

# A Surface Exhibiting Superoleophobicity Both in Air and in Seawater

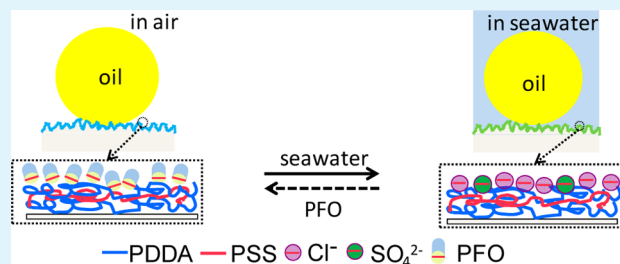
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## S Supporting Information

**ABSTRACT:** Superoleophobic surfaces have attracted increasing interest in recent years due to their potential application in various fields. In this paper, we report a surface that exhibits superoleophobicity both in air and in seawater. A polyelectrolyte multilayer (PEM) is assembled on an aluminum substrate with a micro/nano hierarchical surface structure, and the counterion in the PEM is exchanged with perfluorooctanoate (PFO), making the surface superhydrophobic and superoleophobic in air. When submerged in artificial seawater, the surface exhibits underwater superoleophobicity, with a 1,2-dichloroethane contact angle of 163°. X-ray photoelectron spectroscopic analysis and controlled experiments reveal that, upon exposure to seawater, the PEM spontaneously exchanges the PFO counterion with the chloride and sulfate ions in the seawater, making the surface hydrophilic and hence oil-repelling underwater. When withdrawn from seawater, superoleophobicity in air is restored by treating the surface in a PFO solution shortly to reinstall the PFO counterion. The switching between the two wetting states (superoleophobicity in air and underwater) is completely reversible. This simple and versatile approach can be readily extended to other substrates, making it a promising method for introduction of dual superoleophobicity to surfaces used in many fields.

**KEYWORDS:** polyelectrolyte multilayers, counterion, ion exchange, superoleophobicity, surface, wettability



## INTRODUCTION

In recent years, marine oil spills caused by tanker ships and offshore drilling have raised worldwide environmental concerns.<sup>1–4</sup> Besides the devastation to the ecological system, oil spills in seawater can damage aquatic devices and cause severe economic losses.<sup>5</sup> To help cleanup the spills and protect aquatic equipment from oil contamination, design and fabrication of superoleophobic surfaces has become an important task. In addition, superoleophobic surfaces also find extensive application in other fields, such as marine antifouling coating, oil/water separation, industrial metal cleaning, oil pipeline treatment, and fluidic drag reduction.<sup>6–8</sup> Therefore, research on superoleophobic surfaces has aroused worldwide interest in the past several years. Traditionally, superoleophobic surfaces refer to surfaces that exhibit an oil contact angle greater than 150° and low contact angle hysteresis in air, and have been extensively investigated. For instance, in their pioneering work, Tsujii and co-workers demonstrated that a combination of a fractal rough surface topography and a low surface energy trifluoromethyl coating is essential to superoleophobicity;<sup>9</sup> Jiang and co-workers demonstrated superoleophobicity with micro/nano hierarchically textured surfaces of a fluorine-containing polymer;<sup>10</sup> Tuteja and co-workers showed that re-entrant curvature can play a crucial role in surface superoleophobicity.<sup>11</sup> Very recently, Jiang and co-workers extended the concept of superoleophobicity to surfaces underwater.<sup>6,7</sup> Inspired by natural structures that are oil-repellent underwater, such as fish scales, short clam's shell, and the lower part of lotus leaves, various underwater superoleophobic surfaces have been

fabricated.<sup>6,12,13</sup> They pointed out that roughness with dual length scales is necessary for superoleophobicity both in air and underwater, but the surface energy requirements for the two cases contradict each other: superoleophobicity in air is realized with low surface energy materials, such as fluoro compounds, whereas, for superoleophobicity underwater, hydrophilic materials are needed, so that water can wet and be trapped in the hierarchically rough structure to repel the oil, just like air does in the former. Consequently, a surface that is superoleophobic in air would lose its oil repellent capability when going into water, and vice versa.<sup>14,15</sup> So far, there has been no report in the literature on surfaces that are superoleophobic both in air and underwater. However, in some practical applications, such as coatings for aquatic devices operating in seawater where the upper part of the device is exposed in air and the lower part submerges in seawater at the same time,<sup>16</sup> oil repellency both in air and underwater is highly desirable. Polyelectrolyte multilayers (PEMs), which can be facilely fabricated via the layer-by-layer assembly technique on a large variety of substrates, including polymers, oxides, and metals, of different sizes and shapes, have emerged among others as promising coatings for surface wettability manipulation.<sup>17,18</sup> In this paper, we report a surface that exhibits dual superoleophobicity in air and in seawater based on a PEM coated on a rough aluminum substrate. We show that the counterion of

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the PEM is critical to spontaneous alteration of the surface energy that can lead to dual superoleophobicity.

## EXPERIMENTAL SECTION

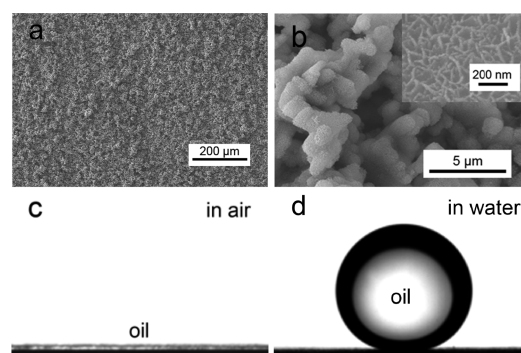
**Materials.** Sodium perfluorooctanoate (PFO,  $\text{CF}_3(\text{CH}_2)_6\text{COONa}$ , 97+%) was purchased from J&K Scientific. Perchloric acid was purchased from Aladdin Chemical Reagent Co. Ltd. Sodium chloride, magnesium chloride, magnesium sulfate, calcium chloride, ethanol, chloroform, acetone, and 1,2-dichloroethane were purchased from Sinopharm Chemical Reagent Co. Ltd. Poly(diallyldimethylammonium chloride) (PDDA, 20 wt % in water,  $M_w \sim 200\text{--}350\text{K}$ ) and polystyrene sulfonate (PSS,  $M_w \sim 70\text{K}$ ) were purchased from Aldrich. All chemicals were used as received without further purification. Ultrapure water ( $18.2\text{ M}\Omega\text{ cm}$  at  $25\text{ }^\circ\text{C}$ ) was purified with a PGeneral GWA-UN4 system and used in all experiments. Commercial flat aluminum sheets of 0.5 mm in thickness were purchased from a local metal materials store and cut into small pieces of  $70 \times 16\text{ mm}$  in size, which were then ultrasonically cleaned in ultrapure water, ethanol, chloroform, and acetone sequentially, each for 2 min, to get rid of possible inorganic and organic surface contaminants. The cleaned aluminum plates were electrochemically polished in a perchloric acid/ethanol solution (25 mL of  $\text{HClO}_4$ , 4 mL of  $\text{H}_2\text{O}$ , 290 mL of  $\text{C}_2\text{H}_5\text{OH}$ ) for 3 min at 60 V, rinsed with water, and dried with a stream of nitrogen. The smooth aluminum plates were then etched in a HCl solution (2.5 M) for 8 min at room temperature, rinsed with water, and immersed in boiling water for 20 min, and then dried with nitrogen flush.<sup>19,20</sup> Artificial seawater was formulated as follows:<sup>16</sup> NaCl: 2.6726 g;  $\text{MgCl}_2$ : 0.2260 g;  $\text{MgSO}_4$ : 0.3248 g;  $\text{CaCl}_2$ : 0.1153 g;  $\text{H}_2\text{O}$ : 100 mL.

**PEM Deposition.** A (PDDA/PSS)<sub>1.5</sub> film was fabricated on the rough aluminum plate following a literature procedure<sup>17,18</sup> by alternate dipping of the substrate into a PDDA (1.0 mg/mL, with 1.0 M NaCl present) and a PSS (1.0 mg/mL, with 1.0 M NaCl present) aqueous solution for 15 min each for 1.5 cycles with water rinsing after each dipping step. The PEM was then immersed in a PFO aqueous solution (0.1 M) for 2 min, removed, and rinsed with a copious amount of water and dried with a stream of nitrogen.

**Characterization.** Scanning electron micrographs were acquired on an FEI XL30 field-emission scanning electron microscope; X-ray photoelectron spectra were obtained on a Thermo-electron ESCALAB 250 spectrometer equipped with a monochromatic Al X-ray source (1486.6 eV). The spectra were recorded at a  $90^\circ$  takeoff angle (between the sample surface and the detector) with a 20 eV pass energy. Water contact angles and oil contact angles were measured on a ramé-hart 200-F1 standard goniometer at room temperature with ultrapure water (5  $\mu\text{L}$ ), and 1,2-dichloroethane (2  $\mu\text{L}$  for in air, 4  $\mu\text{L}$  for underwater). Each contact angle value reported is an average of at least five independent measurements.

## RESULTS AND DISCUSSION

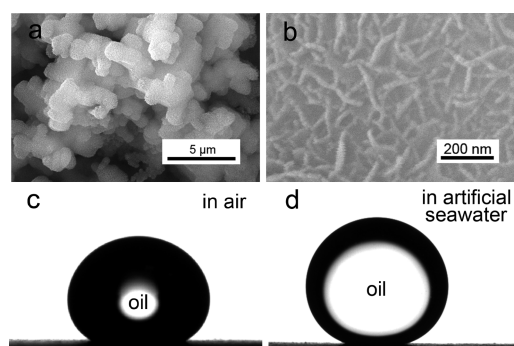
A small aluminum plate was etched with hydrochloric acid and then boiled in water, following a literature procedure, to create a micro/nano hierarchical structure on the surface.<sup>19,20</sup> As seen in the scanning electron microscopy (SEM) images in Figure 1, numerous microscale flakes (size in the order of 1  $\mu\text{m}$ ) are present on the surface randomly, on top of which are many nanoscale puckers of  $\sim 10\text{ nm}$  in size (Figure 1b, inset), after the boiling water treatment. The micro/nano hierarchical structured aluminum surface exhibited a 1,2-dichloroethane contact angle of  $162.6 \pm 3.9^\circ$  and nearly  $0^\circ$  underwater and in air, respectively (Figure 1c,d). That is, the rough aluminum surface is superoleophobic underwater, but superoleophilic in air. This is not unexpected, considering that polished aluminum (same surface chemistry, normally with an oxide surface layer) has a high energy and hydrophilic surface, with a water contact angle of  $\sim 80^\circ$  (Supporting Information). In air, oil can spontaneously wet the high energy aluminum surface and be



**Figure 1.** (a, b) SEM images of a rough aluminum surface at different scales, and the inset shows nanopuckers on a microscale flake in (b). (c, d) Optical image of a 1,2-dichloroethane droplet (c) completely wetting the rough aluminum surface in air and (d) sitting on the rough aluminum surface in water, with a contact angle of  $162.6^\circ$ .

drawn into the cavities due to the three-dimensional capillary effect,<sup>21</sup> and the resulting oil/solid composite surface exhibits oleophilicity. In water, on the other hand, water wets the hydrophilic surface and intrudes into the cavities to create a water/solid composite interface, which can be described by the underwater Cassie model<sup>22</sup> and is superhydrophilic, and in water, a superhydrophilic surface cannot be wetted by oil because replacing the water molecules spreading on the surface with oil molecules is energetically unfavorable. That is, superhydrophilic surfaces repel oil in water.<sup>6</sup> Similar underwater superoleophobicity has been observed with rough silicon<sup>6</sup> and copper oxide surfaces.<sup>5</sup>

To reduce the surface energy and realize superoleophobicity in air, we coated the rough aluminum plate with a PEM carrying a fluorinated counterion. We have previously demonstrated that a PEM assembled from typical polyelectrolytes, PDDA and PSS, can be readily utilized to tune surface wettability by using various counterions.<sup>17,18</sup> On a rough substrate, such PEMs carrying a low surface energy counterion, PFO, introduced via ion exchange, can exhibit superhydrophobicity<sup>23</sup> and superoleophobicity.<sup>19</sup> It was found that the contact angle of 1,2-dichloroethane on the (PDDA/PSS) PEM deposited on the rough aluminum plate decreased with increasing number of bilayers in the PEM, and the one containing 1.5 bilayers was most oleophobic (Supporting Information), due to the highest fluorine content in the PEM.<sup>19</sup> Therefore, in all subsequent experiments, all the rough aluminum plates were coated with this (PDDA/PSS)<sub>1.5</sub> PEM carrying PFO counterion, and are denoted as PEM-Al hereafter. The thickness of the 1.5 bilayer PEM was about 10 nm based on our previous research,<sup>23</sup> a value so small that the surface topography of the rough aluminum substrate was largely preserved after deposition of the PEM. As seen in Figure 2, the micro/nano hierarchical structure critical to surface wettability remains essentially the same as the bare substrate. In air, the PEM-Al surface was superhydrophobic (water contact angle =  $154.8 \pm 1.7^\circ$ ) and, more importantly, superoleophobic, with a 1,2-dichloroethane contact angle of  $151.0 \pm 1.8^\circ$ . However, to our surprise, a same PEM-Al plate submerged in artificial seawater<sup>16</sup> exhibited a 1,2-dichloroethane contact angle of  $163.0 \pm 1.9^\circ$  (Figure 2). Similar wetting behavior was observed when other types of oil, such as *n*-hexadecane and rapeseed oil, were used as the probe fluid for contact angle measurement (Supporting Information). That is, the PEM-Al surface is superoleophobic both in air and in seawater.

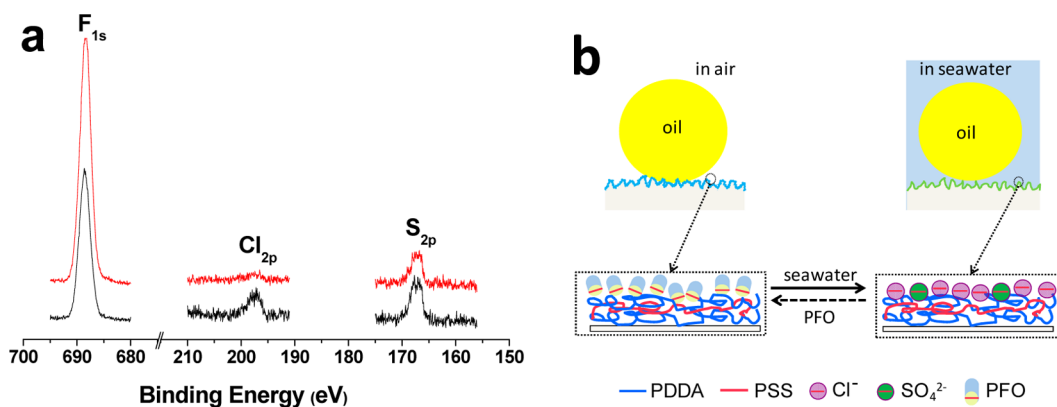


**Figure 2.** (a, b) SEM images of a PEM-Al surface at different scales. (c, d) Optical image of a 1,2-dichloroethane droplet on a PEM-Al surface (a) in air with a contact angle of  $151.0^\circ$ , where the droplet is significantly deformed due to gravitational force, and (b) in artificial seawater with a contact angle of  $163.6^\circ$ .

To understand this unusual phenomenon, that a surface can be superoleophobic in air and underwater, the surface composition was examined. Figure 3 displays the  $F_{1s}$ ,  $Cl_{2p}$ , and  $S_{2p}$  regions of X-ray photoelectron spectra (XPS) of a PEM-Al plate as prepared and after exposure to the artificial seawater, the latter rinsed with water and dried before the analysis. For the as-prepared surface, a strong  $F_{1s}$  peak at 684.9 eV is observed, and no chlorine is detected. For the surface exposed to artificial seawater, on the other hand, the  $F_{1s}$  signal is dramatically lower, a  $Cl_{2p}$  peak emerges at 198.5 eV, and the  $S_{2p}$  signal at  $\sim 166.8$  eV becomes more intense. This piece of evidence clearly indicates that, when submerged in artificial seawater, the PFO counteranion in the PEM was exchanged by the rich  $Cl^-$  and  $SO_4^{2-}$  anions, which are hydrophilic,<sup>17</sup> in the artificial seawater. Since PFO ions in PDDA/PSS PEMs can be completely exchanged by  $Cl^-$ ,<sup>16,17</sup> the residual fluorine detected by XPS probably was due to PFO adsorbed to the Al substrate. In fact, the PEM-Al surface became superhydrophilic and superoleophilic in air after submerging in artificial seawater (Supporting Information). In contrast, a PEM-Al plate submerged in ultrapure water exhibited an underwater 1,2-dichloroethane contact angle of only  $32^\circ$  (Supporting Information). These results prove the critical role that the counterion in the PEM plays in the unusual dual superoleophobicity phenomenon. The as-prepared PEM carries a rich low surface energy PFO counterion, making the surface oleophobic in air, as discussed above; when in contact with

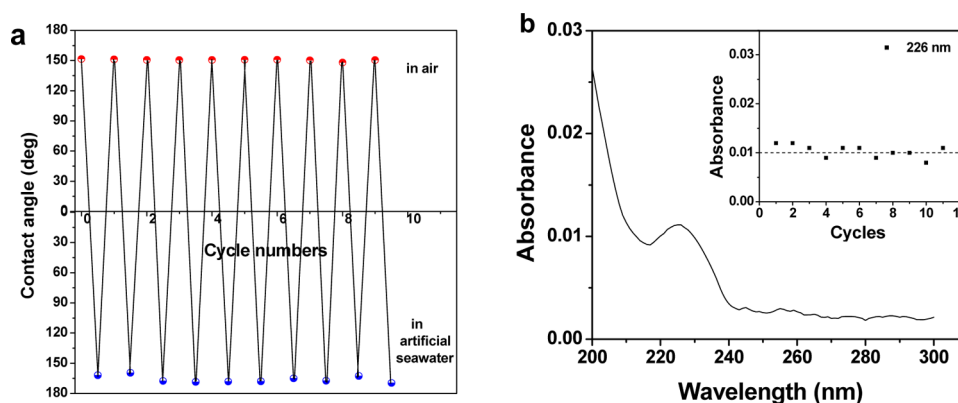
seawater, the PFO counterion is exchanged by the hydrophilic chloride and sulfate ions in the seawater spontaneously, which makes the surface hydrophilic and hence oleophobic underwater. The micro/nano hierarchical structure of the aluminum substrate amplifies the effects, and the PEM-Al can be superoleophobic both in air and in seawater. Apparently, the PEM layer (or other coating species that carry ions) is essential for the unique wetting behavior, whereas the chemical nature of the substrate (aluminum in this study) is insignificant as long as it supports the coating and the micro/nano hierarchical structure. Because PEMs can be conformally deposited on numerous substrates ranging from metals to oxides and polymers, in large scale via techniques such as spraying,<sup>24</sup> this approach is likely to find extensive application.

Although the PFO-carrying PEM-Al surface switches spontaneously from superoleophobic in air to superoleophobic in seawater, as discussed in the previous section, the inverse transition does not occur automatically when the surface is withdrawn from seawater. However, superoleophobicity in air for the PEM-Al surface can be easily restored by treating it with a PFO solution to reinstall the PFO counterion into the PEM. To explore the reversibility of the process, a PFO-carrying PEM-Al was subjected to sequential contact angle measurements in air and then in artificial seawater using 1,2-dichloroethane as the probe fluid, and then the plate was withdrawn from the artificial seawater, rinsed with ultrapure water, and then submerged in a 0.1 M PFO aqueous solution for 2 min, removed, and dried to complete a cycle. Figure 4 shows the contact angle data for the PEM-Al for 10 cycles. It can be seen that the surface can switch quickly between superoleophobicity in air and in seawater, and the process is completely reversible. A same PEM deposited on a quartz slide was subjected to the same treatment cycles, and was monitored by UV-vis spectroscopy. As seen in Figure 4b, the absorbance at 226 nm characteristic of PSS remains constant over the 10 cycles, indicating that the PEM is stable and intact over the process. The reversibility persisted even after the sample had been exposed to ambient laboratory conditions for more than 1 month, and the surface remained superoleophobic in air and underwater after it was submerged in artificial seawater for 7 days. The water contact angle for the surface remained the same after the surface was rubbed with a finger wearing a latex glove (Supporting Information). These results show the robustness of the PEM coating. On the other hand, PEMs assembled based on electrostatic interactions are known to fall



**Figure 3.** (a)  $F_{1s}$ ,  $Cl_{2p}$ , and  $S_{2p}$  regions of XPS spectra of the PEM-Al surface as prepared (red) and after exposure to artificial seawater (black). (b) Schematic illustration of surface structure and composition leading to dual superoleophobicity in air and in seawater.





**Figure 4.** (a) 1,2-Dichloroethane contact angle measured on the PEM-Al surface in air and in artificial seawater, showing the reversible switching between superoleophobicity in air and in artificial seawater. The switch of superoleophobicity from in air to underwater is spontaneous, whereas the inverse transition is accomplished by exposing the surface to a 0.1 M PFO solution for 2 min. (b) UV-vis spectrum of a same PEM deposited on a quartz substrate. Inset plots the absorbance at 226 nm, characteristic of the PSS, as a function of ion exchange cycle, showing the stability of the PEM.

apart when exposed to concentrated salt solutions,<sup>25</sup> and their stability can be improved by cross-linking.

## CONCLUSION

We have fabricated a PEM surface that is superoleophobic in air and remains superoleophobic in seawater by utilizing the ionic species in the PEM and in the seawater. The inverse transition back to superoleophobicity in air when withdrawn from seawater is easily accomplished by treating the surface with a solution of a fluorinated ion, and the switching between the two wetting states is completely reversible. Although the substrate used in this study is aluminum, the simple and versatile approach can be readily extended to many other substrates, making it a very promising method for introduction of dual superoleophobicity to surfaces used in many fields.

## ASSOCIATED CONTENT

### Supporting Information

More contact angle data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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