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Enabling phase transition of infused lubricant in porous structure for exceptional oil/water separation

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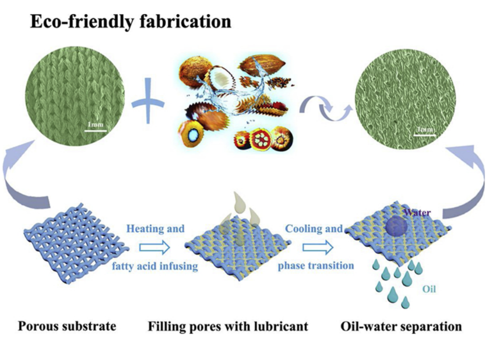
GRAPHICAL ABSTRACT



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ABSTRACT

The fundamental mechanism behind oil/water separation materials is their surface wettability that allows either oil or water to pass through. The conventional materials for oil/water separation generally have extreme wettability, namely superhydrophilic for water separation and superhydrophobic for oil separation. Using easily accessible materials that are medium hydrophobic or even relatively hydrophilic for preparing highly efficient oil/water separators have rarely been reported. In this work, a new strategy by triggering phase transition of infused lubricant from liquid to solid state in porous structure is realized in fabricating slippery lubricant infused porous structure for oil/water separations. By infusing polyester fabric with coconut oil, after phase transition, excellent water repellency and oil permeability by an absorbing-permeating mechanism are achieved, despite the low water contact angle on the new material. Although the new phase transformable slippery lubricant infused porous structure, features much milder hydrophobicity than conventional oil/water separators, it can remove diverse types of oil from water with high efficiencies. The phase transformable slippery lubricant infused porous structure is able to maintain their water repellency after immersing in high concentration salt (10 wt% NaCl), acid (25 % HCl), alkaline (25 % $NH_3{\cdot}H_2O$) solutions for 120 h, showing remarkably functional durability in harsh environment. The lubricant phase transition mechanism proposed in this study is universally applicable

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to porous substrates with various chemical compositions and pore structures, such as porous sponges or even daily life breads, for creating efficient oil/water separators, which can serve as a novel accessible design principle of phase transformable slippery lubricant infused porous structure for eco-friendly oil/water separators.

1. Introduction

The leakage of oil and discharge of liquid industrial wastes result in release of tremendous toxic chemical compounds into environment and obviously threats to the global ecosystem. (Peterson et al., 2003; Schrope, 2011; Incardona et al., 2005; Joye, 2015) Conventional methods for the treatment of large-scale oil spill event, including in-situ burning, vacuum suction, and chemical dispersants-assisted degradation, are highly costly and relatively inefficient (Kleindienst et al., 2015; Fritt-Rasmussen et al., 2015, 2016). Novel strategies that can split oil and water in a cost-effective, efficient and eco-friendly manner are desired. Nowadays, the rapid research and development of colloid and interface introduce new branches for oil/water separation. (Feng et al., 2004) Advanced interface materials that can separate the mixture of oil and water effectively attract tremendous interest since the pioneer study by Jiang et al. in 2004 (Feng et al., 2004). There are currently three main types of oil/water separation materials, the superhydrophobic and superoleophilic materials (Feng et al., 2004; Gao et al., 2013; Cao et al., 2013; Zhang and Seeger, 2011), the superhydrophilic and under-water superoleophobic materials (Xue et al., 2011; Wen et al., 2013; Zhang et al., 2013a), and the superhydrophilic and superoleophobic materials (Yang et al., 2012; Kota et al., 2012; Pan et al., 2018; Ponzio et al., 2016), being actively investigated. These interface materials possess attractive oil/water separation properties originated from their varied affinities to oil and water, namely special surface wettability (Wang et al., 2015; Liu et al., 2014a).

The surface wettability can be quantified by the intrinsic wetting threshold (θ*) of the substrate materials. (Li et al., 2018) A surface holding liquids with contact angles (θ) larger than θ* is regarded as lyophobic, and otherwise lyophilic. With the integration of surface roughness and hierarchical structure, superlyophobic/superlyophilic materials with tailored wettability to oil and water were fabricated and applied for oil-removing or water-removing purposes. (Wang et al., 2015; Ma et al., 2016; Liu et al., 2010) One material with special wettability function is the slippery lubricant infused porous structure (SLIPS) that has already been widely utilized in multiple applications (Wilson et al., 2013; Epstein et al., 2012; Kim et al., 2012). The first SLIPS was fabricated by Aizenberg et al. in 2011 by infusing perfluorinated fluids into hydrophobic porous substrates (Wong et al., 2011). The SLIPS materials are generally omniphobic and show potentials in water repellence, anti-icing and anti-frost, antibiofouling, antibacterial, and so on (Wilson et al., 2013; Epstein et al., 2012; Kim et al., 2012). Interestingly, the SLIPS was also adopted for oil/water separation (Wang et al., 2017). With design concept discussed in the supplementary materials S1, there are intrinsic drawbacks of the traditional SLIPS applied in practical oil/water separation, namely the liquid lubricants in the porous structure of SLIPS can be easily displaced by the incoming oil and the resulted short lifespan of the materials. Furthermore, the infused lubricants in SLIPS are highly unstable if the porous structure has hydrophilic walls (supplementary Figure S3b), given that the water molecules have higher chemical affinity to the porous substrate. (Wong et al., 2011) A recent report by Wang et al. introduced a polarity-based strategy for separating immiscible liquids through SLIPS (Wang et al., 2017), which attempts to maintain stable lubricants in hydrophilic porous membranes. It turns out that the infused lubricants are also easily replaced by oil species of higher polarity, largely owing to their liquid states. A feasible way to maintain lubricant stably in the SLIPS for oil/water separation is missing, which can broaden the applicability of SLIPS in oil/water separation.

The aim of this work was to provide an eco-friendly strategy for separating diverse oil species using daily accessible materials. By enabling phase transition of the lubricants from liquid to solid in the porous structure, a new phase transformable slippery lubricant infused porous structure (PTSLIPS) was fabricated, which possesses exceptional oil/water separation performance at room temperature (20 °C). The fabrication principle of PTSLIPS was realized in various hydrophobic and hydrophilic porous substrates, all of which exhibited outperforming ability of removing oil from water by filtration. Strikingly, the prepared PTSLIPS samples maintained excellent oil/water separation function after immersing in radical solutions of salt, acid and alkaline for 120 h, confirming its robustness in harsh environment. The approach for fabricating PTSLIPS was also practical in daily life. Examples of PTSLIPS prepared from daily accessible porous sponges, including bread, were provided in this study. The wide adaptability and feasibility of PTSLIPS make it a competitive material for an eco-friendly society.

2. Experimental section

2.1. Materials

Coconut oil, with high melting point of 25 °C was chosen as lubricant for PTSLIPS in this study. The coconut oil was purchased from Acros Organics (Belgium). Ethanol (> 99.8 %) and tetraethyl orthosilicate (TEOS, > 99.8 %) were purchased from Sigma Aldrich (USA), which were used for fabricating silica nanoparticles. Wipers and paper used in the experiments as porous substrates were purchased from ITW Texwipe (USA). Foams (skuresvamper) and bread (Klover Toastloff) used in the experiments as porous substrates were purchased from Kiwi (Norway). All porous substrates can be wetted by water (supplementary Figure S11). Various oil types, namely chloroform, n-pentane, cyclohexane, n-heptane, dichloromethane and toluene, were purchased from Merck KGaA (Germany). Dye stuffs (oil red O, methylene blue, sudan black B and sudan I) were purchased from Sigma Aldrich (USA). Ammonia solution (25 %) and the hydrochloric acid solution (25 %) were purchased from Merck KGaA (Germany). Sodium chloride was purchased from Sigma Aldrich (USA) and was dissolved in deionized water to make a solution with concentration of 10 wt%. The steel mesh was purchased from Sigma Aldrich (USA). It should be noted that solid coconut oil chosen in this work for the purpose of demonstrating the fabricating strategy of PTSLIPS. Given that coconut oil can dissolve in certain liquid oil types at room temperature, for instance chloroform, other phase-transferable lubricants but coconut oil should be adopted as the infused phase of PTSLIPS for separation of such oil species from water.

2.2. Preparation of SiO_2 nanoparticles and PTSLIPS

SiO_2 nanoparticles were synthesized based on the method reported for coating glass slides to obtain porous structures. (Wang et al., 2019a) The coated glass slides were used to probe the stability of SLIPS in oil/water separation (Figure S3-S4). Firstly, 5 ml ammonia solution (25 %, Merck KGaA), 95 ml absolute ethanol and 5 ml deionized water were mixed and stirred in a three-necked flask for 10 min. The system was kept at 26 °C, and then added with 3 ml TEOS. Finally, after stirring for another 12 h, the ethanoic suspension of silica nanoparticles with particle size 394.9 nm were obtained (the particle morphology and particle size distribution were given in supplementary Figure S5). Glass slides (25 mm * 75 mm) were cleaned and dipped into the as-prepared suspension to get SiO_2 coated glasses. To achieve hydrophobic surfaces, the SiO_2 nanoparticles coated glasses were silanized with trichloro (1H,1H,2H,2H-perfluorooctyl)silane (Sigma Aldrich) in a vacuumed chamber for 8 h.

To prepare PTSLIPSs, coconut oil was first heated up to 50 °C to be liquid lubricant. Porous substrates were then immersed into the liquid and kept for 1 h. The porous materials were taken out and sloped under 50 °C to remove extra lubricant on the surfaces. After cooled down to room temperature (20 °C), PTSLIPSs were ready for use.

2.3. Oil/water separation

For separating oil/water mixture by filtration, PTSLIPS membrane was fixed at the bottom of a filter. Six types of organic solvents, including chloroform, n-pentane, cyclohexane, n-heptane, dichloromethane and toluene were used in this study. The oil/water mixtures (50 %, v/v) were poured onto the as prepared PTSLIPS membrane for separation. The separation efficiency of the PTSLIPS membranes were calculated through the equation below (Yi et al., 2019)

$$\eta = \frac{W_1}{W_0} \times 100\% \qquad (1)$$

where W_0 and W_1 are the mass of oil before and after the separation. In the separation efficiency test, the PTSLIPS membranes were pre-wetted by the separating oil before test to minimize the deviation by absorption of oil into the membranes. All oil/water separation experiments were carried out at room temperature (20 °C) in a fume hood.

2.4. Characterizations

The morphology and structure of the porous substrates and SiO_2 nanoparticles were investigated by the field emission scanning electron microscope (FEI APREO SEM). All samples were sputter-coated with a 5 nm platinum/palladium layer before SEM tests. The compositions of the wipers and paper were examined by FT-IR spectroscopy (Thermo Nicolet Nexus FT-IR spectrometer) combined with production information. The water contact angle was measured by the CAM 200 contact-angle system (KSV Instruments Ltd., Helsinki, Finland) with 4 independent measurements. The water used for the contact angle measurement was supplied via a syringe with sessile droplets (~5 μL). The size distribution of SiO_2 particles was calculated by the N5 submicron particle size analyzer from Beckman Coulter.

3. Results and discussion

The wettability of the state-of-the-art advanced surfaces were mostly superhydrophobic or superhydrophilic as shown in Fig. 1. Superhydrophobic materials were designed as superoleophilic to remove oil from oil/water mixtures. (Cao et al., 2013; Zhou et al., 2013; Zhang et al., 2013b, c; Liu et al., 2013; Hsu et al., 2013; Crick et al., 2013; Wang et al., 2010; Arbatan et al., 2011; Wang and Lin, 2013; Zhang et al., 2013d; Qiang et al., 2018; Kang et al., 2019; Yuan et al., 2019) Superhydrophilic separation materials were designed to be either superoleophobic or under-water superoleophobic to remove water from oil (Xue et al., 2011; Kota et al., 2012; Zhu et al., 2013; Ge et al., 2018; Xie et al., 2019; Zhou et al., 2016; Zhu et al., 2017; Su et al., 2017; Liu et al., 2014b). The water contact angle of these advanced surfaces are distributed in two extreme ranges, θ > 140° or θ = 0° (as indicated in Fig. 1), which restricted the choice of materials in design separators in practise. In this work, by introducing the PTSLIPS, oil/water separators with high separation efficiencies and wide tailorable water contact angle range of 75.7° ~ 145.9° (Fig. 1) were achieved. Herein, the strategy of achieving high oil/water separation efficiency by PTSLIPS is not by realizing extremely high surface water contact angle for sliding the water away, but by implementing a unique absorbing-permeating mechanism for intrinsic water repellence and broadening the materials options for practical applications.

The SLIPS was known to possess low contact angle hysteresis that can enable water droplet sliding. (Wong et al., 2011) A successful oil/water separation SLIPS material relies on the correct selection of substrate, infused lubricant and oil to be separated based on wettability, as detailed discussion on interfacial energy of wetting systems provided in supplementary Section S1. One key deficiency of the conventional SLIPS used for oil/water separation is weak stability of the infused lubricant in the porous medium. It is quite common that the lubricant is easily washed away in practice. Although Wang et al. had formulated a polarity-based strategy for enhancing the stability of the lubricant in SLIPS (Wang et al., 2017). It is still highly challenging for separating oil species of higher polarity. A more efficient method for universal oil remove is needed. Based on our previous work, (Wang et al., 2019b) the new PTSLIPS dramatically increased the stability with solid-state lubricants that tightly adhered to the wall of the porous structure. Comparing with the conventional SLIPS materials, PTSLIPS has stable infused lubricants disregard the hydrophobicity of the porous wall (supplementary Figure S3c-d) (Wang et al., 2019b). In this work, the PTSLIPS samples were found with exceptional capacity to effectively filter toxic oil species from water, despite of their medium hydrophobic nature, through a novel absorbing-permeating mechanism as discussed in supplementary S2.

3.1. Oil/water separation ability of PTSLIPS

Based on the analysis and design principles in supplementary S1 and S2, PTSLIPS was fabricated and investigated. The PTSLIPS samples were infused with liquid lubricant, coconut oil, at 50 °C. Once cooled down to room temperature, the coconut oil solidified via phase

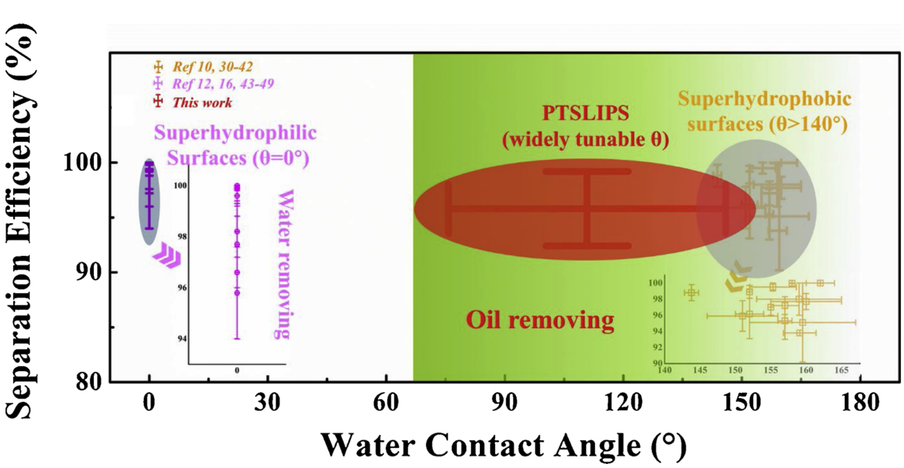

Fig. 1. A comparison between the state-of-the-art advanced oil/water separation surfaces and PTSLIPS. The water contact angle and oil/water separation efficiencies of various reported materials were listed and compared with PTSLIPS. The error bars in the figure represent the ranges of the water contact angle and separation efficiency in the references and the results in this work. The water contact angle range of PTSLIPS covers a wide regime that is uncovered by former studies.

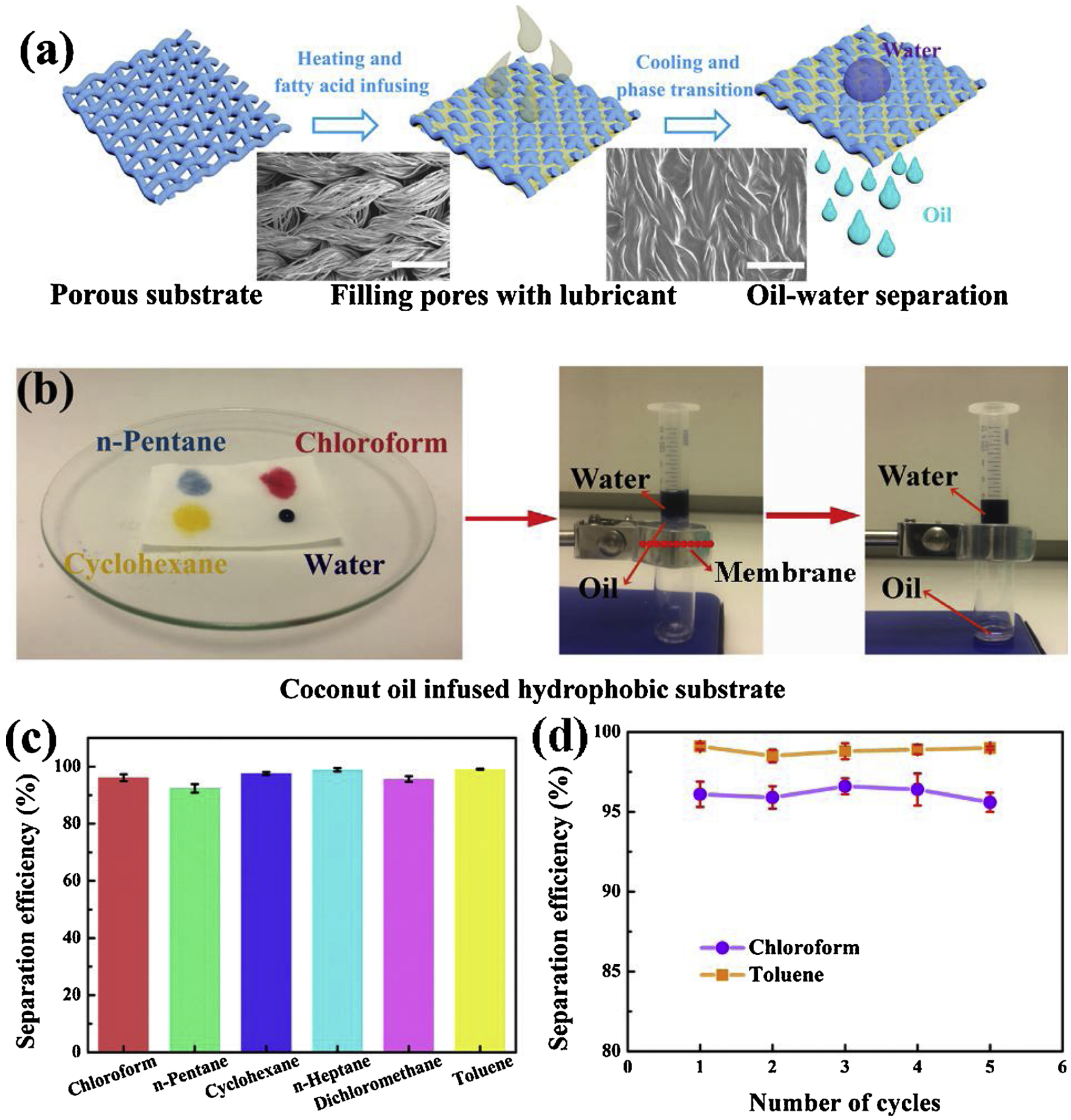

Fig. 2. Fabrication of PTSLIPS for oil/water separating. (a) Schematic of the fabrication process of PTSLIPS. The process involved heating and cooling steps for triggering phase transition of the infused lubricant. The morphology of the fabric before and after coconut oil infusing were given, with scale bars of 400 µm. (b) Wettability of oil and water on the PTSLIPS in air (left panel). Specifically, n-pentane was colored with Sudan black B, chloroform was colored with Oil red O, cyclohexane was colored with Sudan I and water was colored with methylene blue. The middle and the right panels were the filtration system and the process of oil/water separation, with chloroform and water in the system. This filtration system separated oil with higher density than water. For lighter oil species, a new filtration system was provided in supplementary Movie S1. (c) Separation efficiency of the coconut oil infused fabric of various oil/water mixtures (50 %, v/v = 10 ml/10 ml). (d) The separation efficiencies of the coconut oil infused fabric for separating chloroform and toluene from water in 5 cycles. The filtration system in (c) and (d) was shown in supplementary Movie S1. All the experiments in (b) ~ (d) were performed at 20 °C.

transition and was firmly locked in the porous structures. The morphologies of the samples (Fig. 2a) by SEM combined with FT-IR spectra (Figure S6) showed the differences before and after lubricant was infused. It was obvious (Fig. 2a) that pores in the fabric were totally filled by the solid lubricant. The identifying peaks of C=O stretching vibrations from ester at 1740 cm^{-1} and the C–H vibrations from aliphatic CH_2 at 2851 cm^{-1} and 2920 cm^{-1} were observed in FT-IR spectra as shown in supplementary Figure S6, which further confirmed the fatty acid composition in the PTSLIPS samples. (Zhang et al., 2013b)

The infused coconut oil as lubricant altered the wettability of the PTSLIPS samples. In the wettability tests (Fig. 2b), water droplets stably stayed on the top of PTSLIPS while oil droplets (n-pentane, chloroform and cyclohexane) spread and permeated into the membrane, which indicated the potential of PTSLIPS in oil/water separation. In the experiment in Fig. 2b, the PTSLIPS sample served as the filtration membrane at the bottom of a test tube was able to separate mixtures of oil and water. The separating process was extremely fast and efficient as shown in supplementary Movie. S1 with chloroform as an example. All the oil species, chloroform, n-pentane, cyclohexane, n-heptane, dichloromethane and toluene, were utilized to study the separation efficiency of the PTSLIPS. The oil contents before and after separation were monitored for quantifying the separation efficiencies through the Eq. (1). As shown in Fig. 2c, the separation efficiencies of different oil species fell in the range of 92.4 ~ 99.1 %, reaching the efficiency of prior-art interface materials for oil/water separation. (Wang et al., 2015; Li et al., 2018; Fan et al., 2015) It should be noted that there was no visible oil left in the water after the separation. The residual oil was in the PTSLIPS filters. Because the solid lubricant fully saturated the texture of the porous structure (Fig. 2a), the mechanism of oil/water separation was an absorbing-permeating process, meaning the oil was absorbed into the body of PTSLIPS first and then passed through after saturated. The cycling tests of PTSLIPS were carried out with chloroform-water and toluene-water mixtures. After 5 cycles, both filters maintained their separation efficiency (Fig. 2d). As the morphologies of the samples after 5 cycles shown in supplementary Figure S7, limited lubricants were washed away in the cyclic separation process. When compared with Fig. 2a, most of the pores were still filled by solid lubricant after the cyclic tests, which indicated the durability of PTSLIPS for oil/water separation. The solid lubricant in the pores was crucial for the robustness of the PTSLIPS.

As mentioned above that the poor durability of SLIPS for oil/water separation can be attribute to the unstable infused liquid lubricants. The PTSLIPS solved the deficiency of SLIPS with a solid lubricant phase and showed excellent oil/water separation efficiency with novel absorbing-permeating mechanism. As detailed discussion provided in supplementary S1 and S2, the enhanced lubricant layer can enable PTSLIPS for separating various oil species, regardless of the interfacial energy between different configurations.

3.2. Durability of PTSLIPS in harsh environment

Oil/water separation is commonly operated at demanding chemical environments. To test the durability of the as-prepared PTSLIPS in such environment, high concentration of salt, acidic and alkaline solutions were used. The PTSLIPS samples were immersed in sodium chloride solution (10 wt%), hydrochloric acid solution (25 %) and ammonia solution (25 %), respectively. The treated samples were cleaned with deionized water and dried before the following tests. As the morphologies of the sample after immersing for 120 h shown in Fig. 3a-c, abundant lubricant still strongly adhered in the pores of each fabric. It is interesting to note that the water contact angle on each sample showed a significant increase from 129.5° on the initial as-prepared membrane (Fig. 3d) to values higher than 140° (140.7° ~ 145.9°, Fig. 3e-g). These results can mostly be attributed to the change in the surface roughness. As proposed by the modified Young's equation from Wenzel (Wenzel, 1936; Miwa et al., 2000)

$$\cos\theta^* = r\cos\theta \tag{2}$$

where θ^* is the contact angle at a rough surface, θ is the contact angle at a smooth surface, and r is the roughness factor which is defined as the ratio of the actual area of a rough surface to the geometric projected area. As r is always lager than 1, any increase in the roughness of hydrophobic surfaces will result in higher contact angle. The higher water contact angle means higher hydrophobicity and better water repellence. Since the oil was separated by the absorbing-permeating mechanism, these samples can separate oil from water-based solution as long as there were lubricants in the pores. The oil removing ability of samples after immersed in harsh environment was characterized. As shown in the supplementary Figure S8, samples after immersing maintained their high oil removing efficiency around 94.6 ~ 98.4 %, suggesting the robust of PTSLIPS in harsh environment. In the case that the lubricant in the pores was etched away by the chemicals and only remained on the walls of the pores, the samples might still maintain their oil/water potential by direct oil permeating (detail explanation was given in the following parts) similar to other reported superhydrophobic and superoleophilic materials. (Feng et al., 2004; Gao et al., 2013; Cao et al., 2013; Zhang and Seeger, 2011) All these results suggested that the PTSLIPS can serve as a resilient candidate for oil/water separation in harsh chemical conditions.

3.3. Oil/water separation ability of PTSLIPSs from various substrates

In the PTSLIPS, solid lubricants block the pores and repel water, thus enable water repellence on various substrates (both hydrophobic and hydrophilic materials). (Wang et al., 2019b) It is possible to utilize the intrinsic advantages in fabricating different oil/water separators from various daily-life porous materials in an eco-friendly method, including hydrophilic substrates. Various daily accessible porous materials were taken to fabricate PTSLIPS, with their detailed compositions given in supplementary Figure S9. These porous materials had various pore size and pore structure as exhibited in Fig. 4a–d. All samples were infused with coconut oil inside their pores (Fig. 4e–h). Different to the hydrophobic substrates shown above, all these daily materials were hydrophilic, with water contact angles in the range of 75.7° ~ 88.1°. Despite the hydrophilicity, these samples repelled water droplets and at the same time efficiently absorbed oil droplets (Fig. 4i–l). In the filtration experiments showed in Fig. 4m–p, the chloroform was successfully separated from water by various samples. These results indicate the design of PTSLIPS can be adapted to a large family of materials for oil/water separation.

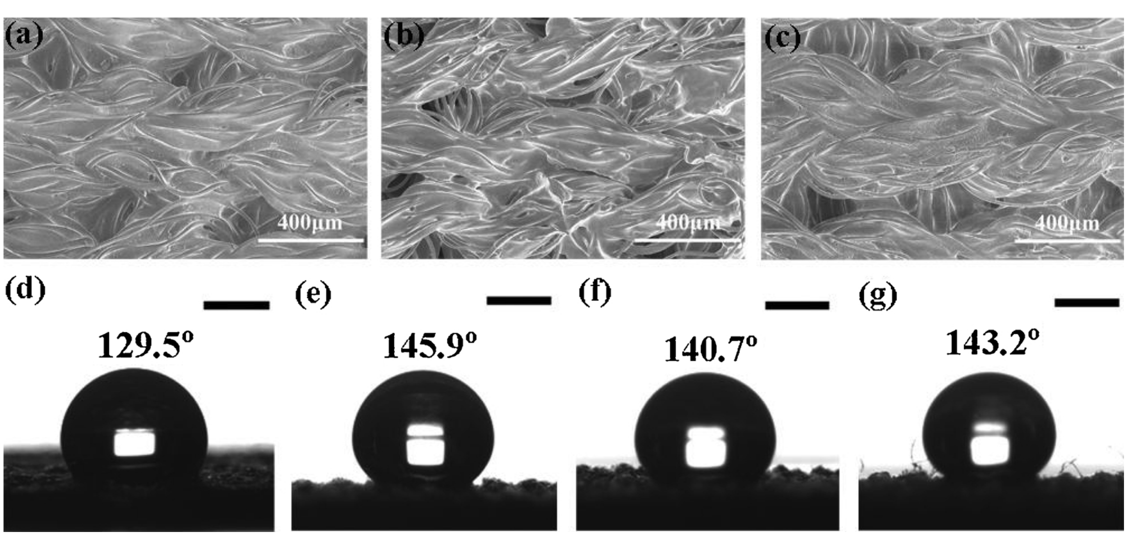

Fig. 3. Surface morphologies of the PTSLIPS samples before and after immersed in various solutions and the corresponding water contact angles. (a) ~ (c) Samples immersed in 10 wt% sodium chloride solution, 25 % hydrochloric acid solution, and 25 % ammonia solution for 120 h, respectively. (d) Water contact angle of as-prepared PTSLIPS, the scale bar was 1 mm. (e) ~ (g) Water contact angle of PTSLIPS samples from (a) ~ (c), respectively, with scale bars of 1 mm in each figure. The water droplet was 5 μl in volume in each test (same for the tests below). All the experiments were carried out at room temperature (20 ℃).

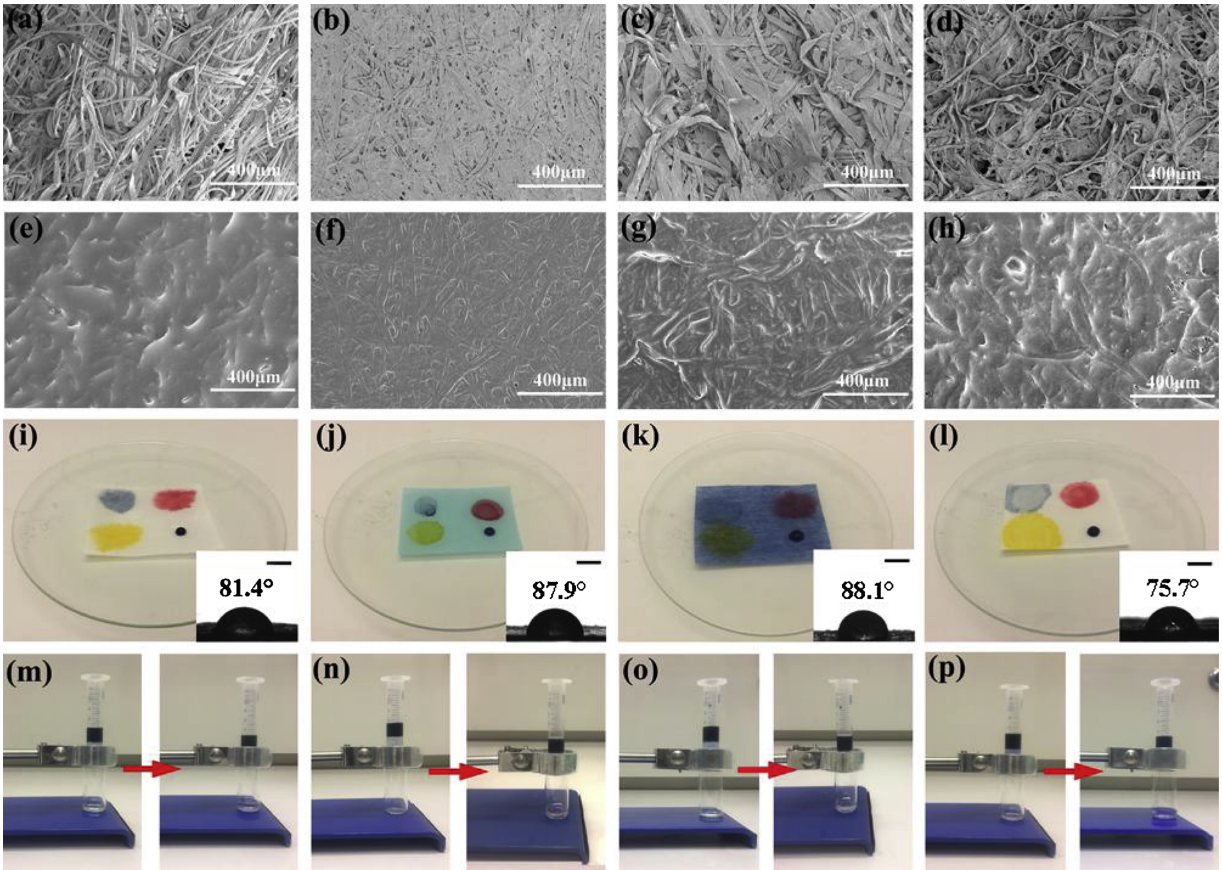

Fig. 4. Surface morphologies, wettability and oil/water separation ability of PTSLIPS samples from various daily porous substrates. (a)–(d) The morphologies and pore structures of substrates of white wiper, green paper, blue wiper and filter paper, respectively. (e)–(h) The corresponding morphologies of the samples in (a)–(d), respectively, after infused with solid coconut oil. (i)–(l) Wettability of the PTSLIPS sample from (e) ~ (h) by oil and water. The colours and types of oil used were the same as these in Fig. 2b. Water contact angle of each sample was shown as insets, with a scale bar of 1 mm. All the samples were hydrophilic with water contact angle lower than 90°. (m)–(p) The filtration systems used and the oil/water separation using corresponding samples from (e)–(h), respectively. The oil component was chloroform. All the experiments were carried out at room temperature (20 °C). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

3.4. Oil/water separation by absorption using PTSLIPS

Besides filtration, another important oil/water separation method is absorption. (Ma et al., 2016) The oil absorption performance of PTSLIPS was also evaluated, as shown in Fig. 5. Two individual sponges with different pore structures were infused with coconut oil following the PTSLIPS fabricating protocol shown above. As wettability tests shown in Fig. 5a and c, the two samples repelled water and at the same time permeated oil components. The two new PTSLIPS samples were then applied for oil absorption in mixtures of cyclohexane and water, both of which separated cyclohexane from water in an efficient manner (supplementary Movie S2). Specially, the fabricating strategy of PTSLIPS can be applied in almost arbitrary porous sponges. As indicated in supplementary Figure S10, the PTSLIPS by infusing coconut oil in a piece of daily bread also showed oil absorption ability.

The self-repairing property of PTSLIPS has been proved in former study. (Wang et al., 2019b) The PTSLIPS can repair not only surface but also bulk damage, the potential of which can be utilized for assembling PTSLIPS from small pieces materials. As shown in Fig. 5e, separate small pieces of wipers and paper were moulded into a PTSLIPS block by thermal treatment under pressure. The liquid lubricant in the experiment flowed into the physical voids by surface-energy-driven-capillary force and spontaneously refilled the gaps. (Ishino et al., 2007) The cooling triggered the reversed phase transition and the solid lubricant adhered these pieces together. The assembled sample showed similar oil/water separation ability as the two PTSLIPS sponges above. The oil in the mixture was successfully removed by the assembled sponge through absorption (Fig. 5f).

3.5. Understanding the mechanisms of oil/water separation in PTSLIPS

The lubricants in the as-prepared PTSLIPS are slowly consumed in many cycles of oil/water separation process. As detail shown in Fig. 6a, the PTSLIPS samples experienced three sequential stages before losing their separation ability, namely oil absorbing-permeating (stage 1), transition stage (stage 2), and oil preferential wetting stage (stage 3). The first and second stages had been confirmed in the sections above (Figs. 2 and 3). The stage 3, perforated holes in the substrate, was observed in other relevant interface materials. (Feng et al., 2004; Gao et al., 2013; Cao et al., 2013; Zhang and Seeger, 2011) To further verify the oil/water separation mechanism change in PTSLIPS membranes, steel mesh was coated with coconut oil and further investigated. The original steel mesh had pore size of ~150 μm without water repellence (supplementary Figure S12 and supplementary Movie S3). After oil infusing, as shown in Fig. 6b and c, both morphology and wettability of the steel mesh differed. The morphologies of the steel mesh in Fig. 6b and c corresponded to the stage 1 and 3, respectively. Importantly, the lubricant partly coated steel mesh possessed even better water repellence with higher water contact angle (137.5°) than the fully immersed steel mesh (98.3°), owing to the enhanced surface roughness. (Wenzel, 1936; Miwa et al., 2000) The contact angle agreed well with the proposed stages in Fig. 6a. The excellent water repellence of partly

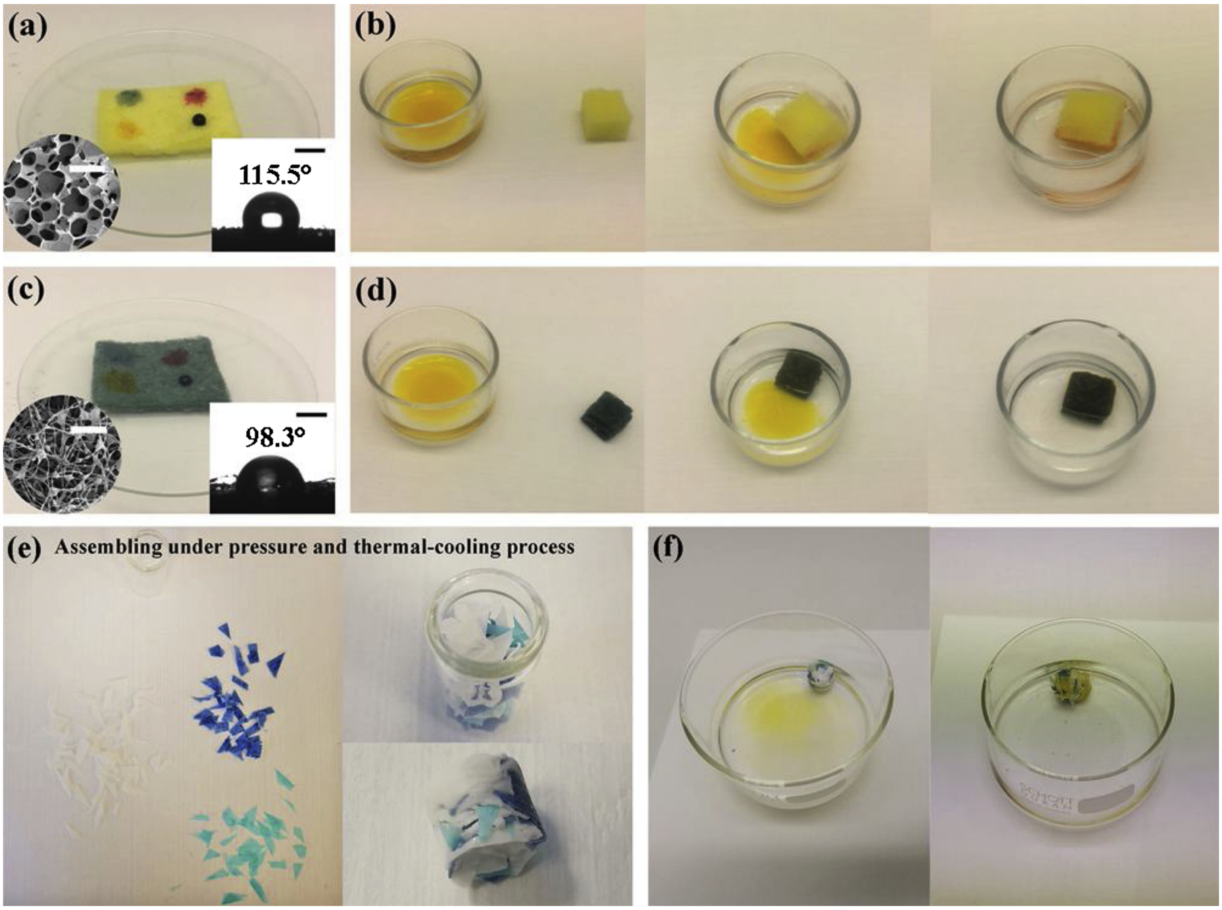

Fig. 5. PTSLIPS sponges from various substrates. (a), (c) Two PTSLIPS sponges with excellent water repellence and oil absorbability. The colours and types of oil used were the same as Fig. 2b. The insets showed the porous structures before infused with lubricant and water contact angle. The scale bar was 1 mm. (b), (d) The oil/water separation abilities of samples from (a), (c). The oil was cyclohexane. All the experiments were carried out at room temperature (20 °C). (e) Assembling PTSLIPS from small pieces to a sponge block. The small pieces of materials were from the samples in Figs. 2b and 4 j–k, coconut oil infused fabric (white), coconut oil infused blue wiper (blue) and coconut oil infused green paper (green), respectively. (f) The oil absorption property of assembled sponge block. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

coated steel mesh was shown in supplementary movie S4. For the fully coated mesh (Fig. 6b), oil was separated through absorbing-permeating mechanism as discussed above. In contrast, oil was separated by partly coated steel mesh through wettability difference, which shared similar separation mechanism as superhydrophobic and superoleophilic materials. (Feng et al., 2004; Gao et al., 2013; Cao et al., 2013; Zhang and Seeger, 2011) Fig. 6d showed the ability of partly coated steel mesh in oil/water separation and proved the proposed mechanism. With the oi/water separation mechanisms in PTSLIPS, one can predict a wider water contact angle distribution of this strategy.

4. Conclusions

This work implemented a new oil/water separation strategy and fabricated PTSLIPS which can utilize medium hydrophobic and even relatively hydrophilic materials for exceptional oil/water separation performance. The PTSLIPS can filtrate various oil/water mixtures with efficiency among 92.4 ~ 99.1 %. The samples after immersing in high concentration salt (10 wt% NaCl), acid (25 % HCl), alkaline (25 % $NH_3{\cdot}H2O$) solutions for 120 h demonstrated improved water repellence and maintained excellent oil removing efficiency, which verified their durability in harsh chemical environments. The strategy of PTSLIPS was further proved to be widely adaptable on membranes with various porous structures and chemical components (both hydrophobic and hydrophilic materials). The phase transition made it possible of stabilize the lubricants in porous structure with wide pore size distributions and various porous morphologies. All the PTSLIPS samples from different wipers and papers successfully repelled water and permeated oil. Moreover, by infusing coconut oil into porous sponges, the obtained PTSLIPS sponges separated oil from water by direct absorption, which broadened the applicability of this strategy. Numerous porous sponges from daily life (like bread) could be easily modified through this method and possessed great oil/water oil removing capacity. The PTSLIPS also possessed self-repairing property, which allowed assemble PTSLIPS from pieces to a block. By the combination of oil absorbing-permeating mechanism and oil preferential wetting mechanism in oil/water separation, PTSLIPS greatly broaden the boundary of materials chosen. The water contact angle of materials used in this research had a wide distribution between 75.7° ~ 145.9°, which covered the ranges of both hydrophobic and hydrophilic materials. Therefore, the design of PTSLIPS is a feasible and widely adaptable method to achieve oil/water separators from various porous substrates, and of course, an eco-friendly fabrication method.

In summary, the design of PTSLIPS enabled materials that are medium hydrophobic and even relatively hydrophilic for oil/water separation, which greatly broaden the domain of materials options for creating oil/water separators. It is important to note that the PTSLIPS should be used at room temperature (or the temperature lower than melting point of lubricants used) for longer durability, which opens room for testing and optimization of the materials. New strategy of utilizing PTSLIPS for oil/water separation at higher temperature is a topic of importance for future study.

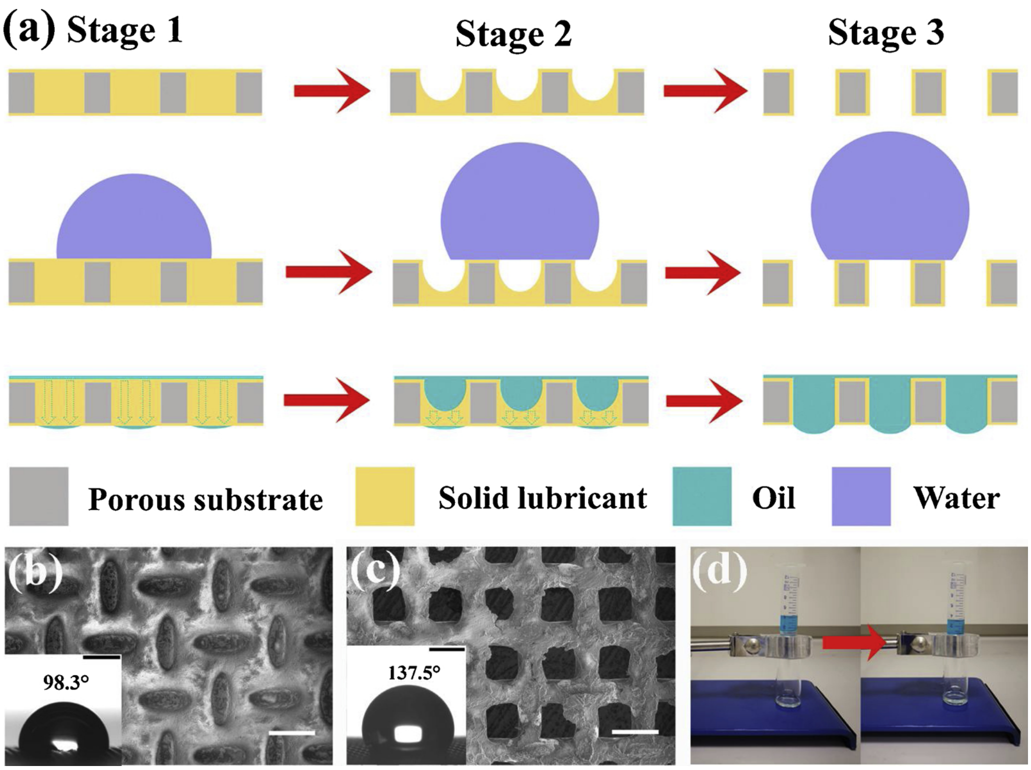

Fig. 6. The mechanisms of oil/water separation in PTSLIPS. (a) Schematic showing the changes of PTSLIPS in long term oil/water separation. Three stages were observed in the process. (b) SEM morphologies of steel mesh after fully infused by lubricant, which showed the stage 1. (d) SEM morphologies of lubricant partly coated steel mesh, which showed the stage 3. The scale bars are 200 μm in (b) and (c). The insets in (b) and (c) showed the water contact angle on the sample, the scale bars are 1 mm. The water contact angle of as received mesh was 0˙. (d) The oil was successfully removed from the mixture with the filtration system used in the process. The oil was chloroform, and the water was colored with methylene blue. All the experiments were carried out at room temperature (20 ℃).

CRediT authorship contribution statement

Feng Wang: Conceptualization, Methodology, Writing - original draft, Methodology, Validation, Formal analysis, Visualization, Investigation, Data curation. **Sihai Luo:** Resources, Investigation, Data curation, Writing - review & editing. **Senbo Xiao:** Writing - review & editing. **Wenjing Zhang:** Resources, Investigation. **Yizhi Zhuo:** Resources, Investigation. **Jianying He:** Conceptualization, Resources, Supervision, Writing - review & editing. **Zhiliang Zhang:** Conceptualization, Resources, Supervision, Writing - review & editing, Project administration.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jhazmat.2020.122176.

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