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Underwater Superoleophobic Meshes Fabricated by Poly(sulfobetaine)/Polydopamine Co-deposition

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Porous meshes with superhydrophilicity and underwater superoleophobicity have attracted much attention for oil/water separation. In this work, poly(sulfobetaine methacrylate) (PSBMA), were co-deposited with polydopamine (PDA) to decorate steel meshes and to endow them with those characteristics for oil/water separation. Compared with the PDA-modified meshes, the oil contact angle increases to 158.6 ± 8.0° and the sliding angle decreases to 3.9° for the PSBMA/PDA-modified ones, indicating superoleophobic underwater and ultra-low adhesive towards oil. These results are mainly attributed to the superhydrophilicity of PSBMA and the highly rough surface morphology in micro-nanoscale introduced during the co-deposition process. The PSBMA/PDA-modified meshes show excellent performance in gravity-driven oil/water separation. They are stable towards organic solvent treatment, and retain the wettability in sea water for long time. This one-step PSBMA/PDA co-deposition method provides a convenient and effective approach to modify porous materials with underwater superoleophobicity for oil/water separation.

1. Introduction

In recent years, oil spill accidents have occasionally happened, causing catastrophic consequences to marine environment.1,2 There is a growing demand for technologies that can separate oil and water selectively and effectively during the oily wastewater treatment. Materials with superwetting properties are deemed as one of the most promising solutions to this problem. Both superhydrophobic and superhydrophilic (underwater superoleophobic at the same time) materials can be applied for oil/water separation. In the former case, oil passes through hydrophobic pores and is retained.3-5 However, the main problem is oil pollution caused by oleophilicity in the presence of water, which is hard to remove and leads to secondary pollution, thus greatly affecting the flux.6 In addition, it is unsuitable for gravity-driven oil/water separation due to the low density of most oil over water. The concept of underwater low-oil-adhesion superoleophobicity has been introduced to fabricate novel oil/water separation materials due to their affinity to water and blocking to oil. It is inspired by fish scales which can keep their surfaces clean in oil-polluted water.7 Hydrophilic surface with micro-nano hierarchical structures allows water being trapped at the interface, serving as a barrier to repel oil drops. Following this idea, Jiang and co-workers fabricated hydrophilic hydrogel coating with underwater superoleophobic property to separate water from an oil/water mixture.8 After that, various superhydrophilic and underwater superoleophobic surfaces were also proposed, based on the same principle.9-12 Hydrophilicity and rough surface morphology are the two key factors in fabricating underwater superoleophobic surface. Hydrophilic polymers are considered as the most attractive materials, due to their superior wettability and excellent flexibility for coating fabrication.13 Polyacrylamide8 and polyethylene glycol14,15 have been widely used, which can bind with water molecules via hydrogen bonds. However, the hydrogen bonds are generally known not stable, which may affect the stability of the hydration layer and its application in the practical use.17,18 Zwitterionic polymers provide us an alternative choice, which can be strongly hydrated via the ion-ion or ion-dipole bonding with water molecules.19,20 They have been widely studied as antifouling materials to resist protein/bacteria adsorption for biomedical applications.21-24 Besides, the zwitterionic polymers are now attractive to become a new generation of coating in oil/water separation. Zhu et al. has fabricated poly(sulfobetaine methacrylate) (PSBMA), a zwitterionic polymer, on poly(vinylidene fluoride) membranes via a surface-initiated atom transfer radical polymerization technique for separating oil from water effectively.25 However, it needs to simplify the multi-step procedures and to overcome the choice limitation of porous. Polydopamine (PDA), generally known for its universal adhesion with flexibility of coating formation, can be used to decorate on various forms of substrates such as sponges, microfiltration membrane and meshes.26-30 Recently, we have reported a PDA-assisted PSBMA deposition method to decorate polypropylene microfiltration membranes to realize resisting protein adsorption.31 It is reasonable for ones to envisage that this method has great potential for constructing underwater superoleophobic and ultra-low adhesive surfaces on materials to separate oil/water mixtures.
Materials in various forms, such as membranes,\textsuperscript{32,33} powders,\textsuperscript{34} sponges\textsuperscript{35,36} and meshes,\textsuperscript{37,38} have been modified and proposed for the separation of oil/water mixtures. Among them, metallic meshes, especially stainless steel and copper meshes, are two-dimensional pore-structured materials, which provide the most prevailing substrates for the studied aims.\textsuperscript{39} It is mainly due to their regular and rough morphology and furthermore the modified meshes can realize the gravity driven oil/water separation. Since a spray-and-dry method reported by Feng et al. in 2004,\textsuperscript{40} various approaches, such as physical modification, layer-by-layer assembly, polymer grafting and chemical-based oxidation, were employed to fabricate superhydrophobic or superoleophilic oil/water separation meshes.\textsuperscript{41-45}

Here, stainless steel meshes were used as a model substrate and we report a facile method to endow them with underwater low-oil-adhesion superoleophobicity by simply co-depositing PSBMA and PDA (Fig. 1). We explored the reasons for low-oil-adhesion of PSBMA/PDA-modified meshes and studied the effects of PSBMA/dopamine (DA) ratio in the deposition solution on the performance of our meshes. Furthermore, the meshes were applied in the gravity-driven oil/water separation.

**2. Experimental section**

**Materials.**

Stainless steel meshes (1/300 in, pore size) were purchased from Xing-An mesh manufacturer (China) and washed with acetone overnight before use. Dopamine hydrochloride and N-(3-sulfopropyl)-N-(methacyrloyloxyethyl)-N,N-dimethyl ammonium betaine (sulfobetaine methacrylate, SBMA, 97\%) was obtained from Sigma-Aldrich (USA) and used without further purification. PSBMA was synthesized by free radical polymerization according to our previous work.\textsuperscript{31} It was further characterized by NMR (Fig. S1 in ESI). $^1$H NMR (400 MHz, D2O, δ): 4.43 (2H, peak c), 3.74 (2H, peak d), 3.52 (2H, peak f), 3.16 (6H, peak e), 2.90 (2H, peak h), 2.20 (2H, peak g), 1.93 (2H, peak b), 0.93-1.20 (3H, peak a) and GPC (Table S1 in ESI). Other reagents, such as tris(hydroxymethyl)aminomethane, 1,2-dichloroethane and hexane were procured from Sinopharm Chemical Reagent Co., Ltd (China) and used as received.

**Co-deposition of PSBMA and PDA on the meshes.**

DA and PSBMA mixtures were dissolved in Tris buffer (pH 8.5, 50 mM). The DA concentration was kept at 2 mg/mL and the ratio of PSBMA/DA varied from 0:1 to 1:1, 5:1 and 10:1 to prepare a series of reaction solutions. The mesh samples were directly immersed in the freshly prepared solution, and shaken for 18 h at 25 °C. Then, the samples were washed three times with deionized water, and dried in a vacuum at 40 °C overnight.

**Characterization and measurement.**

Chemical composition of the mesh surfaces was analysed by X-ray photoelectron spectroscopy (XPS). It was performed on a spectrometer (PerkinElmer, USA) with Al Kα excitation radiation (1486.6 eV). Field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan) was used to characterize the surface morphology of the meshes. Samples were spurted with Au for 1 min before FESEM observation. Surface wettability of the meshes was obtained by measuring oil contact angle (OCA) and sliding angle (SA). Both static and dynamic contact angles were detected using a DropMeter A-200 contact angle system (MAIST VisionInspection & Measurement Co. Ltd., China). Oily drop was set at 5 µL and the angle values were averaged from three measurements.

**Oil/water separation experiment.**

One of the as-prepared meshes were first immersed in water for 10 min and fixed between two O-rings. A mixture of water and hexane (50\% v/v) was poured immediately down the top glass tube. The permeated liquid was then collected. The driving force for the separation was the gravity of the solution itself.

**Stability of the PSBMA/PDA-modified coating.**

To investigate the stability of the PSBMA/PDA co-deposited coating, the modified meshes were rinsed by organic solvent, deionized water and sea water in a shaken bath at 25 °C under 150 rpm. The samples were then taken out, dried, and the underwater OCAs were measured once every a period of time. The organic solvents were commonly-used as water-soluble, including ethanol, N,N-dimethyl-Formamide (DMF), N-methyl-2-pyrrolidone (NMP) and acetone. The samples were washed for 24 h. The test for salt stability was proceed in sea water and continued until 7 days.

**3. Results and discussion**

**3.1 Surface composition and morphology of the PSBMA/PDA-modified meshes**

It is well-known that the surface wetting behaviour is mainly related to two crucial factors, i.e. hierarchical micro- and nanostructures and surface composition. In our previous work, we found that the PSBMA concentration significantly affects the deposition density of PSBMA/PDA on polypropylene microfiltration membrane, resulting in controllable membrane surface properties.\textsuperscript{31} Herein, different ratios of PSBMA/DA, i.e. 1:0 to 0:1, 1:1, 5:1 and 10:1, were chosen to investigate the influence of PSBMA. The mesh surfaces were characterized by XPS and FESEM, respectively.

XPS spectra in Fig. 2 and chemical composition in Table 1 confirm the formation of PSBMA/PDA co-deposited coatings on the mesh surfaces. For a PDA-modified mesh (Fig. 2a), the major peaks at 284.6 eV, 401.0 eV and 534.0 eV are ascribed to the binding energy of C\textsubscript{1os}, N\textsubscript{1s} and O\textsubscript{1s} respectively. When PSBMA is introduced for co-deposition (Fig. 2b-d), an additional peak appears at 169.0 eV for S\textsubscript{2p}. The content of sulfur element rises gradually with the feed ratio of PSBMA/DA as shown in Table 1. The molar ratio of S/N can be used to analyse the relative content of PSBMA and DA on the mesh surfaces. PSBMA on the mesh surface is 22\% when the PSBMA/DA feed ratio is 1:1, and increases alongside with the ratio. However, the increased content is slight for the case of 10:1, compared with the case of 5:1. It indicates that the further addition of PSBMA is not beneficial for the PDA-assisted deposition of PSBMA on the mesh surfaces.
Table 1 Chemical composition of the modified meshes from XPS spectra (in at%).

<table>
<thead>
<tr>
<th></th>
<th>C1s (%)</th>
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<th>N1s (%)</th>
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<td>d</td>
<td>69.5</td>
<td>23.6</td>
<td>5.3</td>
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</table>

3.2 Wettability of the PSBMA/PDA-modified meshes

It is expected that the as-modified meshes realize superhydrophilc behaviours underwater by combining the micro-nanoscale rough structures with the superior hydrophility of PSBMA. The superoleo-phobicity of the mesh surface was evaluated by contact angle measurement using 1,2-dichloroethane as a model oil. A 5 µL oil droplet was suspended on the micro-syringe tip and slowly lowered to reach the mesh surface. OCA on the studied mesh surfaces is shown in Fig. 4a. It is about 137.6 ± 3.2° on the nascent mesh surface underwater, which indicates not an underwater superhydrophobic surface.

Fig. 3 Typical FESEM graphs of the studied meshes: (a) nascent, (b) PDA-modified, PSBMA/PDA-modified with PSBMA/DA ratios of (c) 1:1, (d) 5:1, and (e) 10:1. (f) It is the enlarged image from (c).

Fig. 4 (a) Underwater OCAs of the studied meshes modified with different ratio of PSBMA/DA for co-deposition. Photographs of the dynamic underwater oil-adhesion measurements and the sliding behaviour on (b) PDA-modified and (c) PSBMA/PDA-modified meshes.
After PDA deposition, the oil droplet is difficult to be transferred to the mesh surface and must be forced to fall off for an accurate measurement of OCA. The OCA increases to 147.2 ± 4.8° on the PDA-modified mesh surface. It further increases to 158.6 ± 8.0° when PSBMA is co-deposited with DA at 1:1 ratio. This means underwater superoleophobicity (OCA > 150°) is achieved on the PSBMA/PDA-modified meshes, due to the strong hydration of PSBMA combining with the high roughness of the mesh surface. However, the OCA no longer increases with further increasing the ratio of PSBMA/DA, because the mesh surface becomes smooth. Therefore, we finally adopt 1:1 as an optimized PSBMA/DA mass ratio for the surface modification of stainless steel meshes by co-deposition. The underwater superoleophobicity can also be confirmed by dynamic underwater oil-adhesion measurements and sliding behaviour of the oil droplet on the mesh surface (Fig. 4b, c). A 5 μL oil droplet was lowered to contact with the surface and then allowed to leave. The oil-adhesion behaviours were captured by camera set at continuous mode. Although the OCA is approach to 150°, the PDA-modified mesh exhibits high adhesion with oil as shown in Fig. 4b. The oil droplet is stretched to deformation after the syringe is lifted up, even though it is slightly pushed downward. Besides, the oil droplet hardly rolls off the surface until the mesh is sloped to 28.9°. Compared with the PDA-modified mesh, the behaviour of PSBMA/PDA-modified one is much different (Fig. 4c). The oil droplet can leave more easily from the surface and there is almost no deformation to happen, even the oil droplet is squeezed against the surface with high preload. Moreover, the oil droplet can easily roll off from the PSBMA/PDA-modified surface (SA = ~3.9°).

Our PSBMA/PDA-modified mesh also has excellent underwater superoleophobicity towards various oils, including diesel, gasoline, hexane, and petroleum ether. Fig. 5 shows the underwater OCAs for a selection of oils, and the typical photographs of oil droplets on the mesh surface are shown as the insets. The OCAs is all over 150°, which is similar with the result of 1,2-dichloroethane.

![Fig. 5](image)

### 3.3 Separation of oil and water

The PSBMA/PDA-modified meshes with excellent low adhesion property have great potential in oil/water separation process. Typical measurements were performed as shown in Fig. 6a. Hexane (dyed with methyl red) was used as a model oil and the oil/water mixture (50% v/v) was poured onto the mesh. Water with high density can selectively penetrate through the mesh, while oil is blocked. The oil content in the filtrate is 3.75 ± 0.27 ppm, which was measured by the total organic carbon analyser (TOC). Therefore, the separation efficiency is over 99.9%. It is mainly due to the underwater superoleophobicity and low oil-adhesion property of the as-prepared mesh. Besides, the modified mesh can be reused after a washing process, benefited from its super-oil-repellency. As shown in Fig 6b, the oil on the mesh surface can be easily washed away. The surface retained its original property after being used several times. A video illustrating the washing process is provided as ESI, Movie S1.

![Fig. 6](image)

### 3.4 Stability of the PSBMA/PDA coating

It is important to sustain the underwater superoleophobicity during practical applications. Therefore, the stabilities of PSBMA/PDA coating were examined by washing the modified meshes in various organic solutions and sea water at 25 °C for different periods (Fig. 7). As mentioned previously, the PSBMA/PDA coating has high oil-repellency of water-insoluble organic solvent. Herein, we adopted four water-soluble organic solvents for stability measurement. As shown in Fig. 7a, the PSBMA/PDA-modified meshes remain the low oil-adhesion after washing for 24 h. The coating is also stable under a long-term washing with deionized water. In general, metal ions can chelate with the phenol groups in PDA, which play central roles in the adhesion of PDA on meshes. In our work, the PSBMA is only 22% in the coating. Therefore, the coating has shown good stability, which is similar to that of PDA coating. More appealing, the underwater OCAs remain unchanged during the whole experiment, even after the meshes were continuously washed.
subjected to sea water for 7 days (Fig. 7b). It is generally known that the intra- or inter-chain associations of the charges in PSBMA moieties will be shield in the presence of inorganic salts, such as sodium chloride. PSBMA will turn to a more extended molecular conformation in this case. It is called the “anti-polyelectrolyte effect”.46,47 However, the PSBMA moieties are anchored in the PDA coating in our cases and cannot be washed away until the dissolve of PDA coating. The “anchor” effect between PSBMA and PDA ensures the modified meshes with excellent stability under sea water.

The mechanical durability of the coating is also a key issue for practical application. Therefore, the tear test with an adhesive tape was conducted according to the procedure described by Wang et al.48 to detect the mechanical stability of the PSBMA/PDA coating. After 30-cycle test, the underwater OCA is only slightly decreased and still higher than 15°. The results indicate the PSBMA/PDA coating has good mechanical durability, which is promising in environmental and energy applications.

Conclusions

In conclusion, we used a convenient and facile method of PSBMA/PDA co-deposition to endow stainless steel meshes with underwater superoleophobicity and ultra-low adhesion towards oil. These results are derived from the combination of the superhydrophilicity of PSBMA with the rough surface morphology in micro-nanoscale introduced during the co-deposition process. The meshes prove to be selective and effective in separating water from oil/water mixture. The oily residues can be washed away easily, ensuring the prepared meshes reusability. Furthermore, the wettability can be retained towards organic solvents and sea water treatment. As PDA is able to decorate various materials, this work provides a universal method for underwater superoleophobic materials fabrication and application, especially in oily wastewater treatment.

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Notes and references

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