elemental information of the surfaces was investigated using energy-dispersive X-ray spectroscopy (EDX, Oxford Instruments, Model 7426) attached to a SEM. The interior of the samples was characterized with a transmission electron microscope (TEM, JEOL JEM-2100). The surface chemical composition of the samples was analyzed by using an AXIS Ultra X-ray photoelectron spectrometer (Kratos Analytical Ltd., U.K.) equipped with Al K α radiation ($h\nu$ =1486.6 eV). Fourier transform infrared (FTIR) spectroscopy was recorded on a PerkinElmer Spectrum Two FT-IR. Water contact angles (WCAs) of the fabrics were determined with a Dataphysics OCA 20 contact angle system (DataPhysics Instruments GmbH, Germany) by using 2 μ L of water droplets as the indicators at ambient temperature. The average WCA value was acquired by measuring five different positions on the same sample.

Self-healing tests. To test self-healing ability of the superhydrophobic fabrics, three different methods including air plasma, acid and alkali treatments were employed to deteriorate the superhydrophobicity of the fabrics, as illustrated in Scheme 1. For air plasma treatment, those superhydrophobic fabrics were treated in a plasma machine (ZEPTO, Diener Electronic, Germany) for 1 min at a power of 50 W. This air plasma treatment made superhydrophobic fabrics completely superhydrophilic (WCA=0 $^{\circ}$). To recover the superhydrophobicity, the plasma-treated fabrics were either heated at 120 $^{\circ}$ C for 2 h or rubbed with hands for 5 min. The superhydrophobicity of the

surface was then completely restored. In the treatment with acid/alkali, the superhydrophobic fabrics were immersed in the highly acid (pH 1)/alkali (pH 14) solutions at ambient temperature for 24 h. Subsequently, those samples were collected and rinsed with ultrapure water, and then dried at ambient temperature in sequence. In this way, the fabrics became superhydrophilic, and the superhydrophobicity of the surface was recovered by heating the fabrics at 120 °C for 2 h.

Oil/water separation performance. For the oil absorption tests, the typical organic solvents, such as *n*-hexane and tetrachloromethane, were poured into water to simulate the oil spills. Then, superhydrophobic cotton fabric was dipped into the oil/water mixtures to separate oil from water. When the superhydrophobic cotton fabric was completely saturated by the absorbed organic liquids, it was immediately retreated for weight measurement. The absorption capacity (*k*) was determined according to Eq. (1):⁹

$$k = \frac{M_{after} - M_{before}}{M_{before}} \quad (1)$$

where M_{before} and M_{after} are the masses of the cotton fabric prior to and after the adsorption of organic liquids, respectively. Each *k* is obtained by averaging three results.

In the oil/water separation evaluation, this superhydrophobic fabric served as the filter, which was installed between two glass fixtures with two glass beakers attached. The superhydrophobicity of the fabric allowed the oils passing through while water repelling. The separation performance can be quantified with the separation efficiency (*R*) in accordance to Eq (2):⁴²⁻⁴³

$$R(\%) = \left(\frac{M_2}{M_1} \right) \times 100 \quad (2)$$

where M_1 and M_2 are the masses of the overall oils and the separated oils, respectively. Each *R* is the results of averaging values from the same sample.

RESULTS AND DISCUSSION

Scheme 1 schematically describes the synthetic strategy on how to prepare self-healable superhydrophobic fabrics via an environmentally benign two-step approach. In this process, two key chemicals: octadecyltrimethoxysilane (ODTMS) and dopamine hydrochloride (DA) are used to make the fabric's surface superhydrophobic. First, the coating solution is prepared by integrating ODTMS, DA, and aqueous ammonia in an aqueous media under ultrasonication for 30 min. Then, the fabric substrates are immersed into the coating solution. After magnetic stirring for 24 h, the superhydrophobic surfaces are finally formed regardless the materials, and surface chemistry and morphology of the substrates.

Figure 1a, b show that the pristine cotton fabric is inherently white in color and hydrophilic, enabling the immediate absorption of dyed (with rhodamine b) water droplets. After its surface is modified with PDA and ODTMS under ultrasonication, this fabric (denoted as Cotton fabric@PDA-ODTMS) looks brownish, and becomes highly water repellent as the water droplets with spherical shapes sit stably on its surface (Figure 1d). In comparison, the surface morphologies and structures of the pristine and the coated cotton fabrics are visualized by scanning electron microscopy (SEM). The pristine fabric exhibits a clean and smooth surface, as shown in Figure 1b and c. After coating, the Cotton fabric@PDA-ODTMS exhibits a particulate hierarchical surface (see Figure 1e, f), which is the one of the key elements to build superhydrophobic surfaces. By measuring the water contact angle ($157.8 \pm 2.4^\circ$, see inset in Figure 1f) and oil contact angle (0° , see Figure S1), this Cotton fabric@PDA-ODTMS is shown with the superhydrophobic and superoleophilic property feature, hinting that the surface of fabric is covered with low-surface-energy chemicals. This is confirmed with the X-ray photoelectron spectroscopy (XPS) characterization, in which the surface compositions of the fabrics prior to and after the surface

modification are analyzed. In contrast to the pristine cotton fabric, the new N1s, Si2s and Si2p signal peaks are present in the XPS results of the Cotton fabric@PDA-ODTMS, which are originated from PDA and ODTMS, respectively, as shown in Figure 1g. The signal intensity of N1s is far lower than the signals assigned to Si, suggesting that the ODTMS concentrates on the surface of the coating, while PDA is hidden within the coating. Furthermore, the EDX elemental mapping of the Cotton fabric@PDA-ODTMS shown in Figure 1h presents the elemental distribution of the C, N, O and Si, in which PDA is homogeneously deposited on the substrate, while ODTMS is not only fully coated but also is abundant in the nano-roughness of the surface. These results elucidate the formation of the superhydrophobic surface from the combination of the hierarchical surface morphology and the surface with a low surface free energy.

In addition, the versatility of the approach is demonstrated by using different materials as the substrates. As demonstrated in Figure 1i, j and k, our method enables to endow nylon, silk and fiber glass to be highly water repellent with the water contact angles (WCAs) higher than 150°, i.e., superhydrophobicity. This is a strong advantageous evidence to further enlarge the applicable scope of the approach.

As well known that the surface wettability of the solid substrate is determined by both the geometrical microstructure and the surface chemical composition.¹⁴⁻¹⁵ To gain a better insight into the possible formation mechanism of this process, a series of control experiments are designed to explore the role of each ingredient in the formation of superhydrophobic fabrics. As shown in Figure 2a, the cotton fabric modified with ODTMS-only (denoted as Cotton fabric@ODTMS) retains a smooth surface, which is analogous to the surface morphology of the pristine fabric (see Figure 1c). While, the surface of the Cotton fabric@ODTMS is hydrophobic with a WCA of $139.7 \pm 1.5^\circ$, hinting the coating of ODTMS. This is verified by XPS results as shown in Figure 2c.

In contrast, we, this time, treat cotton fabric solely with DA (denoted as Cotton fabric@PDA). Although the PDA coating does not disturb the microstructures of the cotton fabric, the PDA nanoparticles derived from dopamine polymerization attach to the microstructures of the fabric, leading to nano-roughness (see Figure 2b). Similarly in the XPS results, the main C1s, O1s peaks including the new N1s peaks are detected (see Figure 2d) after PDA coating, and the surface elemental ratio of oxygen-to-carbon (O/C) from the Cotton fabric@PDA is observed higher than that from the pristine cotton fabric, which is attributed to the oxygen-abundant PDA coating. Based on these results, we speculate that PDA would be the main source for constructing the rough surfaces and ODTMS would serve as the low surface energy chemicals for surface coating. However, this speculation cannot exactly elucidate the formation of hierarchical superhydrophobic surfaces on the cotton fabrics with the aid of DA and ODTMS.

To further explore the mechanism, we carry out a series of parallel comparative experiments in the absence of cotton fabrics. At the initial stage of mixing, ODTMS can be dispersed in the aqueous medium to yield oil-in-water emulsions under ultrasonication (see Figure 3a). These oil droplets are stable with a mean size of 4.63 μm (see the inset in Figure 3a), which have been shown already by others can be utilized as the soft cores for the preparation of colloidal capsules.⁴⁴⁻⁴⁵ Subsequently, the addition of DA and aqueous ammonia induces the self-polymerization of DA into PDA, which preferably coats onto the surfaces of ODTMS emulsion droplets because of the hydroxyl groups of ODTMS. These hydroxyl groups are assumed induced by the hydrolyzation of ODTMS under alkaline conditions,⁴⁶ as demonstrated in Figure S2. Finally, micro-sized PDA@ODTMS composite capsules are yielded (see Figure 3b). Note that when ODTMS is absent in this parallel experiment, only solid PDA colloidal particles are obtained (see Figure S3). A close inspect on these PDA@ODTMS capsules by TEM reveals that the exterior of the capsules are with

nanostructures as demonstrated in Figure 3c and d, giving rise to micro-/nano-hierarchical surfaces once they are attached to the substrates (see Figure 1e and Figure S4). Apart from that, the cavity of the PDA@ODTMS composite capsules allows for the reserve of ODTMS molecules (see Figure S5), providing possibilities towards self-healable superhydrophobic surface.

In practice, the robustness and the durability of the hierarchical superhydrophobic surfaces are critical properties. As such, the chemical resistant, mechanical durability and environmental stability of the superhydrophobic Cotton fabric@PDA-ODTMS are evaluated. As shown in Figure 4, we note that this superhydrophobic surface have excellent durability against different treatment. For instance, by dipping Cotton fabric@PDA-ODTMS in diverse organic solvents for 1 day, it retains superhydrophobic (see Figure 4a). Besides the chemical durability, the washing durability of this superhydrophobic fabric is also examined by an accelerated laundering durability test with the AACC 61-2006 standard test method. This Cotton fabric@PDA-ODTMS can withstand at least 25 accelerated laundering cycles without losing its superhydrophobicity (see Figure 4b). Additionally, this Cotton fabric@PDA-ODTMS also shows excellent abrasion resistance. After 100 cycles of abrasion with sandpaper by loading 200 g of a weight, the superhydrophobicity of the surfaces is not deteriorated (see Figure 4c), demonstrating its good mechanical durability. Moreover, when exposing them under different extreme environments, such as UV exposure (wavelength: 365 nm; intensity: 500 W; duration: 24 h), in a high temperature (200 °C, 24 h), and a low temperature (in liquid nitrogen: -196 °C for 24 h), no deterioration in superhydrophobicity is observed (see Figure 4d).

Interesting, we notice that the Cotton fabric@PDA-ODTMS is capable of self-healing to be superhydrophobic after its superhydrophobicity has been damaged by either air plasma or acid/alkali treatment. Upon exposing the Cotton fabric@PDA-ODTMS under air plasma for 1 min,

the superhydrophobicity is lost and the surface becomes superhydrophilic with a WCA of 0° (see Figure 5a and c). These results hint that the treatment by air plasma may generate oxygen-containing hydrophilic functional (e.g. carbonyl, carboxyl and hydroxyl) groups to the cotton fabric's surfaces,⁴⁶ which can alter the surface chemical composition and results in the reverse in wetting property from superhydrophobic to superhydrophilic. However, when these plasma-damaged cotton fabrics are placed in air for days or treated either by heating at 120 °C for 2 h (see Figure 5a) or by simply rubbing with hands for 5 min (see Figure 5c), the superhydrophobicity of the surface is restored, indicating that this superhydrophobicity is self-restorable and the treatment of heating and rubbing enable a significant acceleration of this process. More importantly, this self-healing ability is repeatable by consecutive cycles of air plasma treatment and heat or rubbing treatment, as shown in Figure 5b, d. After multi-cycles, the Cotton fabric@PDA-ODTMS surface still retain its superhydrophobicity, indicating the robust self-healable function of the surfaces.

Apart from self-recovery against air plasma treatment, the Cotton fabric@PDA-ODTMS also exhibits the similar self-healing ability against the acid/alkali treatment. By immersing the Cotton fabric@PDA-ODTMS into the pH extreme aqueous solutions (acidic pH 1 or alkaline pH 14) for 24 h, the superhydrophobic surface turns superhydrophilic (WCA= 0°). Similar, this turn can be reversed by heating the surfaces at 120 °C for 2 h (see Figure 5e and g). This self-healing ability is repeatable and last for at least 6 cycles (see Figure 5f and h). Additionally, we also note that this self-healing ability is universally applicable for other substrates that undergo the same procedure to be superhydrophobic (see Figure S6), suggesting a general strategy to endow the substrates with self-healable superhydrophobicity.

To gain a better understanding of the self-healing process, both the geometrical microstructure and the surface chemical composition, and the wetting property of the surfaces both after the air

plasma and heating treatment are analyzed with SEM, EDX, FTIR, and water contact angle measurement, respectively. As clearly evidenced by the SEM images in Figure 6a-c, the air plasma and heating treatments show little effect on the surface geometrical microstructure of the Cotton fabric@PDA-ODTMS, which still retain its hierarchical structures. In contrast, the surface chemical composition varies significantly depending the treatment. After the treatment by plasma, both the elemental ratios of Si to C (Si/C) and O to C (O/C) decrease, which may be ascribed to the decomposition of ODTMS by air plasma etching (see Figure 6d). Correspondingly, the surface wettability is turned to be superhydrophilic with a WCA of 0° in good agreement with the fact that the plasma treatment endows the surfaces with polar groups, together with hierarchical surfaces resulting in superhydrophilic surfaces. Upon heating, both the elemental ratios of Si/C and O/C are recovered to the status prior to the air plasma treatment (see Figure 6d), which would be the main reason for restoring the surface superhydrophobicity. In parallel, FTIR spectroscopy is employed to examine the variations of the functional groups during the process. As shown in Figure 6e, after the air plasma treatment, the vibration peaks at 2910, 2855 and 720 cm^{-1} , which are assigned to the asymmetric, symmetric and rocking vibrations of methylene ($-\text{CH}_2-$), are decreased in intensity. While, the absorption peaks of the stretching vibrations of $-\text{OH}$ and $-\text{C}=\text{O}$ appearing at 3335 cm^{-1} and 1651 cm^{-1} , are increased respectively. On the contrary, after heating treatment, the intensity of the peaks assigned to methylene increase while those of the $-\text{OH}$ and $-\text{C}=\text{O}$ groups are reduced inversely. These results, again, further verify that the alkyl chains of ODTMS are decomposed after the air plasma treatment, but reemerge after the heating treatment.

Based on the experiment results that the hierarchical surface microstructures are invariable in contrast to the variable surface chemical composite during self-healing, we infer that the self-healing mechanism is primarily associated to the variation of the surface chemical composition.

From the results in Figure 3 and S2, we speculate that those hydrolyzed ODTMS are preferentially immobilized onto the surfaces of PDA@ODTMS composite capsules, and the unhydrolyzed ODTMS are stored in the cavities. When the Cotton fabric@PDA-ODTMS is subjected to air plasma treatment, some polar groups (e.g. oxygen-containing hydrophilic groups: hydroxyl, carbonyl and carboxyl groups) are created to the cotton fabric's surfaces, which enables the rise in total surface free energy. Nevertheless, the air plasma treatment shows little effect to the hierarchical surface microstructures. A similar mechanism is also applicable to acid/alkali treatment (Figure S7 and S8), in which the silane molecules can be removed from the surface by strong acid or base⁴⁶, leading to a rise in total surface free energy and ultimately making surface superhydrophilic.⁴⁶ Upon heating or rubbing, those ODTMS molecules that are stored in the cavities are released and migrate to the surfaces so as to minimize the overall surface free energy, by which the surface superhydrophobicity is then restored gradually.

The advantageous features of the inherent high porosity, robust stability and self-healing superhydrophobicity make the Cotton fabric@PDA-ODTMS a promising candidate application in oil/water separation. As demonstrated in Figure 7a and b, and Supplementary videos 1 and 2, this superhydrophobic Cotton fabric@PDA-ODTMS allows for a quick absorption of the oils with various densities, for instance *n*-hexane (a low density oil) and tetrachloromethane (a high density oil), from water, without leaving any oil droplets within the water phase. Moreover, it also shows a satisfied recyclability in oil collection, and no apparent decline in absorption capacity (*k*) is observed over 20 repetitions (see Figure 7c). Besides, the superhydrophobic Cotton fabric@PDA-ODTMS can also serve as the filters allowing for the oil/water separation at a large scale. As demonstrated in Figure 7d and Supplementary video 3, as pouring the oil-water mixtures onto this filter, the oil phase is allowed to wet and pass through the filter, arriving at the lower beaker, while

the aqueous phase is repled by the filter, staying in the upper beaker. Again, it also exhibits high separation efficiency in the range of 95%-97% over 20 repetitions (see Figure 7e).

In the end, the oil/water separation property of the Cotton fabric@PDA-ODTMS after 10 cycles of the plasma or heat treatment is evaluated. Thanks to their self-healing ability, this superhydrophobic Cotton fabric@PDA-ODTMS exhibit a nonattenuated efficiency in the separation of oil/water mixtures as demonstrated in Figure 7f and g. This is corroborated by the invariable hierarchical surface morphology and superwettability of the cotton fabric after 10 cycles of self-healing processes (see Figure S9). Based on this advantageous self-healable function, the service lifespan of the superhydrophobic materials can be significantly prolonged.

CONCLUSIONS

In conclusion, a versatile, yet straightforward strategy to endow a rich variety of commercial substrates with self-healing superhydrophobic surfaces has been realized. In this approach, ODTMS and DA under ultrasonication is the key in the formation of hierarchical structured PDA@ODTMS composite capsules with low surface tensions, i.e., superhydrophobic surfaces. The cavity of the capsules offers reservoirs in the storage of ODTMS, which can be released after the surface having low surface tension has been destroyed. We assume that this migration of ODTMS from the cavity to the surface is caused by the minimization of the overall surface free energy in the system. In practice, the treatments of these superhydrophobic surface with air plasma or highly acidic/alkaline solutions would deteriorate the superhydrophobicity, and finally to be superhydrophilic. By heating or rubbing the surface is self-restored back to superhydrophobic, allowing for a renewal lifespan. The advantageous self-healable superhydrophobic property allow for a wide variety of commercial materials serving as the absorbents for the oil/water separation with a considerable prolonged service lifespan. In all, this versatile and straightforward coating

strategy presents a unique pathway to fabricate the durable, self-healing superhydrophobic surfaces on various commercial substrates, which would be promising for practical applications, e.g., environmental remediation, water purification, and many other relevant important fields.

FIGURES

Scheme 1. Schematic illustration of a versatile synthetic route for fabricating self-healable superhydrophobic fabrics.

Figure 1. Surface wetting characterization of (a) the pristine cotton fabric and (d) the coated cotton fabric (Cotton fabric@PDA-ODTMS) with (rhodamine b dyed) water droplets. The corresponding SEM characterization of (b, c) the pristine fabric and (e, f) Cotton fabric@PDA-ODTMS, and the insets in (c) and (f) show the results of WCA measurement. (g) XPS measurements of the samples in (a) and (d). (h) Elemental mapping patterns of the Cotton fabric@PDA-ODTMS. Surface wetting characterization of different fabrics after superhydrophobic treatment: (i) nylon fabric, (j) silk fabric, and (k) fiber glass fabric, the insets show the WCAs of sessile droplets.

Figure 2. SEM characterization of cotton fabric modified with (a) octadecyltrimethoxysilane (Cotton fabric@ODTMS) and (b) polydopamine (Cotton fabric@PDA), respectively, and their corresponding XPS measurements (c) and (d) of samples in (a) and (b), respectively.

Figure 3. (a) Optical microscopic image of ODTMS-in-water emulsion. The inset shows the oil droplet size distribution of the ODTMS droplets. (b) SEM images and (c, d) TEM images of PDA@ODTMS composite capsules formed in the absence of the cotton fabrics.

Figure 4. The wetting property characterization of the Cotton fabric@PDA-ODTMS (a) after immersing in various solvents for 24 h, (b) after laundering for 25 cycles by following the AATCC 61–2006 standard method, (c) after 100 abrasion cycles with sandpaper by loading a 200 g weight, (d) The surface wetting characterization of the Cotton fabric@PDA-ODTMS after the irradiation under UV for 24 h (500 W, $\lambda = 365$ nm), heating at 200 °C for 24 h, and immersing in liquid nitrogen (-196 °C) for 24 h, respectively. Insets: the corresponding WCA measurements.

Figure 5. (a, c, e, g) Surface wetting characterization of Cotton fabric@PDA-ODTMS during a cycle of self-healing processes. (b, d, f, h) Water contact angle monitoring during multi-cycles of self-healing processes:(a, b) air plasma treatment and self-healing at a high temperature, (c, d) air plasma treatment and self-healing by rubbing, (e, f) acid treatment and the high temperature assisted self-healing, (g, h) alkali treatment and the high temperature assisted self-healing.

Figure 6. SEM images of Cotton fabric@PDA-ODTMS (a) prior to and (b) after the air plasma treatment, and (c) after the high temperature-assisted healing. The insets are the corresponding WCA measurements. The corresponding (d) EDX results and (e) FTIR spectra of samples shown in (a-c), respectively.

Figure 7. Photographs for the collection of (a) *n*-hexane (low density oil, dyed with oil red) on the surface of water (i-iii) and (b) tetrachloromethane (high density oil, dyed with oil red) on the bottom of the water (i-iii) by using Cotton fabric@PDA-ODTMS, respectively. (c) The absorption capacity evaluation of this superhydrophobic Cotton fabric@PDA-ODTMS for *n*-hexane and tetrachloromethane over 20 repetitions of the oil collection. (d) Photographs of oil/water separation (dyed tetrachloromethane serves the oil phase) with a piece of Cotton fabric@PDA-ODTMS. (e)

The separation efficiency evaluation of the Cotton fabric@PDA-ODTMS in the isolation of tetrachloromethane from water over 20 cycles. (f) The absorption capacities of this superhydrophobic Cotton fabric@PDA-ODTMS for *n*-hexane and tetrachloromethane over 10 cycles of self-healing processes. (g) The remaining separation efficiencies of the Cotton fabric@PDA-ODTMS for separating tetrachloromethane from aqueous phase over 10 cycles of self-healing processes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Movie S1: This movie demonstrates the absorption of *n*-hexane from the surface of water with a superhydrophobic Cotton fabric@PDA-ODTMS.

Movie S2: This movie exhibits the collection of tetrachloromethane from the bottom of the aqueous phase by a superhydrophobic Cotton fabric@PDA-ODTMS.

Movie S3: This movie exemplifies the oil/water separation by using a piece of superhydrophobic Cotton fabric@PDA-ODTMS.

Time-dependent photographs of an oil (*n*-hexane) droplet falling onto the superhydrophobic Cotton fabric@PDA-ODTMS (Figure S1). Fourier-transform infrared spectra (FTIR) of PDA colloidal particles and PDA@ODTMS composite capsules (Figure S2). SEM and TEM images of PDA colloidal particles formed in the coating solution in the absence of ODTMS and cotton fabric (Figure S3). SEM observation of Cotton fabric@PDA-ODTMS (Figure S4). Dark field TEM and energy-dispersive X-ray spectroscopy-based elemental mapping analysis of PDA@ODTMS composite capsules (Figure S5). Photographs of dyed water droplets on the surfaces of the superhydrophobic nylon fabric, silk fabric, fiber glass fabric during one self-healing process (Figure S6). SEM images of Cotton fabric@PDA-ODTMS after acid treatment (Figure S7). SEM images of Cotton fabric@PDA-ODTMS after alkali treatment (Figure S8). SEM images and water contact angle measurement of Cotton fabric@PDA-ODTMS after 10 cycles of air plasma and heat recovery treatment (Figure S9).

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Author Contributions

B.Y.W. designed research methodology, performed experiments, data acquisition and processing, and manuscript drafting. Y.L.M. performed experiments and data acquisition and processing. H.Q.G designed research methodology, discussed the results and conducted data analysis. J.L. designed research methodology and discussed the results. B. P. discussed the results, conducted data analysis and reviewed and corrected the manuscript. Z.W.D. conceived the research, designed research methodology, conducted data analysis, and wrote the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

Financial support was received from the Program for Science & Technology Innovation Team of Shaanxi Province (No.2018TD-030), the Innovation Capability Support Program of Shaanxi (No.2020TD-024), the Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, Jiangnan University (JDSJ2020-2) and the Fundamental Research Funds for the Central Universities (No. GK202002007). B.P. appreciates the financial support from the Academy of Finland (No. 321443 and No. 328942).

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