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Thesis Title: Room-Temperature Construction and Performances of Low-Cost and Transparent Oil-Repellent Coatings

Room-Temperature Construction and Performances of Low-Cost and Transparent Oil-Repellent Coatings

Abstract

Oil contamination occurred on various kinds of daily used objects and is difficult to be cleaned. Herein, we show a room-temperature layer-by-layer (LBL) assembly approach to achieve transparent, cost-effective oil-repellent coatings on a variety of substrates for self-cleaning of oil-contaminations. In our work, positively charged poly (allylamine hydrochloride) (PAH) polyelectrolyte and negatively charged polyacrylic acid (PAA) polyelectrolyte were alternatively deposited onto various substrates (e.g., silicon, glass, steel, plastic and finished wood) to fabricate polyelectrolyte multilayers (PEMs), followed by incubation of the PEMs coated substrates into ammonium perfluorooctanoate (PFO) solution, resulting in oil-repellent coating of PFO-$(PAH/PAA)_n$, which is transparent and has a smooth and flat surface and a controlled thickness. The PFO-$(PAH/PAA)_n$ coatings exhibited excellent properties including persistent oil-repellency (even including high-temperature oil and condensed vapor oil), anti-oxidation, anti-physical abrasion, and anti-chemical corrosion. Various oil liquids (e.g., hexane, decane, dodecane, hexadecane and toluene) with different surface tensions can easily slide across or off the coated objects at a sliding angle lower than 12°. Also, the coatings demonstrate fascinating chemical-shield performance towards toluene so that they can protect plastics from dissolution by organic solvents. After a long-time (15 days) irradiation by sunlight and a storage in a dark environment for 3 h, the coating effectively recovered its oil-repellent performance, suggesting a good anti-oxidation property. In addition, even abraded by sands for 300 cycles, the coatings maintained their easy-sliding oil-repellency, illustrating a good capability to resist physical abrasions. Importantly, such a smooth coating without any air-pocket structure demonstrates high-efficient repellency towards high-temperature oil and condensed vapor oil.

Compared to currently available superoleophobic coatings, the facile LBL assembly approach for the construction of transparent oil-repellent coatings have solved many problems (e.g., difficulty in production, toxic substance release during high temperature fluorination, substrate-limitation by its shape and size, expensive cost, optical opacity, etc.), therefore, our coatings demonstrate a promising commercial prospect.

Innovation Declaration

The team members declare that the research results and achievements shown in this submitted thesis were obtained under our supervisor’s supervision. To the best of our knowledge it does not contain any materials previously published or written by any team member except where due reference or acknowledgment is made in the text. If there is any dishonesty, I will take all responsibilities for any violation of the declaration.

Team member signature：

Date: 12/08/2016

Room-Temperature Construction and Performances of Low-Cost and Transparent Oil-Repellent Coatings

1 Introduction

Oil contaminations generally refer to saturated or unsaturated organic alkanes pollutants, such as paint in furniture, crude oil in petroleum transportation, cooking oils, animal oil and fat, and so on. In daily life, these oils often adhere to or contaminate the objects, for example, cooking oil pollutions on clothes and cooking utensils, high viscosity oils adhesion to the wall thereof blocking the pipelines, paint's adhesion and contamination to the container, and oily components from finger secretions on electronic products. Importantly, these objects (i.e., electronic products, dinner tables, cooking utensils and clothes) contaminated by oils are difficult to be cleaned, which brings a lot of inconveniences to our lives. In addition, in many industries, such as aviation, electricity and transportation, once the oil pollution occurred, it often severely affects people's activities, and even causes significant economic losses. Therefore, the research on oil-repellent coatings is of great importance.

1.1 The development of oil-repellent coatings

It is known to all, lotus leaf, butterfly wings and peacock feathers, show excellent water-proof property, and water can easily slide off from these animal and plant surfaces. Inspired by these naturally existed surfaces, scientists have artificially developed a variety of water-repellent coatings, which were applied to many products, such as sealing films, water-proof cloth, and water-proof electronics.[1-3] Compared to water-repellent coatings, oil-repellent coatings also show tremendous applications in our daily lives and industries, for instance, self-cleaning oil-repellent clothes, table supplies, oil pipelines, offshore oil-spill cleanup equipment, and the like.[4-6] Due to the fact that the surface tension of oils is lower than that of water, the coating surfaces are easier to be wetted by oil. In other words, oil-repellent coatings are more difficult to achieve than water-repellent coatings.[4-6] Through the continuous exploration, scientists found that two factors were key to be required for construction of water-repellent or/and oil-repellent coatings, one is nano/microscale roughness, the other is the presence of a low surface energy waxy material. However, the difference is that the oil-repellent coatings require more precisely controlled roughness, which is the biggest challenge for fabrication of oil-repellent coatings.

After extensive studies, scientists believed that whether the surface is contaminated by oil or not is determined by two features, i.e., oil contact angle and sliding angle. The surface with a smaller oil contact angle and a larger oil sliding angle is much easier to be contaminated by oil, and vice versa. Contact angle is the angle for liquid on solid surface, which is conventionally measured between liquid/vapor (LV) and solid/liquid (SL) contact lines, as shown in Figure 1, in which θ_e is the contact angle. Sliding angle is the critical angle formed by the tilted surface and the horizontal plane when the liquids begin to slide on the inclined surface. Therefore, two conditions of the traditional oil-repellent coatings can be summarized as below. (1) The oil contact angle on the coating is large (generally, contact angle > 150°, i.e., the coating surface is superoleophobic); (2) the sliding angle on the coating is small (the smaller sliding angle facilitates an easier rolling-off).

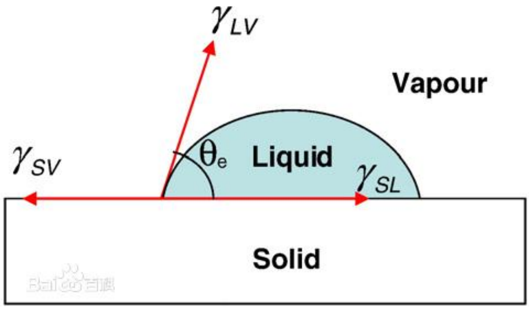

Figure 1. Schematic sketch of the contact angle (cited from Wikipedia).

By summarizing the previous reports, the main approaches for construction of traditional oil-repellent coatings were spin coating method[8-10] and sol-gel method[11,12]. For example, by using spin coating method, Uyanik and co-workers[8] fabricated heat and abrasion resistant, anti-chemical corrosion superhydrophobic/superoleophobic coatings, nevertheless, the raw organic materials they adopted are of high toxicity. Fu and co-workers[9] used the same method to produce a piece of thin polydimethysiloxane (PDMS) film on glass substrates, and the oleophobic coatings were obtained after modification of the PDMS film by perfluorooctyl trichlorosilane (PFOTS). In addition, utilizing sol-gel method, Yan et al.[11] used tetraethoxysilane (TEOS) as the raw material and ammonia as the catalyst, and the hydrophobic/oleophobic transparent SiO_2-based film coatings were obtained after fluorination by perfluorooctyl trimethoxysilane (POTS). However, the above methods have many disadvantages, for instance, the modification process requires a high-temperature fluorination treatment, which not only produces toxicity but also limits available substrates for the coatings. Moreover, all of these coatings must be roughened to increase the amount of air trapped in the coating thereof enhancing the oil-repellency.[13] However, the introducing of roughened surfaces requires additional surface treatment, and not all surfaces are available for roughening, which severely limits their ability to prevent oil contaminations in the practical applications.

To solve the problem that the construction of oil-repellent coatings is limited by surface roughening, scientists recently developed three approaches for fabrication of smooth oil-repellent coatings.[14-16] These new technologies make people realize that the smooth coatings without any roughness can also perform as self-cleaning oil-repellent coatings. The feature of these self-cleaning coatings is that the oil contact angles are smaller than 90 °, but oil can easily slide off the coatings surfaces at a low sliding angle. The first approach relies on the infusion of a low surface energy material, i.e., perfluorinated oil (lubricant), into textured epoxy or porous teflon membrane substrates.[14] The second approach is grafting PDMS onto Si substrate for monolayer modification.[15] The third approach refers to fabrication of a copolymer made of perfluoropolyether-incorporated polyurethane (PU) on these surfaces.[16] The greatest advantage of the three technologies is that the coatings can be prepared without surface roughening and introducing toxic fluorides. However, these techniques also have some drawbacks, i.e., the first two are subjected to the limitation of solid substrates, and the second one based on monolayer modification shows poor mechanical properties. The third one can overcome the shortcomings of the first two technologies, but it requires expensive precursors, toxic organic solvents, and complex organic reactions. Further, the substrates must endure a 120 ℃ treatment process, which is only accessible for some specific substrate materials.

Importantly, in practical applications, the oil-repellent coatings should possess durable anti-oxidation and anti-abrasion properties. For oil-repellent coatings, no matter how excellent oil-repellency they have, if they cannot bear oxidation and abrasion, their practical applications will be greatly limited. In addition, during industrial production process, some containers with coatings inevitably contact with various chemical reagents, which requires these coatings to resist chemicals, especially oily organic solvents.[17] This is one of the key issues that should be solved, and it is also an integral part for performance evaluation of the oil-repellent coatings. It is also worth noting that the kitchen ventilator surface and the inner side of distillation apparatus surface are often contaminated by condensed vapor oil, which results in tremendous inconvenience. However, currently available oil-repellent coatings can only repel liquid oil, the coatings to repel vapor oil and high temperature oil is still rarely reported.

1.2 Research backgrounds and our objectives

According to the above literature review and our life experiences, main problems of the traditional self-cleaning oil-repellent coatings are listed as follows.

(1) Precursors (e.g., highly volatile fluorinated silane) for construction of the coatings are highly toxic, which is extremely harmful to human beings.

(2) The preparation approaches of the oil-repellent coatings require a high temperature fluorination process, and are limited by the substrate material, thus, they cannot be applied to most of the daily objects, i.e., they are not universal.

(3) The coatings are normally prepared by pre-depositing of a layer of inorganic or

organic matrix on the substrate surface, which often leads to an opaque coating and alternates the appearance of the substrates. Moreover, the rough structure in the coating is liable to be occupied by the vapor oil molecules so that the coating cannot repel vapor oil.

Taken together, currently available oil-repellent coatings have many issues mentioned above, so our research is to develop a simple, room temperature approach using cost-effective and non-toxic materials to construct transparent oil-repellent coatings possessing excellent anti-oxidation, anti-chemical corrosion, and anti-abrasion properties. Our fabrication process involves alternate deposition of polyelectrolyte multilayers (PEMs) onto the substrates, followed by incubation of the PEMs coated substrates into a perfluorinated surfactant solution. Through the above process, we can construct the self-cleaning oil-repellent coatings on various kinds of daily used objects, such as glass, metal, wood, plastics, and so on. In additional, the involved oils even included vapor oil and high-temperature oil. So, the present coatings will promote their practical applications in many industries.

1.3 Main innovations

(1) It overcomes the problem that construction of the traditional oil-repellent coatings is limited by the type of substrate. We use a layer-by-layer (LbL) technique to prepare self-cleaning oil-repellent coatings on the surfaces of a variety of daily objects, such as glass, metal, wood, plastics, and silicon wafer.

(2) It simplifies the complicated construction process of the oil-repellent coatings. Here, a simple room temperature dip coating method facilitates the deposition of the coatings on various substrates. This method avoids many complex processes, such as pretreatment, roughening, and high temperature fluorination.

(3) It improves the transparency and durability of the oil-repellent coatings. The coatings are made of transparent polymer materials and surfactants so that they can keep the appearance of the substrates. Moreover, the durability of the coatings is greatly improved due to their anti-oxidation and anti-physical abrasion performances of the polymer matrix materials.

(4) It can extend the application of these oil-repellent coatings to the field of repelling condensed vapor oil. Our coatings are smooth without roughness induced porous structures, in this context, the vapor oil molecules cannot penetrate into the coatings. Consequently, our coatings exhibit high-performance of vapor-oil repellency.

2. Research contents and methodologies

In this study, the oil-repellent coatings were fabricated by a dip coating approach involving two steps. Firstly, the substrates were coated by PEMs matrix via alternate deposition (LbL assembly) of two oppositely charged polyelectrolytes. The LbL assembled PEMs with a controlled film thickness can be constructed on various kinds of substrates with any shapes and sizes.[18-20] Noting that there are many species of polyelectrolytes available for construction of PEMs, herein, we choose cheap and non-toxic positively charged poly (allylamine hydrochloride) (PAH) and negatively charged polyacrylic acid (PAA) for fabrication of $(PAH/PAA)_n$ PEMs matrix. Secondly, the final oil-repellent coatings were obtained by dipping the $(PAH/PAA)_n$ PEMs coated substrates into ammonium perfluorooctanoate (PFO) solution. The detailed experiments are illustrated as below.

2.1 Construction of $(PAH/PAA)_n$ matrix coating

Preparation of PAH and PAA solutions. 1 g of PAH (*Mw* 58000) and 1 g of PAA (*Mw* 1800) powder were respectively dissolved in 1 L of aqueous water under stirring. Adjust pH value of PAH solution to 7.5 by addition of NaOH or HCl. For PAA (weak acid, $pK_a = 4.75$) solution, there is no need to adjust its pH value. As-obtained PAH (1 mg/mL) and PAA (1 mg/mL) solutions were directly used as precursors for construction of PEMs.

Construction of $(PAH/PAA)_n$ PEMs. As exhibited in Figure 2, the substrates, such as a Si wafer, wood, glass, steel and plastics were firstly immersed in the as-obtained PAH solution for 15 min (step 1), and then washed with water (step 2). Afterwards, the substrates were alternatively immersed in the PAA solution for another 15 min (step 3) and washed with water (step 4). Like this, one bilayer of PAH/PAA was coated on the substrate. Repeating steps 1 to step 4 for multi-cycles, one can obtain multi-layers of $(PAH/PAA)_n$, where "n" denotes the bilayer number of the PEMs. After the final layer deposition, the PEMs-coated substrates were dried in air.

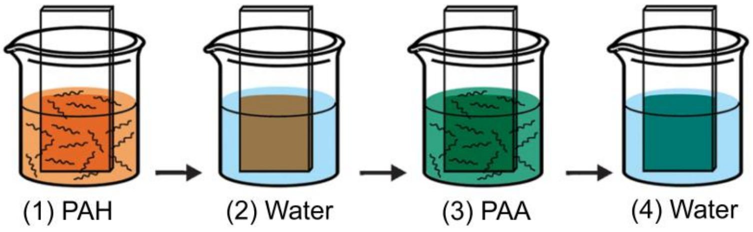

Figure 2. Schematic illustration of the LbL assembly of PEMs on substrates.[20]

Mechanism of the LbL assembly. The mechanism of the LbL assembly processes is schematically demonstrated in Figure 3. The processes can be simply divided into three steps. Firstly, the positively charged PAH can adsorb to the substrate due to electrostatic or hydrophobic-hydrophobic interactions, depending on the surface properties of the substrate. Secondly, the negatively charged PAA molecules can adsorb to the PAH modified substrates after immersion into the PAA solution because of the electrostatic interactions between positively charged PAH coated substrate and the negatively charged PAA. In this step, the surface charge reversed and negatively charged. Thirdly, the positively charged PAH molecules can adsorb to the PAA/PAH-substrate due to strong interactions between PAH and PAA. Therefore, PAH and PAA macromolecules can alternatively deposited on the substrate to form the $(PAH/PAA)_n$ PEMs. Obviously, the key of the coating construction is derived from electrostatic interactions between the positively and negatively charged polyelectrolyte materials (Figure 3).

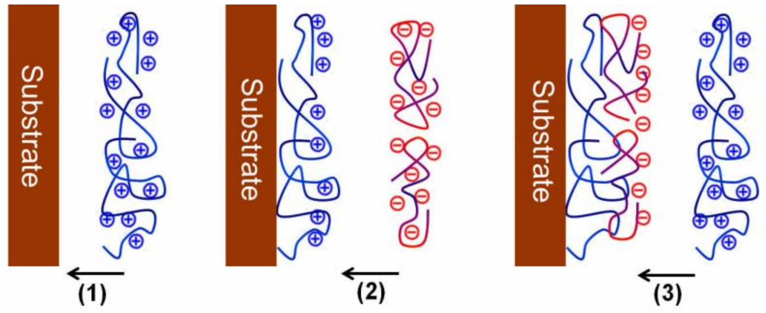

Figure 3. Schematic illustration of the electrostatic interactions triggered LbL assembly of PEMs on substrate.

2.2 Construction of oil-repellent PFO-$(PAH/PAA)_n$ coatings

One of the prior conditions to construct oil-repellent coating is to reduce its surface energy by fluorination for prevention of oil contaminations. However, the fluorination process at high temperatures for preparation of the most currently available oil-repellent coatings not only produces high toxic silane, but also requires heat-resistant substrate materials. To overcome these disadvantages, a fluorination process using non-toxic fluoride at room temperature is desired. In this study, the PEMs matrix is assembled by electrostatic interactions between the oppositely charged polyelectrolytes, the fluorination of the PEMs should be completed by using a fluoride agent that has stronger electrostatic interactions with PEMs. Therefore, the charged ionic surfactants containing fluorocarbons meet the requirements. Here, we chose an inexpensive, non-toxic ammonium perfluorooctanoate (PFO) anionic surfactant as the fluorination agent.

Preparation of the PFO solution. The PFO solution with a concentration of 50 mmol/L was prepared by dissolving 21.56 g of PFO powder in 1 L of aqueous water under stirring, and then stored for use.

Preparation of oil-repellent PFO-(PAH/PAA)$_n$ coatings. The (PAH/PAA)$_n$ PEMs-coated substrates were immersed in PFO solution for 10 s, followed by water washing and drying in air. Thus, the transparent oil-repellent PFO-(PAH/PAA)$_n$ coatings were fabricated on the substrates.

2.3 Methodologies for characterization of oil-repellent coatings

(1) Thickness and morphology of the coatings. The thickness and morphology of the coatings were examined by using a scanning electron microscopy (SEM). To increase the conductivity during the SEM imaging, a 15-nm thickness coating of platinum was deposited on as-prepared PFO-(PAH/PAA)$_n$ coating on the silicon wafer.

(2) Transparency of the coatings. The PFO-(PAH/PAA)$_7$ coating was prepared on the glass surface and its transmittance was measured by an UV-Vis spectrophotometer.

(3) Oil-repellent performances of the coatings. The oil-repellency of the coatings was evaluated by measuring the contact angle and sliding angle of various oil droplets with different surface tensions, such as hexadecane, dodecane, decane, hexane and toluene on the coating surface. The larger contact angle indicates that the coating is more oleophobic, and the lower sliding angle facilitates easier rolling-off.

(4) Chemical resistance of the coatings. The chemical resistant performance of the coatings was studied by dropping a commonly used organic solvent such as toluene onto the coated and uncoated polystyrene (PS) plastic surfaces.

(5) Anti-oxidation and anti-abrasion properties of the coatings. These properties were studied through checking the oil-sliding performances of the oxidized and abraded coatings achieved by sunlight irradiation of the coatings for 15 days and 300 cycles of sand-abrasion, respectively.

(6) Oil-repellency of the coatings towards condensed vapor oil. The oil vapor was generated by heating the liquid hexadecane at 240 ℃, afterwards, the coated sample was placed over the top of the container for condensing oil vapor. Oil-enriched coatings with different condensation times were observed by an optical microscope, and their oil-repellent performance was studied.

3. Results and discussion

3.1 Molecular structure of PAH, PAA and PFO

The molecular structure of three precursors for construction of oil-repellent coatings are shown in Figure 4, where PAH is a positively charged polyelectrolyte with Cl^- as counterions, PAA is a negatively charged polyelectrolyte with H^+ as conterions, and PFO is an anionic surfactant, i.e., negatively charged ammonium perfluorooctanoate with NH_4^+ as counterions.

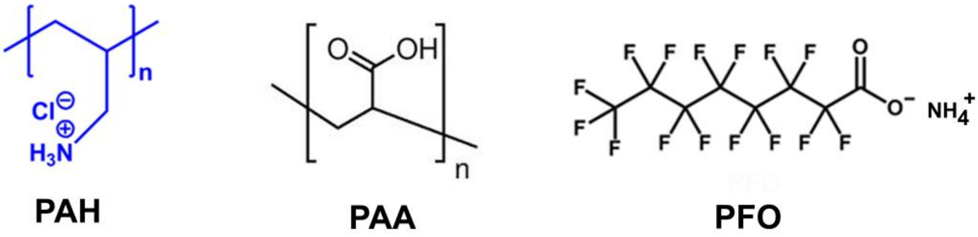

Figure 4. Schematic illustration of the molecular structure of PAH, PAA and PFO.

3.2 Characterization of the PFO-(PAH/PAA)$_n$ coatings

3.2.1 Thickness and morphologies of the coatings

To examine the thickness and surface morphology of the coatings, the coating was firstly deposited on the flat silicon substrate, and then observe by the SEM. As shown in Figure 5a, one can clearly see that the PFO-(PAH/PAA)$_{15}$ coating on the Si wafer substrate has a thickness of approximately 1.25 μm, and the surface is relatively smooth and flat. (Figure 5b).

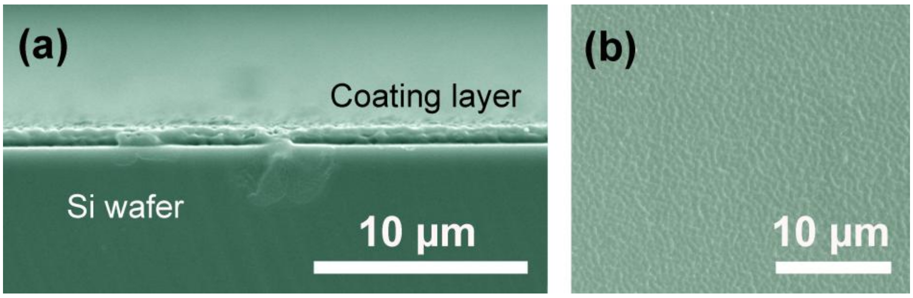

Figure 5. Cross-sectional (a) and frontal (b) SEM images of the PFO-(PAH/PAA)$_{15}$ coating deposited on Si wafer.

3.2.2 Transparency of the coatings

Choosing the coating with good transparency without changing the appearance of the original substrates enables a variety of functions in optical and electronic devices. Therefore, the coatings with a good transparency are very important for their practical applications. Here, the transmittance of the PFO-(PAH/PAA)$_7$-coated and uncoated glass slides is measured by UV-Vis spectrum. As revealed in Figure 6, the commonly used pristine glass shows the transmittance of ~ 91% in the visible light region (400-700 nm), while the PFO-(PAH/PAA)$_7$-coated glass substrate demosntrates a transmittance of 92.5-92.9% in this region. This suggests that the coated glass exhibits a little better optical transparency than the uncoated glass, which can be explained by the fact that the coating is quite smooth with a certain thickness that weakens the Fresnel reflectance.[21]

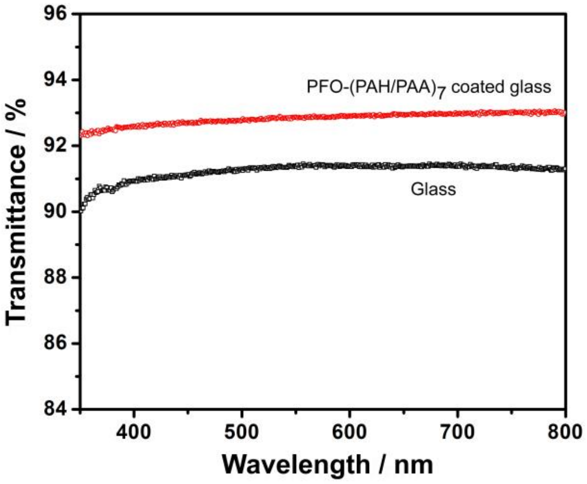

Figure 6. UV-Vis transmission spectra of the PFO-(PAH/PAA)$_7$-coated and pristine glass slides.

3.3 Oil-repellent performances of the PFO-(PAH/PAA)$_n$ coatings

3.3.1 Oil-repellency of the coatings on the flat glass substrates

As the surface roughness can enhance the surface wettability,[2,3] here, we fabricated the coatings on the flat glass or Si wafer substrates to eliminate the roughness-induced effect and then studied their wettability towards various oils. Figure 7a shows that the original (PAH/PAA)$_7$ coating is oleophilic and thus decane can completely wet the coating surface. However, as we expected, after fluorination, the PFO-(PAH/PAA)$_7$ coating demonstrates an excellent oil-repellent performance, as clearly suggested by the fact that the decane droplets quickly slid off without leaving any oil trace on this fluorinated coating (Figure 7b).

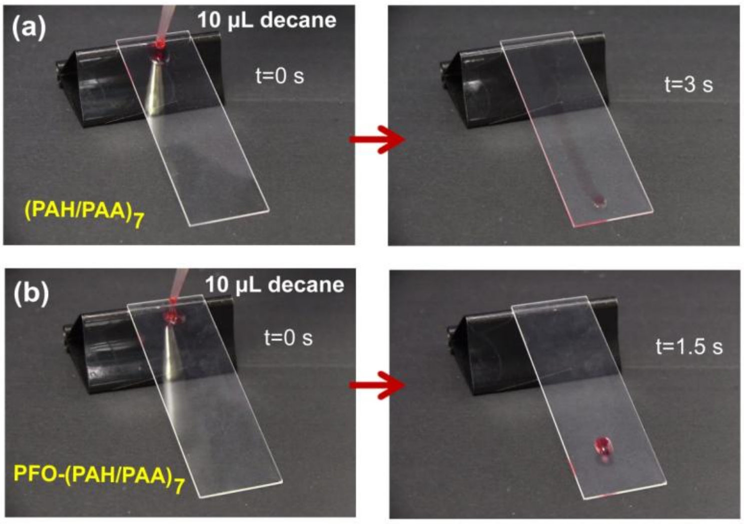

Figure 7. (a, b) Time-lapse snapshots of a sliding decane droplet (10 μL) on the tilted glass substrate-supported $(PAH/PAA)_7$ (a) and PFO-$(PAH/PAA)_7$ (b) coating. The decane was labelled by oil red O, and the tilting angle of the substrates was 15 °.

In order to further investigate the wettability of the coatings, the contact angle and sliding angle of various oil droplets (including hexadecane, dodecane, decane, hexane, and toluene) on the coated surface were measured. The molecular weight, viscosity and surface tension of the oils are shown in Table 1.

Table 1. The molecular weight, viscosity and surface tension of the tested oils.

Tested oil	Molecular weight (g/mol)	Viscosity (mpa•s)	Surface tension (mN/m)
Hexadecane	226.45	2.98	27.35
Dodecane	170.33	1.34	25.35
Decane	142.30	0.85	23.26
Hexane	86.18	0.28	17.90
Toluene	92.14	0.56	28.52

Figure 8 shows the contact angle and sliding angle of these oils on the PFO-$(PAH/PAA)_7$ coating. The results indicate that the contact angle and sliding angle on the coated surface increase with the oil surface tension increasing. For example, the contact angle is measured to be 35 °, 52 °, 56 ° and 65 ° for hexane, decane, dodecane and hexadecane, respectively, and the corresponding sliding angle is measured to be 8 °, 8.6 °, 10.9 ° and 11.8 °, respectively. Very small sliding angles suggest a good oleophobicity of the coating. It is also worth noting that the smaller sliding angle facilitates easier oil sliding-off. Therefore, our coatings with low sliding angles should possess excellent self-cleaning oil-repellency. In addition, as toluene shows a higher surface tension and an easier volatility, the contact angle of toluene is lower than that of hexadecane. Importantly, the sliding angle of toluene on the coating is also small, i.e., 11.1 °, slightly lower than that of hexadecane, indicating that toluene can also easily slide off the coating, which makes the coating a promising chemical shield to protect the substrates from dissolution by toluene.

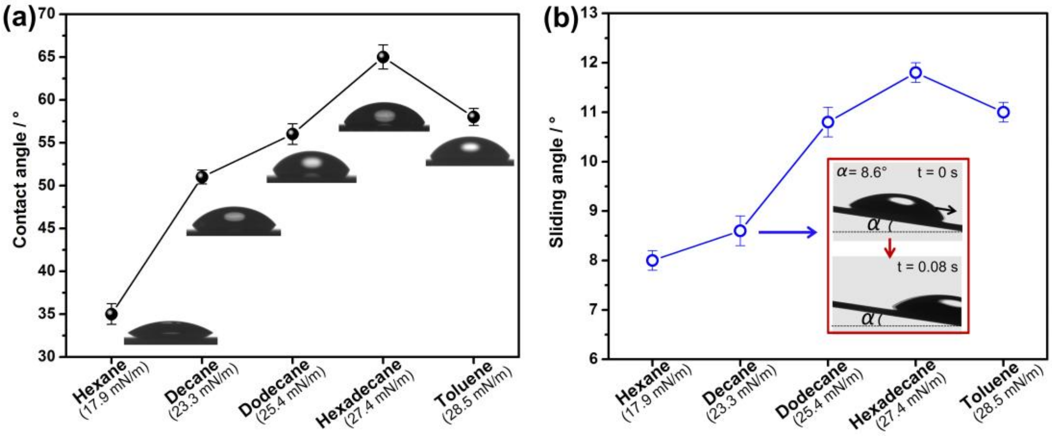

Figure 8. (a, b) Contact angle (a) and sliding angle (b) of the tested oils on Si substrate-supported PFO-(PAH/PAA)$_7$ coatings. Insets of (a) are contact angle profiles of hexane, decane, dodecane, hexadecane, and toluene, respectively. Insets of (b) are time-lapse snapshots of a sliding decane droplet (10 μL) on the coating at a tilting angle of 8.6 °. The volume of oil droplets for contact angle and sliding angle measurements is 2 μL and 10 μL, respectively.

3.3.2 Oil-repellency of the coating on the wood, plastic, steel and inner wall of glass tube

As our coatings can be constructed on various kinds of substrates with any shapes and sizes, typically, we deposited the PFO-(PAH/PAA)$_7$ coating on different daily objects, such as inner wall of the glass tubes, wood, plastics, and steel surfaces, and then studied their oil-repellency. As shown in Figure 9, we compared the oil-repellent performance of the inner wall-uncoated and inner wall-coated glass tubes (a diameter of 3.5 mm). 1 mL of decane was simutaneously injected into two glass tubes, respectively. It was clearly seen that the uncoated glass tube was quickly contaminated by decane, while the coated glass tube kept clean without leaving any oil residue. This result indicates the superiority of our approach to the coating fabrication, which can be simply and effectively applied to the outer or inner wall of a substrate.

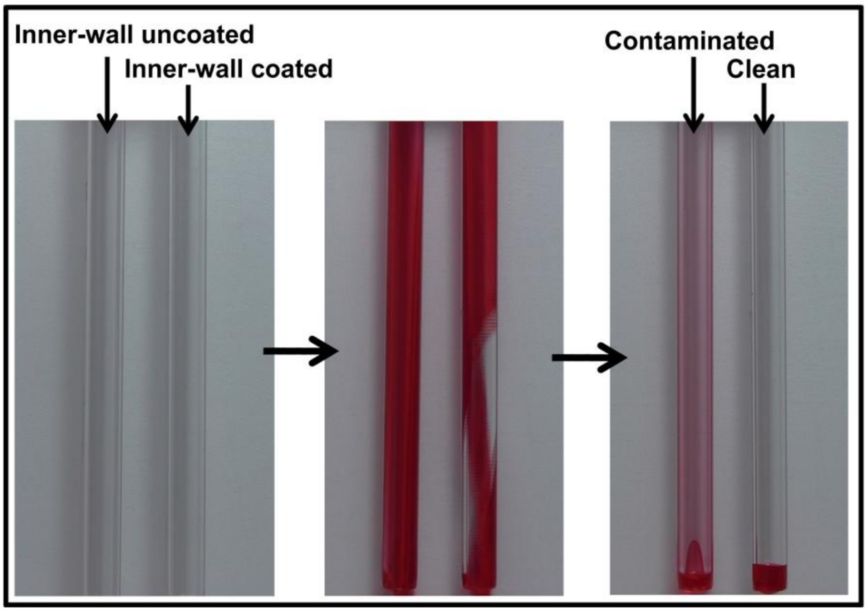

Figure 9. Snapshots taken showing 1 mL of decane flowing inside the PFO-(PAH/PAA)$_7$-coated and uncoated glass tubes with a innner diameter of 3.5 mm.

Moreover, we also compared the oil-repellency on the surface of the coated and uncoated wood, plastics, and steel. As exhibited in Figure 10, hexadecane can quickly slide across the coated surfaces without leaving any oil trace, which occurs at substrate tilting angle of 15 ° (Figure 10a-c). This indicates that the coating can protect various substrate materials from contamination by oils. In contrast, the surfaces of the pristine wood, plastic and steel without such a coating were all contaminated by hexadecane with large amounts of oil traces retained (Figure 10d-f). These results show that the construction of the oil-repellent coatings in the present study is not limited by the substrate material and thus can be used to improve the self-cleaning performance of a variety of daily objects.

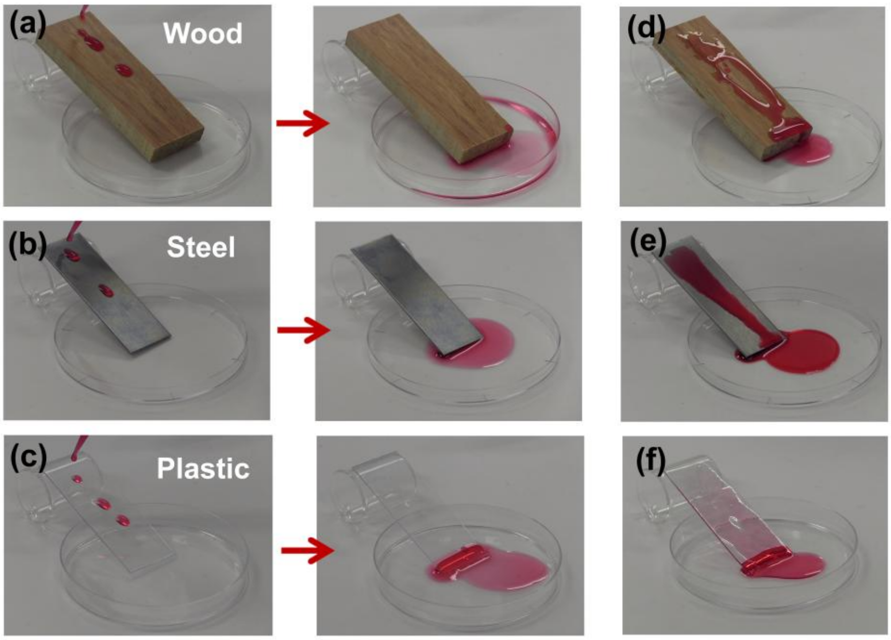

Figure 10. Photographs of sliding (a-c) and spreading (d-f) of decane droplets (1 mL) on the PFO-(PAH/PAA)$_7$-coated (a-c) and pristine (d-f) wood, steel and plastic substrates at a tilting angle of 15°, respectively.

3.3.3 Oil-repellency of the coating on rough substrates

In our daily life, lots of the substrate materials are not smooth. Herein, two rough substrates were chosen for deposition of the coating and their oil-repellent performances were examined. The first rough substrate is a piece of Si wafer abraded by sandpaper, which many rough scratches can be clearly observed (Figure 11a). The second substrate is commercially available plastic mat with macroscopic roughness (Figure 11c). Interestingly, after constructing the PFO-(PAH/PAA)$_7$ coating on the two substrates, they both showed good oil-repellency, which is evidenced by quick decane droplet (10 μL) sliding-off from their surfaces (Figure 11b, d). These results show that our oil-repellent coatings can be applied not only to flat substrates but also to various rough substrates, thus, extending their application ranges.

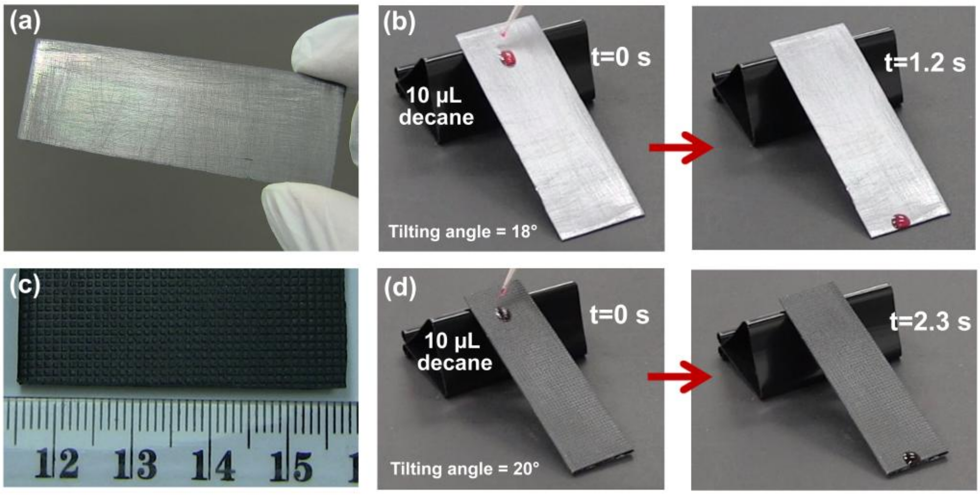

Figure 11. (a, c) Photographs of the rough sandpaper-abraded Si wafer (a) and plastic mat (c) substrates. (b, d) Time-lapse snapshots of a sliding decane droplet (10 µL) on the tilted Si (b) and plastic mat (d) substrate-supported PFO-$(PAH/PAA)_7$ coating.

3.3.4 Chemical-shielding performances of the coating

In many industrial production processes and our daily lives, the plastic products showing anti-dissolution by chemical solvents are highly important. However, up to date, the coatings possessing anti-corrosion by chemical solvents were rarely reported.[17] In Figure 8, we showed that toluene can easily slide off the coated surface with a low sliding angle. Here, we further investigated the chemical-shielding performances of the coated plastics. As shown in Figure 12, a conventional polystyrene (PS) plastic plate was chosen as the substrate. When the toluene droplets were added dropwise onto the pristine PS plate, toluene easily adheres to the PS surface and partially dissolves the plastic (Figure 12a-c). Tilting the substrate, the adhered toluene cannot slide across or off the PS plate (Figure 12b), damaging the PS substrate (Figure 12c). As a comparison, after the PS plate with the PFO-$(PAH/PAA)_7$ coating, toluene maintains a good droplet-shape on the top (Figure 12d), and slides rapidly off the coated-PS surface at a slight tilting angle (Figure 12e), and no chemical-corrosion was observed (Figure 12f). The results show that the coating has an excellent resistance to toluene corrosion. So, it is believed that this coating can perform as a chemical shield to protect plastics from dissolution by organic solvents.

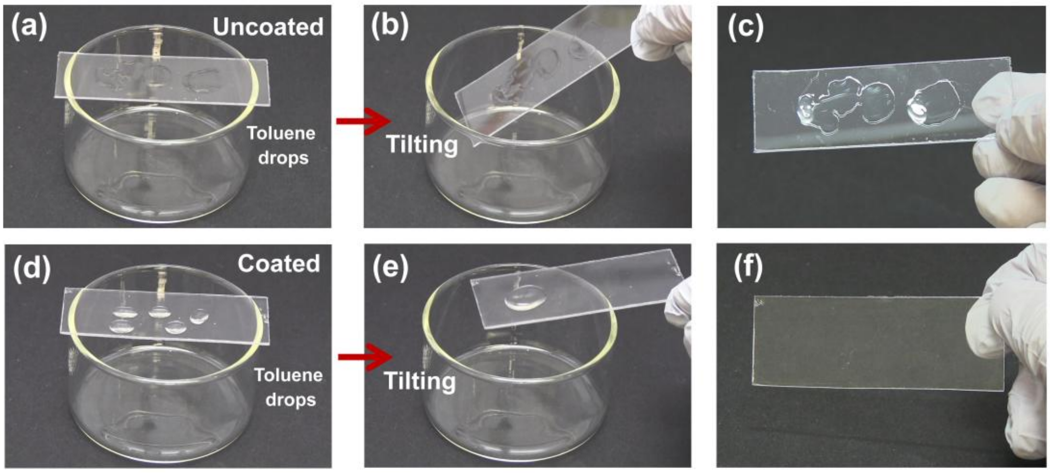

Figure 12. (a-c) Photographs of a PS plate after dropping toluene on the top. (d-f) Photographs showing that toluene droplets can slide off the PFO-(PAH/PAA)$_7$-coated PS plate.

3.3.5 Anti-oxidation and anti-abrasion performances of the coatings

In this study, two methods (sunlight-irradiation and sand-abrasion) resulted in the coating damage were chosen to evaluate their self-healing oil-repellent properties. The PFO-(PAH/PAA)$_7$ coating was deposited on a Si wafer substrate and placed under sunlight for 15 days continuous irradiation. As sunlight contains ultraviolet (UV) light, the coating will have oleophilic oxygen-containing groups after UV light oxidation. After irradiation, the sample was placed in an ambient condition, and the sliding angle of hexadecane on its surface versus storing time was measured. Showed in Figure 13a, the initial sliding angle of the irradiated sample was 55°, indicating that the oil droplet cannot easily slide off from the surface. It is interesting to note that the sliding angle dropped linearly within 2 h of the ambient storing (without light) and reached to 15° in the third hour of the storing. As shown in Figure 13b, after 3 h of the storing, these hexadecane droplets can rapidly slide off from the surface at a substrate tilting angle of 20°, indicating that the oil-repellency of the coating was recovered. These results show that our coatings have an excellent self-healing anti-oxidation property by the sunlight irradiation.

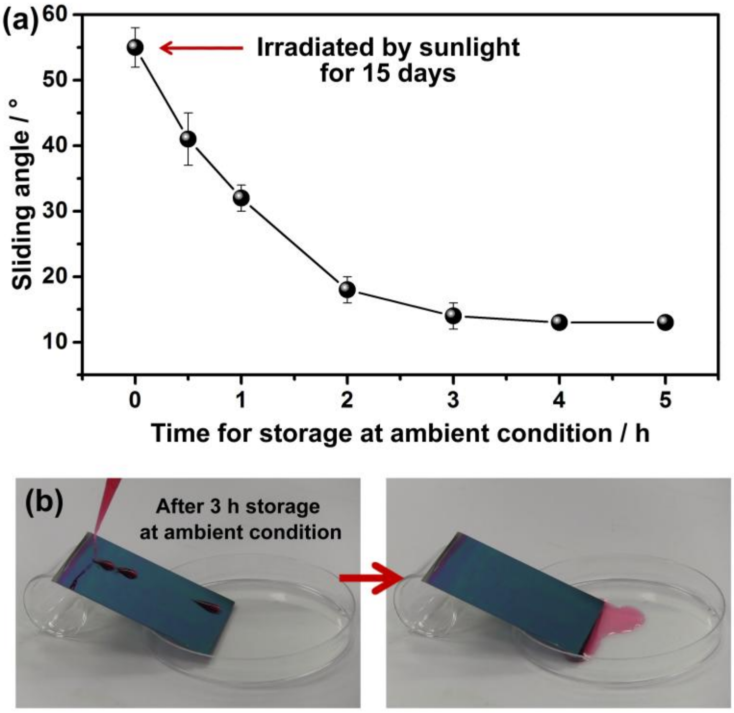

Figure 13. (a) Sliding angles of hexadecane on the PFO-(PAH/PAA)$_7$ coated Si substrate versus storing time at ambient conditions. (b) Photographs of oil-repellent performance of the coating after 3 h of its storing at ambient conditions (without light). The volume of oil droplets for measuring sliding angles in (a) is 10 μL, and the substrate titling angle in (b) is 20 °.

In addition, the coating was scratched by physical sand-abrasion, showed in Figure 14a and Figure 14b. Here, the PFO-(PAH/PAA)$_7$-coated Si substrate was up and down abraded by sands repeatedly for 300 times, and the appearance and the microstructures of the coating are shown in Figure 14c and Figure 14d. It can be clearly seen that the sand-abraded coating exhibited significant damages (Figure 14d), but hexadecane can still easily slide off the coating at a certain tilting angle (Figure 14e-g). These results indicate that the coating exhibits good durability for its oil-repellency.

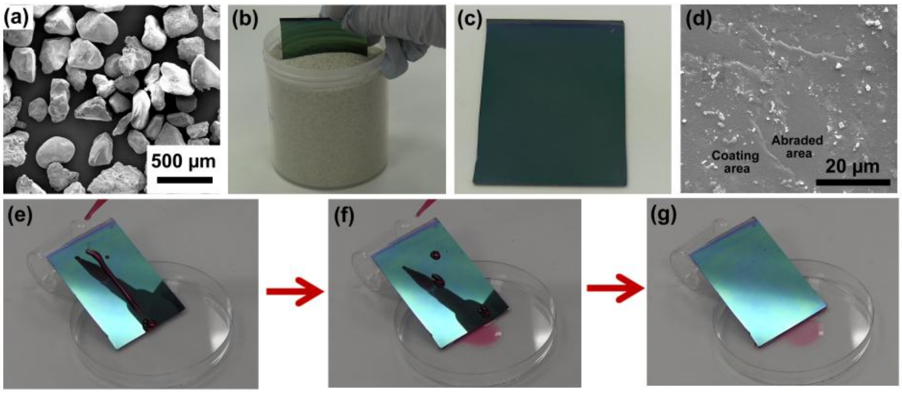

Figure 14. (a) SEM image of sands used for the coating abrasion. (b) Photograph of the Si substrate-supported PFO-(PAH/PAA)$_7$ coating thrusting into the sand, each thrust consisting of downward thrusting followed by upward thrusting of the sample in the sand. (c, d) Photograph and SEM image of the coating after 300 cycles of sand-abrasion. (e-g) Snapshots of hexadecane (1 mL) sliding on the sand-abraded sample.

3.3.6 Oil-repellency of the coatings towards condensed vapor oil and high temperature oil

The PFO-(PAH/PAA)$_n$ coatings developed here also have excellent oil-repellent properties towards condensed vapor oil and high temperature oil. As shown in Figure 15, the hexadecane liquid was heated and kept at 240 ℃ to generate hexadecane vapor, and the Si substrate-supported PFO-(PAH/PAA)$_7$ coating sample was placed on the top for vapor oil condensation. The vapor oil condensed on the sample was characterized by optical microscope, as shown in Figure 16. With the extension of the condensation time, the hexadecane vapor accumulated on the surface and formed oil droplets, and the size of the droplets increased with condensation time increasing. For example, after 5 min and 120 min, the size of the oil droplets increased from several micrometers to hundreds of micrometers.

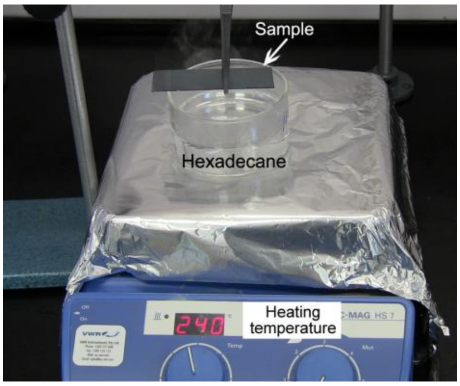

Figure 15. Photograph of the hexadecane vapor oil condensation on the surface.

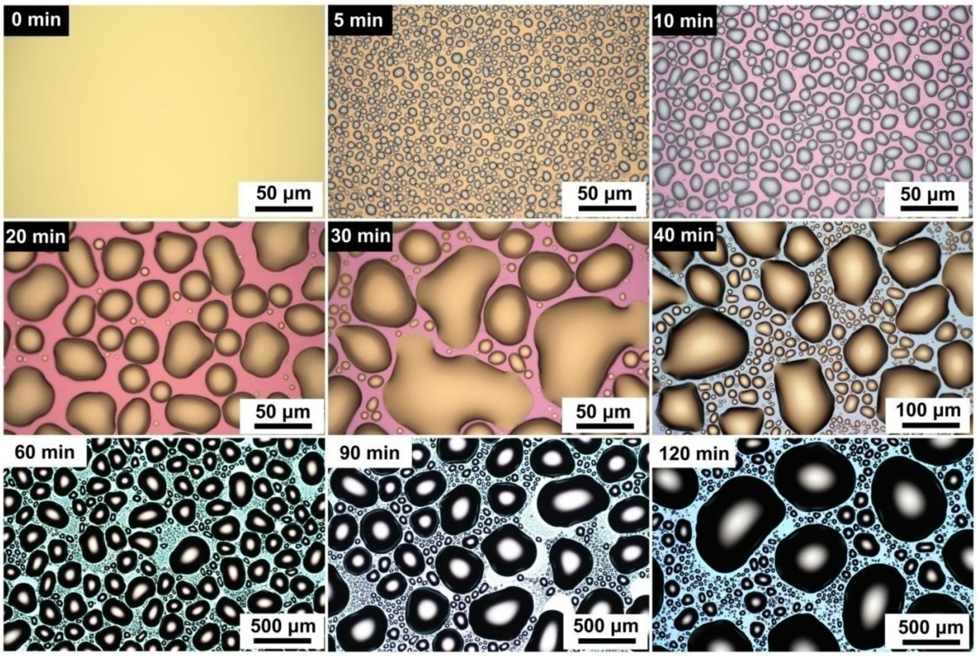

Figure 16. Optical microscopy images of the hexadecane vapor accumulated on the Si substrate-supported PFO-(PAH/PAA)$_7$ coating with different condensation time.

Since our coatings are flat without porous air-pocket structures (as shown in Figure 5), the gaseous oil molecules can hardly penetrate into the coatings. Thus, these coatings can effectively resist the infiltration of oil vapors. Showed in Figure 17a, after 10 min condensation of hexadecane vapor on the coating, a large amount of fog-like oil droplets were attached to the surface. When the liquid hexadecane droplets were dropped onto the coating, they can easily slip away from the surface together with the fog-like oils (Figure 17b). Optical microscopy image indicates that the oil-slipped area does not have any fog-like oil droplets left (Figure 17c). These results illustrate that the coating exhibits good oil-repellency towards condensed vapor oil.

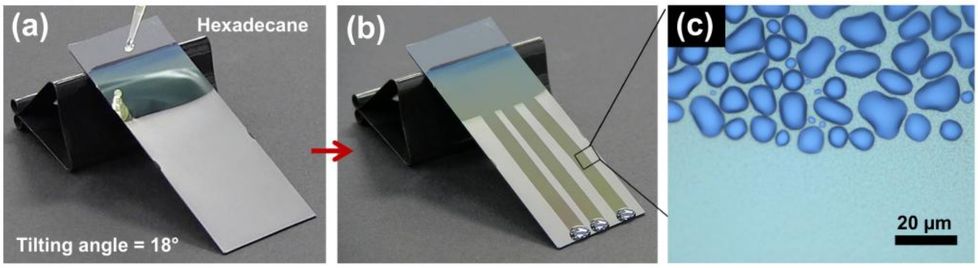

Figure 17. (a, b) photographs of 3 sliding droplets of liquid hexadecane on the Si substrate-supported PFO-(PAH/PAA)$_7$ coating, which was pre-condensed by the hexadecane vapor for 10 min. (c) Optical microscopy image showing the boundary of the coating after hexadecane sliding.

In addition, such a coating can also prevent the infiltration of high-temperature oils. As demonstrated in Figure 18a-c, the hexadecane was heated to 240 ℃, followed by immersing the coating into hot hexadecane for tens of seconds, afterwards, the sample was taken out and characterized by optical microscope. It can be seen that the coating surface was very clean without any hexadecane adhered (Figure 18d). Furthermore, it was found that even if the immersion time was extended to several minutes, the coating remains intact and shows good oil-repellency. This is because the $(PAH/PAA)_n$ matrix polymer has a high decomposition temperature, therefore, the coatings can resist high temperature oils.

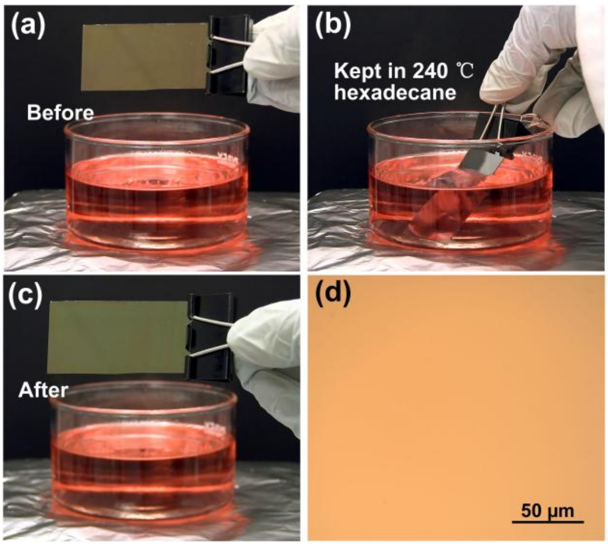

Figure 18. (a-c) Photographs of the Si substrate-supported PFO-$(PAH/PAA)_7$ coating before immersion (a), in immersion (b) and after (c) immersion in hexadecane at 240 ℃. (d) Optical microscopy image of the coating after immersion in hexadecane at 240 ℃.

4. Conclusions and prospects

4.1 Conclusions

This study developed a room-temperature construction of low-cost and transparent oil-repellent PFO-$(PAH/PAA)_n$ coatings using LBL assembly technique. This approach is facile and the coatings can be deposited on a variety of daily objects, such as glass, steel, plastic, wood, silicon and so on. The PFO-$(PAH/PAA)_n$ coatings exhibit excellent oil-repellency that various oils with different surface tensions such as hexane, decane, dodecane, hexadecane and toluene can easily slide off the coatings at a sliding angle lower than 12 °. In addition, the coatings can effectively prevent plastics from chemical corrosion by organic solvents (e.g., toluene). Moreover, the coatings also show self-healing oil-repellency upon UV light oxidation and physical abrasion as well as high-temperature oil and condensed vapor oil repellency.

4.2 Prospects

Our facile LBL assembly approach for the construction of transparent oil-repellent coatings have solved many problems, such as difficulty in production, toxic substance release during high temperature fluorination, substrate-limitation by its shape and size, expensive cost, optical opacity, etc. Therefore, our coatings demonstrate promising commercial prospects. However, in this study, two works have not been conducted yet. Firstly, the substrates we used are mostly hard substrates, yet we have not considered the coatings deposited on other flexible substrates, such as table cloth, clothing, etc. In future work, we will further fabricate coatings on the flexible substrates, and study their oil-repellent performances. Secondly, by taking advantage of vapor oil-repellency, we will fabricate the coatings on the kitchen ventilators and study their oil-repellent performances towards condensed cooking oils. After this technology is well developed, we will absolutely promote their applications in many industries.

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