Polydopamine-based hybrid materials with tailored surface wettability for immiscible liquid separation

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**NANYANG
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SINGAPORE

**Polydopamine-Based Hybrid Materials with Tailored Surface
Wettability for Immiscible Liquid Separation**

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Interdisciplinary Graduate School

Nanyang Environmental and Water Research Institute

2019

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Wettability for Immiscible Liquid Separation**

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Interdisciplinary Graduate School

Nanyang Environmental and Water Research Institute

A thesis submitted to Nanyang Technological University

in partial fulfilment of the requirement for the degree of

Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarized materials, and has not been submitted for a higher degree to any other University or Institution.

May 06th, 2019

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Date

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Van Cuong Mai

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

May 06th, 2019

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Date

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Assoc. Prof. Hongwei Duan

Authorship Attribution Statement

This thesis contains materials from 3 manuscripts that will be submitted in peer-reviewed journals in which I am listed as an author.

Chapter 3 is from the manuscript: Van Cuong Mai, Paramita Das, Jiajing Zhou, Teik Thye Lim, and Hongwei Duan, Mussel-Inspired Dual-Superlyophobic Biomass Membranes for Selective Oil/water Separation.

The contribution of the co-authors are as follows:

- I and Prof. Hongwei Duan designed the study together. I performed the laboratory works at the School of Chemical and Biomedical Engineering and Nanyang Environmental and Water Research Institute.
- Dr. Jiajing Zhou assisted in the drawing of the general scheme.
- Dr. Paramita Das and Prof. Teik Thye Lim discussed the data and comments on the manuscript.
- I wrote the draft of the manuscript. The manuscript was revised together by Dr. Paramita Das, Prof. Teik Thye Lim and Prof. Hongwei Duan.

Chapter 4 is from the manuscript: Van Cuong Mai, Desmon Lim, Paramita Das, Shuai Hou, Teik Thye Lim, and Hongwei Duan, Polydopamine-mediated Superlyophobic Coating for Efficient Separation of Immiscible Liquids.

The contribution of the co-authors are as follows:

- I and Prof. Hongwei Duan designed the study together. I performed the all laboratory works at the School of Chemical and Biomedical Engineering.
- Desmon Lim assisted in the initial steps of the fabrication of superlyophobic paper.
- Dr. Paramita Das and Prof. Teik Thye Lim discussed the data and comments on the manuscript.
- Dr. Shuai Hou assisted in the drawing of the general scheme.
- I wrote the draft of the manuscript. The manuscript was revised together by Prof. Teik Thye Lim and Prof. Hongwei Duan.

Chapter 5 is from the manuscript: Van Cuong Mai, Paramita Das, Goei Ronn, Jiajing Zhou, Zheng Fang, Teik Thye Lim, and Hongwei Duan, Hierarchical Graphene-Metal Organic Frameworks: from Superamphiphobic Coatings to Membranes for Separating Immiscible Liquids.

The contribution of the co-authors are as follows:

- I and Prof. Hongwei Duan designed the study together. I performed the all laboratory works at the School of Chemical and Biomedical Engineering.
- Dr. Goei Ronn assisted in the characterization of X-ray photoelectron spectroscopy.
- Dr. Jiajing Zhou assisted in the drawing of the general scheme.
- Dr. Zheng Fang assisted in the preparation of graphene oxide.
- Dr. Paramita Das and Prof. Teik Thye Lim comments on the manuscript.

- I wrote the draft of the manuscript. The manuscript was revised together by Dr. Paramita Das and Prof. Hongwei Duan.

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List of Abbreviations

2D	Two dimensional
3D	Three dimensional
Au	Gold
AuPBs	Gold plasmonic black bodies
ATR-FTIR	Attenuated total reflectance-fourier-transform infrared
CA	Contact angle
CAH	Contact angle hysteresis
CA _o	Oil contact angle
CA _{o/w}	Oil contact angle underwater
CA _w (CA _{w/a})	Water contact angle (in air)
CA _{w/o}	Water contact angle underoil
CF	Chloroform
CNF	carbon nanofiber
CTC	Carbon tetrachloride
DA	Dopamine
DCM	Dichloromethane
DEE	Diethyl ether
DEG	Diethylene glycol
DI	Deionized
EG	Ethylene glycol
GLY	Glycerol
FM	Formamide
FSMS	Fluoro-silicone microsheet
FSL	Fluoro-silicone layer
FTIR	Fourier-transform infrared
GO	Graphene oxide
HDC	n-hexadecane
HL	Hydrophilic
HEX	n-hexane
KP	Kapok
IWT	Intrinsic Wetting Threshold
ICA	Intrinsic contact angle
IL	Ionic liquid
LBL	Layer-by-layer
LCST	Lower critical solution temperature
MAPs	Mussel adhesive proteins
MeOH	Methanol
MOFs	Metal organic frameworks
MTS	Methyl trichlorosilane
Ni	Nikel
ODTS	octadecyl trichlorosilane
OTS	octyl trichlorosilane
OSHB	Underoil superhydrophobic

PDA	Polydopamine
PDDA	Poly(diallyldimethylammonium chloride)
PDMS	Polydimethylsiloxane
PEG-SH	Thiol-polyethylene glycol
PEMs	Polyelectrolyte layer-by-layer multilayer
PEI	Polyethyleneimine
PFDTs	1H,1H,2H,2H-perfluorododecyl trichlorosilane
PFOTS	1H,1H,2H,2H-perfluorooctyl trichlorosilane
PHCs	Petroleum hydrocarbons
PNIPAAm	Poly(N-isopropylacryamide)
PSS	Poly(styrenesulfonate)
PS	Polystyrene
PTE	Petroleum ether
PVDF	Polyvinylidene
PUF-RC	Poly(ureaformaldehyde)
SA	Sliding angle
SE	Surface energy
SEM	Scanning electron microscope
SMS	Silicone microsheet
SPI	Sodium periodate
ST	Surface tension
STY	Styrene
TMB	1,3,5-trimethylbenzene
TOL	Toluene
UIO-66	Zirconium 1,4-dicarboxybenzene MOF
RO	Radial outward
XYL	o-xylene
ZIF-8	Zeolitic imidazolate framework
WSOB	Underwater superoleophobic

Caption of Figures

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Figure 5.8. SEM images (top) and schematic illustration (bottom) for the curved three-phase contact lines with side view and top view. Droplet deposited on the (a) thin ($D_1=1/\kappa_1$) and (b) thick microscale pore coating surface ($D_2=1/\kappa_2$).

Figure 5.9. SEM image of (a) bare Ni foam, (b) silanized Ni foam, and (c) silanized GH-PDA-Z₄ coated Ni foam. A droplet of 3 μ L formamide on top of the respective membranes is shown as insets in (a - c). (d) static contact angle of different surface tension liquid droplets on surface of bare Ni foam, silanized Ni foam and silanized GH-PDA-Z₄ coated Ni foam, respectively.

Figure 5.10. (a) separation efficiency of mixture between different polar solvents and carbon tetrachloride. (b) and (c) separation efficiency and calculated flux through the membrane of mixture between formamide and nonpolar solvents. d) re-generation and filtration flux of membrane using formamide and chloroform after 20 cycles.

Figure 5.11. Optical images represent separation of formamide/chloroform mixture with a) bare Ni form, b) silanized GH-PDA-Z₂ coated Ni form and c) silanized GH-PDA-Z₄ coated Ni form. Formamide is colored by methylene blue.

Figure 5.12. Optical photographs of separation of chloroform/formamide mixture using silanized Ni foam. First, formamide stays on top and chloroform passes through the membrane. However, when more liquid comes, a part of formamide also penetrates through the membrane due to intrusion pressure.

Figure 5.13. Optical photographs of separation of n-hexane/formamide mixture using silanized GH-PDA-Z₄ coated Ni foam. n-hexane quickly passes through the membrane while formamide stays on top.

Figure 5.14. Optical photographs of separation of n-hexane/formamide mixture using silanized GH-PDA-Z₂ coated Ni foam. n-hexane quickly passes through the membrane while formamide stays on top.

Summary

Polydopamine-Based Hybrid Materials with Tailored Surface Wettability for Immiscible Liquid Separation

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My thesis work focuses on employing the properties of wettable materials to separate immiscible liquids, including the separations of oil/water and immiscible organic liquids. We take advantages of polydopamine (PDA) such as amphiphilicity, adhesion and chemical versatility to fabricate novel wettable materials. PDA is a mussel-inspired polymer that is formed by the self-polymerization of its monomer, dopamine under the presence of oxidizing agents. Herein, PDA acts as both surface coating and intermediate layer for designing novel materials with tailored wettability, which selectively allow the penetration of liquids.

First, I deposit PDA nanoparticles on surface of cotton and kapok biomass fibers to fabricate dual-superlyophobic membranes. The formation of PDA nanoparticles is induced by the introduction of a strong oxidizing agent such as NaIO_4 in acetate buffer ($\text{pH} = 5$). Compared to the conformal layer, the formation of PDA nanoparticles enhances the surface roughness of the biomass fiber. As a

result, when the membranes are wetted by water they can effectively repel oils. On the other hand, when the membranes are wetted by oils they can effectively repel water. The interesting wetting behavior of the membranes allows the selective penetration of water or oil, leading to successful separation of oil and water. More importantly, the as-prepared membranes show the great regeneration with high flux and high efficiency compared to previous reported articles.

Second, I employ PDA nanoparticles as the template to grow silicone micro-sheets (SMSs) derived from hydrolysis of octadecyltrichloro silane to fabricate a broad range of superlyophobic materials. It suggests that superlyophobic materials repel other high surface tension liquids such as formamide and diethylene glycol more effectively than superhydrophobic materials. The key point here is the mass loading of PDA on surface of pristine materials decides the morphology of the SMSs. The larger mass loading of PDA nanoparticles generates the lath-like structure of SMSs, leading the increase in surface roughness. The more air fraction encapsulated into the rough surface enhances the repellency of the materials towards high surface tension liquids; while the liquids with surface tension lower than 30 mN/m penetrates quickly. This interesting phenomenon is true with a broad range of pristine materials, including 2D and 3D structure. As a result, the as-prepared materials are then applied to separate immiscible liquids by both absorption and membrane filtration.

Finally, the self-polymerization of dopamine reduces and functionalizes graphene oxide, forming GH-PDA porous particles with assistance of ionic liquids. Unlike the bulk structure of GH-PDA with cylindrical shape, the porous

GH-PDA particles are dispersed well and stable under a mid-sonication. ZIF-8 nanocrystals are grown on to modulate pore sizes of porous graphene. The increasing amount of ZIF-8 narrows the wall thickness of the GH-PDA composite. After the surface modification with 1H,1H,2H,2H perfluorodecyltriethoxysilane, the GH-PDA-ZIF-8 composite coating results the transition from superamphiphobicity to omniphobicity; while air fraction diminishes from 0.97 to 0.8. The tailorable wettability of the composite coating allows for the penetration of certain liquids. Ni foam coated with these tailored wettability graphene composite can effectively separate immiscible liquids at different levels.

Chapter 1. Introduction

1.1. Problem Statement

Purification and separation of mixtures of solvents or liquid reactants which are commonly used in various industrial processes, such as petrochemical, food, texturing or medicinal industries are extremely necessary. The purification process ensures a harmless discharge and recovery of liquids, as well as products.^{1, 2} By far, many strategies have been developed to separate the liquid mixtures, particularly oil-water separation, by combining biological, chemical and physical approaches. In spite of displaying advantages those strategies, including centrifugation,³ solvent extraction (including distillation),⁴ forth flotation,⁵ solidification,⁶ , ultrasonic irradiation,⁷ land farming,⁸ bio slurry,⁹ pyrolysis,¹⁰ and microwave irradiation¹¹ have a number of drawbacks, among which high energy consumption and long processing time are very common. In addition, low flux and low efficiency were also reported to reduce the economic benefits and feasibility.^{12, 13, 14, 15, 16, 17, 18} The detailed comparison of those commercial methods, including both advantages and disadvantages of the commercial methods is shown below in table 1.1, which is summarized according to A.F. Ismail et al.¹⁹

Separation method	Advantages	Disadvantages	Ref
Centrifugation	The process is simple, no solvent required	The process requires a large amount of energy, less economic benefit and it is difficult to settle down small size molecules/particles	[3]
Solvent extraction	The process is very fast and efficient	High cost and no environmental friendliness	[4]
Forth flotation	The process requires less energy and is easy to apply	Highly viscous oil cannot be removed using this method	[5]

Stabilization/solidification	The process is fast and cost effectiveness, able to stabilize petroleum hydrocarbons (PHCs)	Hardly to recycle and the process is not effective	[6]
Ultrasonic irradiation	The treatment is fast and effective, no chemicals required	High cost for equipment	[7]
Land farming	The treatment is low cost, available for large scale capacity and no heavy maintenance required	The oil leakage causes pollution of sand and ground water	[8]
Bio slurry	The process is the fastest approach for degradation and PHCs removal	The treatment takes high cost for small scale application	[9]
Pyrolysis	The process is fast, effective and able for large scale treatment	High entrance fee, high cost for maintenance and operation	[10]
Microwave irradiation	The process is fast, efficient and no chemicals required	Special equipment design, high cost and not applicable for large scale	[11]

Table1.1. The comparison between various methods for oily water purification. The table is summarized according to A.F.Ismail et al.'s report.

Recently, superwetting materials have received considerable attention. The surface wettability of these materials allows for controlling repellency or penetration of liquids by mean of tailored interaction with solid interface, thus find widespread uses in various applications, such as anti-corrosion, self-cleaning, water harvesting, anti-icing, anti-fogging, textile, liquid-liquid separation, etc. Filtration membrane with tailored surface wettability has been extensively applied for separation of oil and water with high flux, low energy required and cost-effectiveness.^{20, 21, 22, 23} The hydrophilic (superhydrophilic) nature of membranes allow water to pass through while the hydrophobic (superhydrophobic) property repels water and allows oil to penetrate, thus successfully separating oil/water mixture. Over the past decade, various types of membranes, including metal meshes,^{24, 25} porous polymeric membranes,²⁶ electrospinning fiber membranes,²⁷ etc. have been fabricated with excellent oil/water separation efficiency. Notably, the application of membrane for

separation of organic immiscible liquids is still rarely explored. Owing to high surface tension ($ST = 72.7 \text{ mN/m}$), water, therefore, can be easily removed from mixtures with oils using either (super)hydrophobic or (super)hydrophilic membranes. The key factor here is the opposite surface wettability of membranes toward water or oils. However, it is more difficult to separate immiscible organic liquids. The closer surface tension difference between organic liquids (and obviously much lower ST than water) causes oleophilicity to almost any surfaces, which make the membranes unable to separate small difference surface tension liquids with common hydrophobic membranes. Generally, to successfully separate immiscible organic liquids, it is undoubtedly required membranes that show oleophobicity to one liquid while displaying oleophilicity to the other one in the mixture. Although several studies have been reported for the application of wetting materials to separate immiscible liquids as well as selective oil water separation, there are still challenges that may obstruct the practical application. For example, many researches still employ expensive raw materials or complicated synthesis route. In order to approach practical application, it is highly necessary to develop special wetting/antiwetting materials with low cost and simple method.

1.2. Typical (Super)wetting Structures for Phase Separation

Wetting and anti-wetting behaviors of solid surfaces reveals how liquids and solids interact in different medium, for instance in air or underoil or underwater. The chemical composition of solid surfaces determines intermolecular forces at the interfaces of the solid, liquid and air, while the surface morphology is also an

important factor.²⁸ The synergy of surface chemistry and surface morphology have created various wetting/superwetting states as well as anti-wetting/super anti-wetting states. Within the scope of this thesis, several wetting/anti-wetting states, such as hydrophilic/superhydrophilic, hydrophobic/superhydrophobic, superhydrophobic-superoleophobic (in air) and superhydrophobic (underoil)-superoleophobic (underwater), which determine the separation ability of immiscible liquids of the corresponding membranes are discussed in more detail. Figure 1.1 shows the limit of contact angles (CAs) of these states.

Figure 1.1. Behavior of water and oil on some typical wetting surfaces. (a): hydrophilic/superhydrophilic surface. (b) hydrophobic/superhydrophobic surface. (c) Superamphiphobic surface and (d) dual-superlyophobic surface.

1.2.1. Hydrophilic/Superhydrophilic Surfaces

In general, a surface is considered hydrophilic (HL) when the water contact angle (CA_w) is below 90° and superhydrophilic (SHL) when the water droplet goes below 5° or 10° (Figure 1.1-a).²⁹ The transition from hydrophilicity to

superhydrophilicity happens when the surface roughness is increased or the surface is coated by high surface energy layers.^{30, 31} The high surface energy coating enhances hydrogen bonding with water. High surface roughness, on the other hand, provides a space for a stable trapped water layer. That means water molecules can cover the entire surface of SHL structure with a thin, sticky layer which possibly prevents the penetration of oil droplets because the trapped water molecules can effectively repel immiscible oils. As a result, a superhydrophilic surface is also possible to display superoleophobic behavior underwater in which the oil contact angle (CA_o) is higher than 150° (WSOB-Figure 1.2-a).³²

As mentioned, high surface tension surfaces are relevant for better hydrophilicity. Therefore, the oleophilicity, penetration ability of oil, is also enhanced due to the lower surface tension of oils compared to water. However, if the surface coating, such as block copolymers, contains both hydrophilic components and oleophobic components, oil droplets can be retained while water still penetrates through the structure (Figure 1.2-b).^{33, 34} Previous accepted mechanism of superhydrophilic/superoleophobic surface states that the rearrangement of hydrophilic component and oleophobic component at initial moment of water contacting results in the penetration of water droplet. Particularly, the rearrangement causes the location of hydrophilic component at solid/liquid interface, inducing interaction between water droplet and solid interface. This rearrangement, however, does not happen when oil contacts to a solid. With the synergistic effect of morphology, the time dependent water penetration is observed, while oil is still retained. Recently, Pan et. al. explained the principle of this wetting state based on dispersion (γ^d) and polarity (γ^p) force

components of surface tension.³³ The intrinsic contact angles of oil and water are then calculated by following equations:

$$\cos \theta_o = (2\sqrt{\gamma_s^d} / \sqrt{\gamma_o}) - 1; \cos \theta_w = ((2\sqrt{\gamma_s^d \gamma_w^d} + 2\sqrt{\gamma_s^p \gamma_w^p}) / \sqrt{\gamma_w}) - 1$$

With a solid surface, a smaller value of γ^d is necessary for higher oil contact angle and a larger value of γ^p is necessary for lower water contact angle. Because these two components can be treated separately, the coating layer should have low γ^d and high γ^p for sufficient repellency of oil but not water. For example, γ^d of the solid surface is 3.04 mN/m and γ^p is 80.2 mN/m after modification with pentadecafluorooctanoic acid. As a result, water contact angle is nearly 0° and hexadecane contact angle is approximately 160° (also Figure 1.2-b).

Figure 1.2. The wettability of water and oil on surface of (a) different superhydrophilic/underwater superoleophobic materials and (b) superhydrophilic/superoleophobic (in air) material. (a) Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA. (b) Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.

The fabrication of HL/SHL surfaces mainly relies on the synergistic effect between high surface energy coating and multiscale surface roughness. Over the past decade, the rapid increase in published reports about HL/SHL structures inspired from wetting behavior of natural creators, such as fish skins, clam shells,

mussels, etc, from which many methods have also developed. Below are some typical methods that are most commonly applied.

Sol-gel synthesis. This method is one of the most commonly applicable strategy. It has been widely used to synthesis inorganic coatings such as SiO₂ nanoparticles or TiO₂ nanoparticles. The method involves in the conversion of monomers to colloidal particles. The composite of SiO₂ and TiO₂ is effective to fabricate long-term stable photo-induced superhydrophilic surface.³⁵ Water droplet is observed to penetrate quickly after UV-irradiation, revealing a superhydrophilic surface.

Electrochemical process. This method includes electrochemical deposition anodization, galvanic cell reaction, and electrochemical polymerization.³⁶ Through this method, surface coatings high roughness are easily obtained. Jin and co-workers introduced superhydrophilic Cu₃(PO₄)₂ nanosheets wrapped copper mesh by applying 1V threshold potential for 30 min on the pristine mesh immersed in precursor solutions.³⁷ The high surface energy and high roughness of the nanosheets induce superhydrophilicity with critical low oil adhesion force underwater. The as-prepared mesh is then applied to separate water and crude oil with extremely high efficiency.

Layer-by-layer (LBL) assembly. This method is widely applied to fabricate hydrophilic/superhydrophilic thin films. The thickness of the films is controlled by the number of deposited layers which are alternatively coated via various non-covalent interactions. The superhydrophilicity can be induced by enhancing surface roughness with micro/nanoparticles or with zwitterionic coating

structures. Wang and co-workers recently developed polyelectrolyte LBL multilayer (PEMs) coating that displays highly hydrophilicity and underwater superoleophobicity.³⁸ PDDA (poly(diallyldimethylammonium chloride)) and PSS (poly(styrenesulfonate)) were alternatively coated on surface of stainless steel mesh and made it possible to separate oil and water. Other methods such as chemical deposition, electrospinning, plasma treatment, phase transfer, etc. are also effective to fabricate hydrophilic/superhydrophilic materials.³⁶

1.2.2. Hydrophobic/Superhydrophobic and Superoleophilic Surfaces

In contrast to the hydrophilic/superhydrophilic, a surface is called hydrophobic when the CA_w is above 90° and superhydrophobic when the CA_w is higher than 150° (Figure 1.1-b). Indeed, the term superhydrophobic was first introduced by Reick in 1976 when the author described that water stays with the spherical shape on the hydrophobic fumed silicon dioxide.²⁹ However, the research on superhydrophobic materials was started in 1907 by Ollivier, and in 1923 by Coghill and Anderson.²⁸ Ollivier reported the observation of spherical shape of water droplet on surface of soot, lycopodium powder, and arsenic trioxide while Coghill and Anderson reported a $CA = 160^\circ$ of water on rough galena surfaces covered by stearic acid. The observation and further characterizations of natural creators is an interesting way to understand superhydrophobicity. For example, the surface analysis of lotus leaf, butterfly wing, gecko foot or mosquito eye reveals that the hierarchical structure and hydrophobic waxy layer induce the superhydrophobicity, helping these plants and animal to have self-cleaning and anti-fogging ability. Consequently, other researchers, inspired by these natural anti-wetting properties, investigated the

dependence of superhydrophobicity to surface chemistry and surface morphology. The conclusion after a hundred reports is that low surface energy is required for hydrophobicity and the high roughness is needed to convert from hydrophobicity to superhydrophobicity. Generally, a normal superhydrophobic surface usually behaves superoleophilicity. It means an oil droplet can easily wet the superhydrophobic surface because of a lower surface tension of oils ($\sim 20\text{--}60$ mN/m) compared to water (~ 72 mN/m).^{28, 39} The low surface tension oils can either pass through the superhydrophobic 2D membranes or quickly be absorbed into 3D sorbents while water is retained and purified (Figure 1.3).⁴⁰ Therefore, superhydrophobic material can effectively purify oil from water in both mixture and emulsion.

Figure 1.3. (a-c) morphology of polyester before and after surface modification by silicone nanofilament; water jet is observed to roll off the surface. (d-e) Morphology of metal mesh before and after surface modification by Cu_2O ; the mesh repels water while oil like toluene penetrates through quickly. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

The key to fabricate both SHL and SHB is tuning surface chemistry and increasing surface roughness. Therefore, almost all methods that are applied to fabricate SHL surfaces also can be used to make SHB surfaces. After SHL is prepared, one low surface energy layer, such as alkyl silane or PDMS

(polydimethylsiloxane) can be introduced to make it SHB. The CA of water is then increased significantly to higher than 150° , showing superhydrophobicity. For example, Su et. al. investigated that the coating of phytic acid/metal ion induced surfaces to superhydrophilic property.⁴¹ Cheng and co-workers applied the same method to modified a fiber membrane. A thin layer of PDMS was coated on as-prepared membrane making it became superhydrophobic membrane.⁴² A simpler method of SHB creation is increasing surface roughness or spacing between HB layers. The higher spacing or roughness increases the air pocket trapped into the HB structure, thus enhancing water repellency. Fischer and co-workers loaded ZIF-8 nanoparticles into hydrophobic HFGO.⁴³ The loading of ZIF-8 increased the spacing between HFGO sheets. The surface area of HFGO-ZIF-8 then increased to $590 \text{ m}^2\text{g}^{-1}$ from $5 \text{ m}^2\text{g}^{-1}$ of HFGO. CA_w also increased from 125° to 160° , revealing the transition from hydrophobic structure to superhydrophobic structure. The as-prepared HFGO-ZIF-8 then obviously displayed higher oil absorption capacity than the HFGO.

1.2.3. Superhydrophobic and Superoleophobic Surfaces

Although superhydrophobic surface shows excellent repellency of water, it fails to repel oils with low surface tension. In fact, oil contaminated surface remains a big problem when it is released to environment. Therefore, using superhydrophobic materials for self-cleaning is limited. In 2007, Tutejia *et al.* introduced superoleophobic surface for the repellency of non-polar oils by the combination of re-entrant curvature and low surface energy modification (fluoro-derived compound).⁴⁴ The surface exhibited excellent repellency of octane ($\text{ST} = 21.6 \text{ mN/m}$). Superamphiphobic⁴⁵ or superomniphobic⁴⁶ are the terminology to

describe the surfaces with both superhydrophobic and superoleophobic nature. The surfaces can be denoted as SHB/SOB, meaning the surfaces can repel oil and water simultaneously in air (Figure 1.1-c), in which SHB denotes superhydrophobicity (repel water) and SOB denotes superoleophobicity (repel oil). As a special case of Figure 1.1c, when both CA_w and CA_o are lower than 150° and higher than their intrinsic angle, the solid surface is called omniphobic (or amphiphobic). Generally, both CA_w and CA_o on superamphiphobic surface should be more than 150° and the value of contact angle hysteresis (CAH) and the SA is as low as 5° to 10° . However, the fabrication of superamphiphobic surface is still challenging due to the excellent wettability of low surface tension liquids to almost all surfaces. It was hypothesized that doubly re-entrant topography could provide higher ability to repel low surface tension liquids. This type of structure allows for trapping more air compared to simple re-entrant topography, thus rendering the formation of air cushion underneath the liquid droplet. There are several re-entrant structures developed to fabricate superamphiphobic surface thus far: T-shaped, mushroom-like, trapezoidal, fibrous, matchstick-like, and microspheres structures.⁴⁷ Recently, a structures that can effectively repel both water and oils have been developed. Consequently, other types of structures also were investigated to understand the nature of superamphiphobicity, such as over-hang structure, or porous structure. For instance, Du and co-workers introduced superamphiphobic coating from microscale porous coating.⁴⁸ The air fraction is calculated up to 0.94. Combined with low surface energy modification, the coating has high availability to repel low surface tension liquids. Indeed, the coating shows versatile super-repellency

to liquids with ST ranging from 73 to 23 mN/m and CA all above 150° (Figure 1.4-a). In addition, over-hang type superamphiphobicity derived from candle soot was also introduced.^{49,50} The few micron thick layer of candle-soot is coated with SiO₂ or TiO₂ and further modified with fluoro-silane. The contact angles of n-hexadecane (ST = 27.5 mN/m) on these surfaces are all higher than 150°. The most basic method to characterize superamphiphobic surfaces is to observe if the liquids droplets retain on the surfaces and both water and oil can roll off when the surfaces are tuned.⁵¹ However, quantitative analysis requires an exact value of CA, SA, and CAH of liquid droplets, and surface characterizations. In some cases, the bouncing behavior was also considered, in which water or oil droplet was observed to jump up to a certain height after it falls down to the superamphiphobic surface (Figure 1.4-b).^{48, 50}

Figure 1.4. (a) Static contact angle and image of liquids with different surface tension on surface of a porous superamphiphobic coating. (b) Bouncing behavior of n-hexadecane droplet on surface of candle-soot derived superamphiphobic coating. (a) Copyright 2016 American Chemical Society. (b) Copyright 2012 American Association for the Advancement of Science.

Not only in air, the SHB and SOB properties also can exist simultaneously under liquid media. It suggests that a solid surface can be superoleophobic underwater (WSOB) and superhydrophobic underoil (OSHB) at the same time. This phenomenon is called dual-superlyophobicity (Figure 1.1-d). When the solid surface is wetted by water, it repels oil; and when it is wetted by oil, water is retained. This phenomenon results from the stably trapped liquid. The key factor to obtain the dual-superlyophobic surface, according to Ras et. al., is the intermediate surface energy of the coating layer.⁵² With the intermediate surface energy, CA_w is maintained between 56° to 74° . Out of this range, the dual-superlyophobicity is no longer existed (Figure 1.5). The dual-superlyophobic surface is useful for self-cleaning under liquid medium and selective oil/water separation.

Figure 1.5. The schematic model of wetting state. $56^\circ < \theta_w < 74^\circ$ is suitable to design dual-superlyophobicity. $56^\circ > \theta_w$ is suitable for hydrophobicity and $\theta_w > 74^\circ$ is suitable for hydrophobicity. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA.

1.3. Research Objective and Outcomes Summary

The above understanding of superwetting materials could provide an effective method to separate immiscible liquids. Indeed, ISI Web of Science displays a rapid increase in the amount of articles fabricated for oil/water separation, using superwetting materials, both organic and inorganic pathways.⁵³ However, there are still several challenges for practical applications.

First, for oil/water separation, the cost effectiveness is very important to promote the application beyond laboratory. Graphene, polymer membranes or graphene/polymer composite are frequently used to separate water and oil.^{54, 55, 56, 57} However, the fabrication of graphene and graphene composite has a relatively high cost. In addition, hydrophobic graphene materials are mostly explored to prepare oil sorbents which have limited sorption capacity. More importantly, composites from graphene and polymer coatings mainly exhibit either hydrophobicity/oleophilicity or hydrophilicity/oleophobicity (underwater). This also hinders the cost effectiveness of materials. Herein, biomass wastes, such as cotton fiber and kapok fiber are introduced as a cheap, easy availability, dual-wettability materials to prepare dual-superlyophobic membranes for effective separation of oil and water.

Second, for other immiscible liquid separation, the significantly lower surface tension of organic liquids than water makes current hydrophobic (or even superhydrophobic) materials impossible to repel those organic liquid, such as formamide or ethylene glycol. To successfully separate immiscible organic liquids, the surface energy of materials must be well controlled. Only limited

number of articles show successful separation of immiscible organic liquids. The fabrication of those materials requires specific pristine substrates to carry the deposition. For example, although the $\text{Cu}(\text{OH})_2$ nanoneedles mesh membrane fabricated by Zhao and co-workers exhibits excellent separation of immiscible organic liquids the membrane strictly requires Cu mesh for the nucleation and growth of $\text{Cu}(\text{OH})_2$ nanoneedles.⁵⁸ This limited option of pristine substrate also renders the practical application of the material. More importantly, the impact of substrate's geometry to final wettability of lyophobic/superlyophobic materials has been investigated. Herein, materials with various geometry such as, melamine sponge, polyurethane sponge, stainless steel mesh, cotton fabric, polyester fabric, filter papers or Ni foam are selected to tailor their surface wettability. The synergistic effect of material's geometry, coating morphology and surface chemistry is then investigated. The chosen substrates are also easy availability and low cost. The 2D materials can be employed to fabricate superwetting membranes for continuous separation, while the 3D materials can be fabricated absorbents for static batch separation, providing more options with low cost for immiscible liquid separation.

Polymer coatings, for example poly(ethylene glycol) coatings, have been widely investigated to control property of solid surface.^{59, 60} More recently, layer-by-layer (LBL) assembly of polymers have been employed to tailor surface wettability of the solid substrates. For instance, Wang and co-workers introduced LBL deposition of polydiallyl dimethylammonium chloride (PDDA) and poly(styrene sulfonate) (PSS) on a hydrophobic stainless steel mesh.³⁸ The $(\text{PDDA}/\text{PSS})_n$ coating (with "n" is the number of assembly cycle) tuned the mesh

to become superhydrophilic after a certain cycles of assembly. The (PDDA/PSS)_n coating is also easily deposit on a hydrophilic surface such as glass slide as post-treatment for a further modification.⁶¹ However, the method involves in time-consuming process that requires many cycles for each layer, thus rendering its application. The alternative approach for fast, simple and robust coating is the use of polydopamine (PDA) with its excellence of chemical property. PDA with a high density of catechol groups has been found to coat on surfaces of almost any materials (Figure 1.6).⁶² Since its first introduction in 2007 by P.B. Messersmith et al,⁶³ the polymer has been utilized as a simple, versatile, adaptive, powerful surface coating in broad fields, such as biomedicine, environment, energy, etc.⁶⁴ The excellent property of PDA is generated from the strong adhesion and versatile reactivity. The strong adhesion of PDA even allows the polymer to coat on very low surface energy substrates with the same principle to the coating on a high surface energy substrate. In addition, the versatile reactivity of PDA can provide a good platform for many other reactions such as Schiff base/ Michael addition reaction, metal ions chelating, redox reaction and reactions based on imine/amine groups.⁶⁵

The work in this thesis take advantages of PDA with robust adhesion and versatile reactivity to develop hybrid materials with tailored surface wettability. In the three systems in this thesis, I have demonstrated that these properties of PDA offered possibilities for fabricating hybrid materials with unique structures and novel wetting properties that have been applied to separate immiscible liquids. In addition, the synergistic effect of surface morphology and surface

chemistry using PDA treatment is also demonstrated, providing further understanding about general separation of immiscible liquids.

Figure 1.6. Typical structure of polydopamine after polymerization from dopamine under slight basic condition. Copyright 2012 American Chemical Society.

In the first system, I employed PDA to functionalize surface of biomass fibers, such as cotton fiber and kapok fiber. The key finding of this system is that the morphology of PDA coating layer determines the wettability of the biomass fibers. PDA was synthesized using a strong oxidizing agent (sodium periodate) under slight acidic condition (acetate buffer, pH = 5). As a result, homogeneous and rough PDA nanoparticles of 100 nm on average grown on surface of the biomass fibers. This micro/nano hierarchical morphology of as-prepared fibers is found to enhance the surface wettability. Cotton fiber is naturally hydrophilic, underwater superoleophobic and underoil superhydrophilic, while kapok fiber is naturally hydrophobic, underwater superoleophilic and underoil superhydrophobic. After modification with PDA nanoparticles, both kinds of

fibers became underwater superoleophobic and underoil superhydrophobic, which were applied to selectively separate oil and water.

In the second system, I took advantage of understanding from the first system to modify surface of various materials, both hydrophobic and hydrophilic, with PDA nanoparticles. The mass of PDA coating deposited on the surface of pristine substrates using this method was higher than the mass of PDA prepared with slow reaction rate. In this work, I employed PDA coating as template to further modify surfaces with hydrophobic alkylsilane molecules. Higher loading of PDA offered more chelating surfaces, on which hydrophobic silicone micro-sheets (SMSs) can grow. The growth of SMS increased surface roughness of hydrophobic surfaces, making them repel liquids with surface tension larger than 30 mN/m. These surfaces are superlyophobic and can repel water and other high surface tension liquids such as formamide and diethylene glycol. Interestingly, the as-prepared materials were then applied to separate immiscible liquid mixtures by both membrane filtration and absorption strategies.

In the third system, I employed PDA as both reducing agent and surface modifier to fabricate GH-PDA porous particles. In the presence of ionic liquid, the GH-PDA formed porous particles, which can be dispersed in solution without losing the porosity that was promising for further surface modification. ZIF-8 nanoparticles were grown to modulate the pore sizes of GH-PDA. Both GH-PDA and GH-PDA-ZIF-8 hybrid structures were then modified by fluoro-silane. The wettability of the hybrid materials can be tailored from superamphiphobicity to omniphobicity when the increasing amount of ZIF-8 nanoparticles were loaded.

The tailored wettability allowed certain liquids to penetrate and retained others when coated on Ni foam, leading to separation of immiscible liquids.

Chapter 2. Literature Review

2.1. Some Basic Theories about Wetting Behaviors

Wetting is one of the most common phenomena that can be observed in anywhere when a liquid droplet contacts with a solid. To classify different wetting states such as hydrophilic and hydrophobic or oleophilic and oleophobic, and their superwetting states, the contact angle is usually measured to characterize the liquid-solid interface. In general, contact angle (CA= θ) of a liquid droplet on an ideally smooth, homogeneous surface is expressed by the classic Young's equation (developed by Thomas Young).⁶⁶

$$\cos \theta = \frac{(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} \quad \text{(Equation 2.1)}$$

where γ_{SV} , γ_{SL} , γ_{LV} , respectively are surface tension of solid-vapor, solid-liquid, and liquid-vapor interfaces. CA is mathematically measured by the tangent lines between liquid-air interface and liquid-solid interface. From equation 2.1, the CA limit between hydrophobic and hydrophilic should be 90° ($\cos \theta = 0$) in which $\gamma_{SV} = \gamma_{SL}$. When $\theta < 90^\circ$ the surface is considered hydrophilic because of the higher value γ_{SL} compared to that of γ_{SV} . Conversely, $\theta > 90^\circ$ is considered hydrophobic because of the higher value γ_{SV} compared to that of γ_{SL} . However, the equation only considers the property of the solid surface. Indeed, chemical and structural state of water droplet also affect the contact angle limit, and research conducted by Berg et al. showed that the actual

limit can be 65° (Figure 2.1-a).^{67, 68} Recent experimental researches from Jiang and co-workers confirmed the value of CA_W on smooth surface, so-called intrinsic wetting threshold (IWT) or intrinsic contact angle (ICA), to be around 63° .^{69, 70} The physical value of 65° has brought more impact of surface design than the mathematical value of 90° when we investigate the impact of oil droplets nature, such as surface chemical structure and the effect of solid surfaces nature, such as surface chemistry and surface morphology.^{29, 71} The values of IWT are different with liquids owing different ST. Liquids with lower ST will have a lower value of IWT (Figure 2.1-b).^{68, 70}

Figure 2.1. (a) The new limit of hydrophilic/hydrophobic with value of water contact angle 65° reported by Berg. (b) Intrinsic wetting threshold of different liquids. (a) Copyright 2017 Nature Publishing Group.

From Young's equation, the main factor affecting CA of liquid droplets is surface energy (SE) of a solid. When $SE_{\text{solid}} > SE_{\text{liquid}}$, the surface exhibits lyophilicity, while $SE_{\text{solid}} < SE_{\text{liquid}}$ the solid surface exhibits lyophobicity. SE is decided by the nature of surface coating, particularly surface chemistry. In practical circumstances, almost substrates, however, are not smooth. Wenzel

investigated the wetting behavior of liquids on a rough surface in 1936 by adding roughness factor to Young's equation.⁷²

$$\cos \theta_w = r \cos \theta = r \frac{(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} \quad \text{(Equation 2.2)}$$

where r is the roughness factor of surface, which is the ratio between the real surface area and the horizontal projection.⁷³ θ_w is the apparent angle or measured angle on the rough surface. When $r = 1$, the equation becomes Young's equation. The model that represents Wenzel's equation so-called Wenzel model. As the surface roughness is always higher than 1, the Wenzel model predicts that surfaces roughness, besides surface chemistry, enhances the surface wettability. In pervasive literatures, the CA limit of 90° ($\pi/2$) is still used for the wettability of water. This means that as r increases, θ_w will increase when liquid CA $\theta > \pi/2$ and surface is more hydrophobic; it will decrease when $\theta < \pi/2$ and surface is more hydrophilic. Similar to Young model, Wenzel model is only valid in a homogeneous surface where the liquid completely wets the solid surface and penetrates into the solid cavities (Figure 2.2-b). As the surface becomes highly hierarchical (heterogeneous) or porous ($r \gg 1$), the Wenzel model is no longer valid.⁷⁴

In many cases, solid surfaces exist with a composite interface which contains significantly trapped air in the cavities of the rough surface, leading to less possibility for liquid droplets to penetrate in these cavities. Cassie and Baxter, therefore, proposed a new equation describing the effect of surface roughness on the wettability. (Figure 2.2-c).⁷⁵

$$\cos \theta_{CB} = f_{SL} (1 + \cos \theta_w) - 1 \quad (\text{Equation 2.3})$$

where f_{SL} represents the solid fraction under the solid-liquid contact regime. Cassie equation suggests that the solid-air fraction also affect the wetting behavior of liquids. Furthermore, Marmur described a wetting state in which the liquid droplet partially wets the solid surface.⁷⁶

$$\cos \theta^* = r_f f_{SL} \cos \theta + f_{SL} - 1 \quad (\text{Equation 2.4})$$

When $f_{SL} = 1$, this equation becomes Wenzel's equation (θ^* is then Wenzel's contact angle), and this state is more likely known as the transition between Wenzel's state and Cassie-Baxter's state.⁷⁷ The Cassie-Baxter's state, thus, is called the meta-stable state. With the introduction of air pocket in the porous structure, the Cassie-Baxter's equation can be written as.^{48, 75}

$$\cos \theta_{CB} = (1 - \phi_{air}) \cos \theta - \phi_{air} \quad (\text{Equation 2.5})$$

where ϕ_{air} represents air fraction of the porous structure ($\phi_{air} \leq 1$). The larger value ϕ_{air} is, the higher CA value is obtained when $\theta > \text{IWT}$. From the above basic theories of surface wettability such as Young model, Wenzel model, Cassie-Baxter model, it can be concluded that surface wettability of materials is affected mainly by surface chemistry, surface roughness, and surface compositions.⁴⁰

Figure 2.2. Illustration of three typical wetting models: (a) Young's model (without roughness), (b) Wenzel's model (with roughness) and Cassie-Baxter's model (with roughness). Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

From both Wenzel's equation and Cassi-Baxter's equation, the surface with CA larger than 150° is defined as superantiwetting. On the other hand, the surface with contact angle as close as 0° is defined as superwetting. However, depending on the wetting state of the liquid droplet, CAH and SA of Wenzel state and Cassi-Baxter state behave differently. CAH is the difference of advancing contact angle and receding contact angle,⁷⁸ corresponding to the compression and release of the droplet on a certain surface, while SA is the tilting angle, below which the droplet starts rolling out of surface.⁷³ Low CAH and SA reveal the low attractive force between the solid and liquid interfaces. Wenzel state usually displays a relatively high SA and high CAH. Thus, the droplet is observed to stick on surface of the material with high adhesion force, while a droplet in the Cassi-Baxter state always shows low SA and low CAH with a minimum adhesion to the solid surface. The liquid droplet in the Cassi-Baxter state easily rolls off the surfaces, leaving almost no residual.

As mentioned, Cassi-Baxter state is meta-stable. The transition from Cassi-Baxter state to Wenzel state happens when the air pocket underneath is disrupted. The decrease in the fraction of air pocket is caused by an external pressure, high temperature of the liquid, low surface tension liquids or contaminated liquids.⁷⁹

The liquid droplet then converts from mobile effect to pinning effect without moving (Figure 2.3-a). When the droplet is in a sticky state, it is nearly impossible to restore to the Cassi-Baxter state without external energy or a special surface treatment. Wong and co-workers have recently reported a new phenomenon that the water droplet still can roll off a solid surface when it converted from Cassi-Baxter state to Wenzel state.⁷⁹ The authors suggested that pretreatment with a layer of perfluoro lubricant (oil) can reduce pinning forces on water droplet (Figure 2.3-b). The use of lubricant is inspired from wax regeneration of plant leaves and slippery surface of the *Nepenthes* pitcher plants in which the lubricant oil is immiscible to water and easily coated on surface of micro/nano structure of solid surface.^{80, 81} The new phenomenon of slippery Wenzel state may open new studies in term of surface wetting, liquid transportation, etc.

Figure 2.3. (a) The impact of external factors to the transition between Cassie-Baxter state and Wenzel state. (b) The behavior of liquid in the slippery Wenzel state. Copyright 2015 American Chemical Society.

2.2. The Tailor of Surface Wettability

2.2.1. Tailor of Wettability Via Bio-inspired Surface Structures

Besides the new surface coating, the tailor in surface morphology (or simply surface roughness) can cause a transition from wetting/anti-wetting to superwetting/superanti-wetting, accordingly. Nature provides us good examples from organisms that well-ordered structures of plants and animals enhance significantly surface wettability. By understanding structure and mechanism of wetting and anti-wetting of organisms, we can build up the rule for material design that can bring tremendous applications. Herein, I will discuss more about the effect of bio-inspired surface morphology on wettability. Figure 2.4 summarizes surface structure of natural wetting and anti-wetting organisms toward water, which were studied by Jiang and co-workers.^{28, 29} From the above explanation of the new CA limit of water, various research works have been designing different states of superhydrophobic and superhydrophilic by modification of surface topography. With static contact angle higher than 65° , the increase in surface roughness of natural hydrophobic surfaces results in various superhydrophobic states such as Wenzel's state (Figure 2.4-a), Cassie's state (Figure 2.4-b) or the transition state (Figure 2.4-d),⁷⁹ the "Lotus" state (Figure 2.4-c)^{82, 83} or the "Gecko" state (Figure 2.4-e).⁸⁴ The Wenzel's state represents to a high adhesion with fully wet superhydrophobic surface, leading a high CA hysteresis value. Thus, the sliding CA is usually higher than 10° .⁸⁵ In the Cassie's state (also called Cassie-Baxter's state), the water droplet is repelled by solid surface with non-wet contact mode. With this mode, the air cushion is normally observed at liquid-solid interface, resulting in a low SA.^{86, 87, 88} The transition

between Cassie's state and Wenzel's state exists when thermodynamic variables are changed, such as external pressure, temperature or external electric field, on which water droplet is hung.⁸⁹ The "Lotus" state represents a unique structure of solid surface that the micro/nano structure of surface looks similar to that of natural lotus leaf. The low SA of liquid on this surface, which is enhanced by micro-nano hierarchical structure of the leaf, reveals the self-cleaning effect or Lotus effect.⁸² Thus, the "Lotus" state can be used as a special case of Cassie's state.⁹⁰ The "gecko" state, in contrast, displays high adhesion of water droplet. The first "gecko" state is originated from superhydrophobic polystyrene (PS) nanotube films.⁹¹ The vertical building of PS nanotubes generates two types of trapped air, one is open air pockets from atmosphere and the other one is sealed-air pockets inside the PS tubes (clearly seen in figure 2.4e). This is different from Cassie's state, which only has open air pockets from atmosphere. The open air pockets contribute to repel water, while the negative pressure generated from the sealed air pockets is believed to enhance the adhesion force.²⁹ As a result, the "gecko" state PS nanotubes film exhibits water CA as high as $162.0 \pm 1.7^\circ$ and the adhesive force is as high as $59.8 \mu\text{N}$ on 6 000 000 vertically aligned nanotubes. On the other hand, the enhancement of the roughness of natural hydrophilic surface with contact angle lower than 65° results in superhydrophilic state such as microscale state,³⁷ micro/nanoscale state⁹² or porous state.⁹³

Figure 2.4. Different superhydrophobic states: (a) Wenzel's state, (b) Cassie's state, (c) the "Lotus" state, (d) the transition state and (e) the "Gecko" state. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.

The surface analysis of natural anti-wetting organisms such as Lotus leaf, water strider's leg, mosquito's eye, gecko's foot or butterfly's wing unveils that these surfaces are not flat.²⁹ Hierarchical, well-ordered structures are observed under SEM. These structures, together with low surface coating, could help to repel water. For instance, it is reported that the synergistic effect of micropapillae and hydrophobic wax of lotus leaf kept the water droplet at around 160°.⁹⁴ Jiang and co-workers later investigated that the micro/nano hierarchical structure prevented water to wet the underside of papillae (Figure 2.5-a).⁹⁵ The authors then removed the nanostructures while leaving the microscale parts, they obtained the adhesion phenomenon of water on the micro-only structure. In 2004, Jiang and co-workers reported that the huge superhydrophobic force on the strider's legs supported the free standing of the insect.⁹⁶ The superhydrophobic force is caused by the special structure of the legs. The authors found a large number of needle-shaped microsetae on the legs of water strider. The helical nano-grooves were also observed on the needles that tilted an angle of about 20° from the surface, forming nano-scale roughness (Figure 2.5-b). These micro/nano oriented structures enhance the air trapped underneath and endows the formation

of robust superhydrophobicity. Therefore, water strider can walk freely on water surface. Another interesting example of super anti-wetting organism is the eyes of mosquito. This insect is famous not only by its vampirism but also by the excellent vision even in the watery atmosphere. In 2007, Jiang et al. investigated that the anti-fogging ability of the eyes induces the excellent vision.⁹⁷ By further analyzing the structure of the eyes the authors found that the hexagonally nonclose-packed nipples decorated on hexagonally close-packed ommatidia of the mosquito eyes, forming micro/nano scale structure and rendering excellent superhydrophobicity of the eyes (Figure 2.5-c). Due to the extreme water resistance, the fog drops were unable to locate on the eye surface. This makes mosquitoes able to see clearly in humid environment. Wing of butterfly is one example of superhydrophobic surface with directional wetting property. Surface analysis from Jiang et. al indicated that the micro/nano hierarchical structure of the wing was mainly resulted from many periodic quadrate scales and well-oriented nanostripes, which were arranged along the radial outward (RO) direction (Figure 2.5-d). As a result, with $CA_w = 152 \pm 1.7^\circ$, water can roll along the RO direction when it tilted by 9° .^{29, 98} However, the droplet cannot roll along the opposite direction as the wing was tilted downward.⁹⁸ Gecko is usually seen to climb on vertical surfaces due to the multiscale structure on its foot causing high adhesion. In addition, Autumn et al. investigated that the foot also exhibited superhydrophobic property with high adhesion to water. The CA_w on the foot were reported to be 160° .⁹⁹ The micro/nano hierarchical structure of gecko foot was built up from $5 \mu\text{m} \times 110 \mu\text{m}$ micro hairs called setae and hundreds of nanoscale

spatulae, which resulted in nano-scale roughness on the surface of setae (Figure 2.5-e).

Various examples of super-wetting surfaces are also observed in many natural creators.²⁸ For instance, Microtextured peristomes on the leaves of *Nepenthes* pitcher was observed to cover with a thin layer of sticky liquid that resulted in the slippery wetting phenomenon (Figure 2.5-f).^{100, 101} Ball showed that skin of some fishes, such as sharks (Figure 2.5-g), exhibited excellent drag reduction based on the super-wetting property.¹⁰² The coarse region of inner walls of clam shells, which mainly consists of hierarchical structures of CaCO_3 was also found to display underwater superoleophobicity with almost no adhesive force of oil droplet.¹⁰³ In contrast, the glossy edge region can hardly repel oil when it was immersed in water (SEM-Figure 2.5-h).

Figure 2.5. The rule of material design in the fabrication of superhydrophobic and superhydrophilic structures inspired from natural anti-wetting and natural wetting organisms. Copyright 2016 American Chemical Society.

Inspired by nature, scientists have developed artificial superhydrophobic or superhydrophilic materials that have the surface structure and wetting behavior similar to the natural organisms with sufficient surface coating. The general principle of design is combining multiscale roughness and hydrophobic or hydrophilic modifiers. The successful mimic of natural organisms provides potential to scale up the fabrication with tremendous applications. For example, Jiang and co-workers reported the composite film consisted of porous microsphere and nanofiber mimicking surface structure of lotus leaves (Figure 2.6-a).¹⁰⁴ The film prepared from solution of 7 wt% PS/DMF displayed superhydrophobic property with $CA_w = 160.4 \pm 1.2^\circ$. The film is promising for large scale fabrication of self-cleaning surface. Gao et.al. reported a superhydrophobic structure, inspired by the compound eye of the mosquito *C. pipiens*.⁹⁷ The authors used top-down approach to fabricate the film with close-packed hemi-sphere PDMS decorated with SiO₂ nanoparticles (Figure 2.6-b). The artificial compound eye with $CA_w = 155^\circ$ then displayed excellent antifogging behavior in a humid environment. Jiang and co-workers then continued to fabricate other biomimetic materials with superwetting property. In 2009, the authors produced artificial fish scale from polyacrylamide (PAM) hydrogel.¹⁰⁵ The hydrogel can trap a stable layer of water. With the structure like mucus of fish scales, the hydrogel displayed hydrophilicity and underwater superoleophobicity with $CA_o = 162 \pm 1.8^\circ$ (Figure 2.6-c). The fish scale-like PAM gel can be applied in underwater self-cleaning surfaces and drag reduction. In 2012, Wang and co-workers reported a underwater self-cleaning surface inspired from wetting behavior of inner wall of clam shell.¹⁰³ The oxidation of

Cu plate in high pH environment resulted high roughness CuO films with micro/nano hierarchical structure. The oil droplet therefore easily rolled off when the plate was immersed in water (Figure 2.6-d). The clamshell-like CuO film has potential for antifouling application. Notably, the multiscale structure tailors the wetting/antiwetting behavior in all the above artificial structures. That means, the as-prepared structures displayed enhanced wettability compared to the flat surfaces with the same chemical components.

Figure 2.6. Natural-inspired wetting/antiwetting materials fabricated with inspiration from (a) lotus leaf, (b) mosquito eye, (c) fish scale and (d) inner wall of clam shell. Inset of (a) and (b) is image of water droplet in air. Inset of (c) and (d) is image of oil droplet underwater. (a) Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA. (b) Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA. (c) Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA. (d) Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA.

Not only superhydrophilic or superhydrophobic, a series of natural superomniphobic (superamphiphobic) surfaces have been reported. For instance,

Aizenberg's group reported that bacterial colonies and pellicles showed anti-wetting property to a low ST liquids such as 80% ethanol solution.¹⁰⁶ R. Rakitov and S. N. Gorb stated that the highly structured particles called bronchosomes that uniformly coat on integuments of leppers can make the leppers exhibit superoleophobicity.¹⁰⁷ Werner and co-workers investigated the repellency for both water and oil without suffocating of springtail.¹⁰⁸ This investigation is one of the most important oil repelling example of a nature organism. The detail examination of cuticle structures showed that the synergistic effect between surface chemistry such as chitin or protein and multiscale roughness of these species rendered the repellency of both water and oil.

Figure 2.7. (a) The omniphobicity of skin of the Springtail that has mushroom-like texture. (b) The comparison of apparent contact angle of different liquids on surface of the mushroom-like structure and cylindrical pillar array. (c) Contact angle hysteresis and sliding contact angle of liquids on the mushroom-like structure. Copyright 2017 American Chemical Society.

The characterization of springtail structure provides inspiration for other fabrications of superamphiphobic surfaces that reproduce natural oil-repellent

surfaces. For example, inspired by oil repellency of springtail, Kim and co-workers have developed flexible and robust re-entrant superomniphobic surface by exploiting localized photofluidization of azopolymers.¹⁰⁹ The mushroom like head of micropillar was obtained mimicking the re-entrant nanostructure in the texture of the insect's skin (Figure 2.7-a). The air mat is believed to form underneath the head of the mushrooms that enhances the repellency of liquids. The apparent CA of liquids from high ST such as water ($ST = 72.8 \text{ mN/m}$) to low ST such as n-hexane ($ST = 18.4 \text{ mN/m}$) were all higher than 150° , which showed significant improvement compared to plain micropillars (Figure 2.7-b). Furthermore, all the liquids displayed low CAH (lower than 20°) and low SA (below 10°), indicating excellent superomniphobicity of the mushroom array (Figure 2.7-c).

2.2.2. Tailor of Wettability via Strategies Beyond Nature

Tailoring surface topography and surface chemistry inspired by nature is an interesting method to tune surface wettability. However, many reports have shown that the surface wettability is also tunable with strategies beyond nature. Smart materials with responsive wettability have been receiving tremendous attention due to the special properties that cannot be found in nature. For example, Jiang and co-workers have first time developed dual-superlyophobic polyvinylidene fluoride (PVDF) membrane.¹¹⁰ A dual-superlyophobic surface is known to display both underwater superoleophobicity and underoil superhydrophobicity. More interesting, these wetting states are tunable depending on the pre-wet solvent (Figure 2.8-a).

Figure 2.8. Stimuli-responsive to superwetting surfaces. (a) Liquid infused tunable underoil superhydrophobicity and underwater superoleophobicity. (b) Thermal responsive tunable hydrophobicity and hydrophobicity. (c) pH-responsive tunable superhydrophilic and superhydrophobic fiber membrane. (d) Ammonium (NH₃) vapor induced transition between superhydrophobic/superoleophobic and superhydrophilic/superoleophobic textile membrane. (e) External electric field induced the transition from superhydrophobic to superhydrophilic mesh membrane. (a) Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA. (b) Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA. (c) Copyright 2017 American Chemical Society. (d) Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA. (e) Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

With another collaborator, Jiang introduced thermal responsive PNIPAAm (poly(N-isopropylacryamide)) coating on a microfiltration membrane.¹¹¹ When the temperature was below the lower critical solution temperature (LCST) of PNIPAAm, the membrane was hydrophilic and underwater superoleophobic; when the temperature was higher than LCST of PNIPAAm, the membrane became hydrophobic (Figure 2.8-b). The thermo-driven wettability of membrane could be explained by the form of hydrogen bonding in PNIPAAm when temperature changes. When temperature is lower than the LCST, N-H and C=O

groups in PNIPAAm are possible form of hydrogen bonding to water molecules due to the major contribution of enthalpy, leading to superhydrophobic behavior of the membrane. On the other hand, when temperature is higher than the LCST, the major contribution of entropy makes the polymer chains condense and collapse, because the N-H and C=O functional groups form intra-molecular hydrogen bonding, leading more hydrophobicity and CA_w is nearly 120° . Chen and co-workers presented a pH-responsive membrane based on the deposition of poly(ureaformaldehyde) (PUF-RC)-coated cotton fabric.¹¹² the authors showed that at $pH = 1$, the membrane was superhydrophilic and underwater superoleophobic. When treated the membrane with a $pH = 13$ solution, it became superhydrophobic (Figure 2.8-c). It suggested that the change in wettability depended on the concentration of N^+ on the surface of membrane which is influenced by pH level. When the PUF-RC-coated fabric was treated with $pH = 1$ solution, the concentration of N^+ increased from 0.58 to 1.46 %, leading higher ability to form hydrogen bonding with water molecules; when the fabric was treated with $pH = 13$ solution, the concentration of N^+ decreased to normal level, inducing hydrophobicity of the membrane. Note that the as-prepared membrane treated with $pH = 7$ solutions had approximately 0.58% of N^+ and showed superhydrophobicity. Zhao et al. reported that ammonium vapor can trigger the transition from superamphiphobicity to superhydrophilicity/superoleophobicity (Figure 2.8-d).¹¹³ This means, after exposing with NH_3 vapor, water can penetrate through the membrane while oil droplets still retain. The transition from superhydrophobicity to superhydrophilicity of the membrane related to the formation of ammonium carboxylate ion. The ammonium salt migrated from

solid-air interface to water-air interface due to the high affinity of the ion and water molecules. The surface coating consequently existed both hydrophilic component and oleophobic component. Surface roughness provided from the attachment of SiO₂ nanoparticles induced repellency of oils and penetration of water. Interestingly, the heat treatment of ammonia exposed membrane can recover the superamphiphobicity, because of the decomposition of the ammonium carboxylate ion bonding. Another work from Jiang introduced the external electric field induced wettability of the mesh membrane (Figure 2.8-e).¹¹⁴ Nanostructured polyaniline was found to coat on the surface of micro scale pores of stainless steel mesh, making it hydrophobic in air ($CA_w = 146^\circ$) and underwater superoleophobic ($CA_o = 166^\circ$). This means both water and oil can stay on top of the mesh, revealing no separation occurred. After applying a 170 V electric current on the polyaniline mesh, the corresponding electric capillary pressure (ECP) is generated, which is proportional to the applied voltage by the following equation $ECP = l\Delta\gamma / A = l\varepsilon_0\varepsilon_1(V - V_T)^2 / 2Ad$.¹¹⁵ Moreover, M. W. J. Prins et. al showed that the applied voltage is inversely proportional to CA_w by the following equation $\cos\theta_v = \cos\theta_0 + \varepsilon_0\varepsilon_1(V - V_T)^2 / 2d\gamma_{LV}$, where θ_v is the CA_w at applied voltage.¹¹⁶ Thus, the water droplet penetrated quickly through the mesh. The mesh membrane then became superhydrophilic and underwater superoleophobic, revealing ability to separate oil and water. In all works, the morphology of materials before and after applying external gradients does not significantly change. In addition, there is also no need to modify with another coating layer. The tune and switch of wettability is only triggered by external gradients such as solvent, electricity, temperature, gas vapor or pH level. The

final purpose of such responsive coatings is to fabricate smart materials for multifunctional ability such as, oil/water separation, antibacterial or antifouling, biosensor or drug delivery.^{117, 118}

2.3. Current Strategies for Separation of Immiscible Liquids Based on wetting Materials

2.3.1. Absorption Strategy

Oil sorbents have been playing a very important role for remediation of oil spills. To enhance the absorption capacity, the oil sorption materials should have hydrophobic and oleophilic property so that the materials can absorb oil but not water. To date, numerous materials have been developed based on natural materials or synthetic materials for oil sorption such as porous resin, 3D graphene, zeolite, natural biomass or so forth.¹¹⁹ These materials, in some cases, display a high absorption ability, good recyclability, high rate of oil uptake and high durability. In addition, the mother materials can combine with other components to strengthen some properties. For example, Zhu et al.¹²⁰ decorated a hydrophobic sponge with magnetic nanoparticles to enhance the surface roughness and simplify the oil collection (Figure 2.9). The materials showed superhydrophobicity with $CA_w = 155^\circ$ because of its large surface roughness and low surface energy. The high roughness of the sponge was resulted from the decoration of nanoparticles, while the introduction of thiolate compound decreased its surface energy. Furthermore, the magnetic nanoparticles immobilized on sponge can direct the motion of the sorbent by using external magnet that makes the easier oil collection. More interestingly, large scale

fabrication of the materials might be achieved via the same method, leading potential of ready-to-use oil separation.

Figure 2.9. Cycle absorption of light oil (blue) out of water batch using superhydrophobic foam driven by an external magnet. Copyright 2014 American Chemical Society.

However, to the best of our knowledge, no sorbents have been fabricated to separate immiscible liquids thus far. Although hydrophobic sorbents display excellent separation of oil from water, they still face challenges to remove low ST liquids such as n-hexadecane (HDC, $ST = 27.3 \text{ mN/m}$) from the mixture with higher surface tension organic liquids, such as formamide (FM, $ST = 58 \text{ mN/m}$). When the hydrophobic sorbents are applied in this mixture, formamide is able to be absorbed together with n-hexadecane, revealing an unsuccessful separation. However, liquid discharge contains more complicated immiscible liquid components rather than just oil and water. Therefore, it is an urgent call to develop sorbents that can separate immiscible liquids. It suggests that wettability of the sorbents should be lyophobic to one liquid and lyophilic to another one. For example, $SE_{FM} > SE_{\text{sorbent}} > SE_{HDC}$.

2.3.2. Membrane Filtration Strategy

Although oil absorbents show high efficiency of oil removal, the slow operation rate, limited absorption capacity, complicated regeneration, etc. are the main challenges.²³ Therefore, scientists have been developing continuous method as an effective choice for oil droplets separation. Currently, several continuous strategies have been applied for oil separation such as gravity separation, flotation. The advantage of continuous separation is that the material can separate a big volume of waste in a short time. However, high cost and low separation flux are the main challenges of these strategies.

Membrane filtration has been showing advantages for its high separation efficiency, high flux, and cost-effectiveness. To date, various kinds of special wettability membranes have been investigated by modifying surface of novel materials, such as metal mesh, textile, polymer membrane, etc.¹²¹ These membranes have displayed great separation efficiency of oil and water, both with hydrophobic or hydrophilic properties. However, the separation of immiscible organic liquids by membrane is seldom reported. Membrane that displays lyophobic to high ST liquids such as water or formamide and lyophilic to lower ST liquid such as carbon tetrachloride (CCl_4) is believed to effectively separate immiscible liquids.⁷⁰ The membrane reported by Jiang and co-workers not only can separate oil and water but also can effectively separate immiscible organic liquids with smaller surface tensions difference, such as formamide and CCl_4 . The key is surface energy of the membrane that exactly exists between surface tension of the two immiscible liquids. For example, the membrane displayed lyophobic to formamide with $\text{CA} = 137.4^\circ$ and lyophilic to CCl_4 with $\text{CA} = 0^\circ$

(Figure 2.10-a). The surface roughness contributed by electro-spinning fibers and sufficiently low surface energy of coating layer endowed the repellency of the membrane toward a series of liquid (Figures 2.10 b-g and j). With a sufficient coating, selective lower surface tension liquids passed through the membrane and the higher surface tension liquids were retained, resulting in a successful separation (Figure 2.10 h and i). More interesting, the surface wettability of the membrane can be tailored from hydrophobicity (coated with C_6HO) to various levels of lyophobicity (coated with C_3F_3 , C_{16}) and omniphobicity (coated with fluoro-based molecules such as C_8F_3 and $C_{10}F_{17}$). Thus, a general strategy to fabricate lyophobic membrane for immiscible liquid separation is precisely manipulating surface of hydrophobic membrane.

Figure 2.10. Separation of formamide (FM) and tetrachloromethane (CCl_4) using lyophobic electro-spinning membrane. Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA.

2.4. Tailor of Surface Wettability with PDA

2.4.1. Chemistry and Characterization of PDA

Recently, bio-inspired materials are investigated intensively for tremendous applications. For examples, the mussel adhesive proteins (MAPs) is found to contribute significantly to the adhesion ability of mussel on almost all surfaces. Furthermore, a high content of catechol amino acid in the structure of MAPs is confirmed by the adhesion property.¹²² Inspired by this mussel adhesion, catecholic compounds such as dopamine has been used as adhesive molecules. PDA is the product of the polymerization of dopamine, incorporating functional groups such as catechol, amine and imine.⁶⁴ However, the mechanism of polymerization is still unclear. Recently, Lee and co-workers proposed a mechanism in which an intermediate oxidative product further reacts to form both covalent bond and physical assembly (Figure 2.11).¹²³

Figure 2.11. Possible pathways to polymerize dopamine starting from 5,6-dihydroxyindole, an intermediate oxidative product: (a) covalent polymerization and (b) self-assembly polymerization. Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA.

PDA shows versatile adhesion and coating on surface of numerous materials from the macroscale to nanoscale, hydrophobic and hydrophilic. The strong adhesion property of PDA may come from metal chelation, π - π interaction, aryl-aryl interaction or Michael-type reaction.^{64, 122} The performance of PDA coated materials, however, is highly depended on the formation of polymerization rate. Among the reported methods, oxidant promotion is found to obtain a thick and highly stable deposition of PDA coating.^{124, 125} More importantly, the coatings of PDA can offer further surface modification both by chemical and physical interaction to obtain new functions (Figure 2.12).¹²⁶ For example, the catechol groups in PDA can react with thiol- or amino-terminated molecules via Michael

addition reaction and/or Schiff-base formations.¹²⁷ Feng et. al. showed that the cross-link of PDA and PEI (polyethyleneimine) via Michael addition reaction strengthened the mechanical stability of PDA coated graphene oxide sheet.¹²⁸ The reaction was conducted in slight basic pH level (~8.5) as similar to polymerization of dopamine. After cross-linking with 30% wt of PEI, the tensile strength increased from 116.06 ± 4.24 MPa to 178.96 ± 3.52 MPa and Young's modulus increased from 30.60 ± 5.23 GPa to 88.84 ± 2.89 GPa. PDA is also found to chelate metal ions or coordinate with metal/metal oxide, from which the metallization or mineralization or reduction of metal ions can be initiated on PDA coating.⁶⁵ Duan and co-workers investigated chelating properties of PDA to synthesize multi-layers nanoparticles. Metals such as Au;¹²⁹ metal oxide such as Fe₃O₄; metal-organic frameworks (MOFs) such as ZIF-8 and UIO-66;¹³⁰ have been reported to grow and form additional layer on surface of PDA coating, which provides new properties to the original nanoparticles, such as plasmonic property, selective catalysis or magnetic property. In addition, the thin layer of PDA can initiate polymerization by the immobilization of the initiators, which react to the phenol group or amino group of PDA. Chan et. al. successfully synthesized anti-bacterial polymer on surface of PDA coated PDMS catheter.¹³¹ Without PDA coating, the polymer layer cannot attach on the inert PDMS surface. In this work, the initiator reacted directly with the PDA layer, from which polymer chain started growing. Due to the strong adhesion, high carbon content and chemical versatility, as shown above, PDA has been displaying great applications in the fields of energy, environmental treatment, and biomedicine. A partial enumeration of PDA applications includes Lithium-battery,^{132, 133, 134}

supercapacitor,¹³⁵ oil-water separation,^{125, 136, 137, 138} organic dye adsorption,¹³⁹ molecular separation,¹⁴⁰ microfluidic devices,¹⁴¹ antimicrobial coating,^{131, 142} catalyst,^{130, 143, 144} cancer theranosis,^{145, 146} and numerous others.

Figure 2.12. Possible pathways for further modification of polydopamine (PDA). Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.

2.4.2 PDA-based Materials for Tailored Surface Wettability

In the past decade, surface modifications using PDA and PDA hybrid materials in which the wettability is tunable has been investigated intensively. The strong adhesion on numerous surfaces, one of the most important properties of PDA, allows for tailoring the surface energy of surfaces. After modification, catechol groups of PDA show a significant enhancement of hydrophilicity of pristine superhydrophobic substrate (Figure 2.13).¹⁴⁷ The high surface energy of PDA is the key so that it can enhance the hydrolysis when the PDA coated surface contacts to water droplet. On the other hand, the growth of PDA nanoparticles, which are prepared by oxidative-induced polymerization, is believed to enhance surface roughness and further increase surface energy through the formation of carboxylic group, thus, resulting in superhydrophilic and underwater

superoleophobic behavior.¹⁴⁸ The tune of surface wettability of PDA coated surfaces brings a great advantage in membrane filtration technology in which PDA is deposited on the porous membrane.¹⁴⁹

Figure 2.13. One step surface modification of hydrophobic AAO membrane by PDA coating. The water contact angle drops significantly after PDA modification (a). The AAO surface after modification is highly hydrophilic then water droplets spread out to the whole area instead of individual droplets (b). The change of surface wettability is confirmed by the change in surface morphology (c) and surface chemistry (d). Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA.

Vecchia, et al. investigated that the key step in the polymerization of dopamine is the oxidation of catechol to o-quinone.^{65, 150} Therefore, controlling the oxidation environment is the most effective strategy to control the polymerization of dopamine, thus, controlling the hydrophilicity of PDA coating. The catechol groups of PDA trigger the Michael or Schiff base reaction with the surface modifiers containing amine or thiol-terminated molecules. Lu and co-

workers take advantage of this property of PDA to modify surface of hydrophilic melamine foam (MF). The PDA coated MF was further reacted with fluorinated thiol compound via Michael addition reaction. After modification, the foam became superhydrophobic and can easily remove oil from water with high efficiency.¹⁵¹ The as-prepared foam showed no significant change in morphology but it can completely repel water (Figure 2.14).

Figure 2.14. SEM images of the pristine melamine sponge (a) and modified sponge (b). The water contact angle on surface of the pristine (c) and as-prepared sponge (d). The modified sponge shows a high repellency of water that it floats on surface of water batch (e). Because the superhydrophobicity water droplet can be easily removed from surface of the as-prepared sponge without remaining any spill (f) Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA.

The Michael addition reaction is also helpful to tune the hydrophilic surface to dual-superlyophobicity. Wang and co-workers reported the modification of a PDA coated membrane with thiolated polyethylene glycol (PEG-SH).¹³⁷ Combining with surface roughness, the as-prepared membrane displayed underwater superoleophobic and underoil superhydrophobic behavior at the same

time, while water and oil can easily penetrate through the membrane in the air. The dual-superlyophobic behavior of the membrane allowed the separation of oil and water selectively depending on the wetting phase. In addition, the high chelating property of catechols also helps to form hydrogen bond with silanol groups and enhances hydrophilicity of the porous membrane.¹⁵² The enhancement of hydrophilicity of a surface not only contributed significantly to separate oil-in-water emulsion but also increased the antifouling ability.¹⁵³ It can be seen that the functionality of PDA brings tremendous applications that only PDA coating cannot and PDA is believed to be a good platform for further coating and modifications.

Chapter 3. Biomass-Derived Dual-superlyophobic Membranes for Selective Oil/water Separation

3.1. Introduction

The oil spillage and the oily water released from oil-refining industrial processes, cause negative impact on vegetation, marine, and agriculture, and need effective solution urgently.^{154, 155, 156, 157} Compared to conventional methods such as coagulation,¹⁵⁸ oil skimmer¹⁵⁹ or air flotation,¹⁶ separation using superwetting materials has shown considerable advantages, for example, environmental friendliness, high separation efficiency and cost effectiveness.^{22, 160, 161} Recently, materials with special wetting properties have shown promise in the separation of oil and water from mixtures in the forms of absorbents and membrane filtration.^{120, 162, 163, 164} Although oil sorbents display high oil/water separation efficiency, they typically have low separation rate, complicated preparation and limited uptake capacity.²³ In contrast, continuous separation methods such as super-wetting membranes can selectively allow water or oil to pass through and retain the other liquid, resulting in high separation efficiency, high flux and easy recovery of separated liquids.¹⁶⁵ In oil/water separation, continuous methods usually are categorized into two strategies: “oil removing” membranes with superhydrophobic property are able to retain water and “water removing” membranes with underwater superoleophobic property to retain oil.^{29, 166, 167, 168} However, under the thermodynamic point of view, these two properties are not expected to simultaneously appear on the same surface. The superhydrophobic state normally displays “lotus effect” which requires low surface energy.¹⁶⁹ In contrast, the underwater superoleophobic property demands high surface energy

which is similar to “fish-scale effect”.¹⁰⁵ Therefore, traditional filters commonly require two kinds of membranes to separate oil and water, making the filtration more costly and complicated. To date, only a few reports show successful separation using one type of membrane for both “oil removing” type and “water removing” type. In these reports, when the membrane is infused with oil, it can retain water. In contrast, once wetted by water, the membrane can retain oil, resulting in simultaneous underwater superoleophobicity and underoil superhydrophobicity.^{110, 137, 170, 171, 172} However, most of them still use either many-step fabrication method or expensive raw materials. More importantly, the impact of surface roughness, surface chemistry to dual-superlyophobicity has not been precisely investigated. It is highly desired to develop dual-superlyophobic membranes using a widely applicable fabrication method and cheap raw materials.

Biomass-derived materials have received considerable attention for the preparation of functional materials due to their low cost, easy availability, sustainability and environmental friendliness.^{173, 174, 175, 176} Recently, oil sorbents generated from pyrolysis of biomass have been applied to absorb oil from water. The pyrolysis produces highly hydrophobic carbonaceous surfaces that repel water effectively (Figure 3.1).⁴⁰ For examples, Yu and co-workers introduced a simple method to produce flexible and ultralight carbon nanofiber (CNF) aerogel from bacterial cellulose.¹⁷⁷ After pyrolysis at 1450 °C for 2h, the CNF was found to interconnect to a porous, 3D structure with $CA_w = 135.8^\circ$, and $CA_o \sim 0^\circ$. The aerogel showed ultrahigh oil absorption capacity from 6000 % to 14000 %,

depending on the oil types. Interestingly, the fire resistance of the aerogel provided an effective method to recover absorbed oil.

Figure 3.1. Oil sorbents generated from various biomass sources, such as bacterial cellulose (a), cotton (b), bamboo (c), waste paper (d), water melon (e) and wintermelon (f). The sorbent show high ability to remove oil from water. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

Zhang and co-workers reported another biomass-based, hydrophobic aerogel.¹⁷⁸ The aerogel was simply made from slowly pyrolysis cotton fiber at 800 °C for 2h. The twisted morphology of the carbon fiber allowed the gel to repel water and absorb various oils with capacity from 5000 % to nearly 19200 %. The aerogel also displayed excellent regeneration by distillation and combustion without decreasing in sorption capacity. The fabrication of carbon fiber aerogel by pyrolysis was also reported by Ma and co-workers.¹⁷⁹ The

authors used bamboo chopstick waste as the biomass source. The porous aerogel showed ultrahydrophobic property with $CA_W = 145^\circ \pm 2^\circ$; and $CA_O \sim 0^\circ$. Therefore, the aerogel exhibited high absorption capacity ranging from 30 to 129 times with different oils. Especially, other carbon-based sorbents derived from fruit's peel also were reported that exhibited high mechanical stability, flame retardancy, highly hydrophobic and great sorption capacity.^{180, 181} However, the pyrolysis of biomass also shows disadvantage. The process may release harmful gases such as carbon dioxide or nitrogen oxides to the air that causes secondary pollution. On the other hand, the drawback of using sorbents to remove oil from water has been already pointed out.

Among the biomass sources, cotton and kapok are the most abundant, renewable, and sustainable materials, thus promising for oil-water separation.^{178, 182} Herein, we report a facile approach to produce dual-superlyophobic fiber membranes using cotton and kapok fibers as substrate materials with the growth of PDA nanoparticles. Using a strong oxidizing agent (sodium periodate) under slight acidic solution (acetate buffer, pH = 5), homogeneous PDA particles of 100 nm on average aggregated on the surface of both hydrophilic (cotton) and hydrophobic (kapok) fibers, which were denoted as cotton@PDA and KP@PDA. Subsequently, the as-prepared brown cotton@PDA and KP@PDA fibers were infused either in aqueous phase to yield underwater superoleophobic membrane or in oil phase to obtain underoil superhydrophobic membrane with both CA_W and CA_O higher than 150° . They were then used to selectively separate oil and water (Figure 3.2). We also demonstrated that the morphology of PDA nanoparticles, which was controlled by reaction conditions, was the key for

fabrication of dual-superlyophobic membrane. Only an extreme roughness of PDA coated fiber resulted in dual-superlyophobicity, while smooth or less rough modification cannot. Our as-prepared membranes performed ultrahigh separation efficiency (higher than 99.98 %) toward different oil-water mixtures with high flux, which is comparative to reported literatures using gravity as driving force for separation.^{23, 137, 171, 183, 184} More over, the filtration of toluene/water mixture using both KP@PDA and cotton@PDA exhibited good regeneration while remaining high efficiency and dual-superlyophobicity. Hence, our approach offers a general solution for the selective separation of water and oil by using cheap, sustainable, bio-based materials, and cost- and energy-effective environmentally friendly process.

Figure 3.2. Scheme illustrates (a) the fabrication of PDA modified cotton fabric and natural kapok fabric, (b) the application of modified fabrics to selectively separate oil and water.

3.2. Experimental Section

3.2.1. Materials

Ceiba pentandra (kapok) fibers were collected from a local garden and cotton fibers were purchased from a medical store. The fibers were used directly without any purification or pre-treatment. Dopamine hydrochloride (DA), sodium periodate (NaIO_4), acetic acid (CH_3COOH) were purchased from Sigma Aldrich. Anhydrous sodium acetate (CH_3COONa), tris (hydroxymethyl) aminomethane hydrochloride (Tris-HCl), n-hexane (HEX), dichloromethane (DCM), chloroform (CF), carbon tetrachloride (CTC), toluene (TOL), o-xylene (XYL), styrene (STY), 1,3,5-trimethylbenzene (TMB) were purchased from Fischer Scientific.

3.2.2. Surface Modification of Kapok Fibers and Cotton Fibers

Surface modification of the fibers in acetate buffer was conducted as follows. Kapok fibers first were wetted in ethanol. After that, the fibers were immersed in acetate buffer ($\text{pH} = 5.0$) containing sodium periodate with concentration 4 mg ml^{-1} in a glass vial dopamine hydrochloride with different concentrations was then added quickly to the solution and the cap of the vial was closed immediately to prevent oxygen entrapment. The solution mixture was kept stirring in dark for 2 hours. After finishing, kapok fibers were taken out and washed under a strong flow of water to remove unbound particles and then dried in an oven at 70°C overnight before using. The same procedure was conducted for cotton fibers without pre-wetting in ethanol. The fibers after modification were denoted as

KP@PDA and cotton@PDA, respectively. The PDA modification on kapok and cotton at different conditions was conducted accordingly.

Surface modification of kapok and cotton in Tris buffer was conducted as follows. Kapok wetted with ethanol was immersed in Tris-HCl buffer (pH = 8.5). Dopamine hydrochloride was then added to the solution with final concentration 2 mg ml⁻¹. The mixture was then stirred well for 1 hour. After that, kapok was taken out and washed under a strong flow of water to remove unbound particles and then dried in an oven at 70 °C overnight before using. The same procedure was conducted with cotton without pre-wetting with ethanol. The fibers after modification were denoted as KP@PDA_{Tris} and cotton@PDA_{Tris}, respectively.

3.2.3. Characterizations

Field emission scanning microscopy (FE-SEM) was used to characterize the surface morphology of pristine and modified kapok and cotton. Surface chemistry was tested by Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photo electron spectrometer (XPS). The water and oil contact angle, under oil contact angle, under water contact angle was tested by Kruss DSA 25 contact angle analyzer. UV-Vis spectrum was used to test oil content and Karl-Fischer titrator was used to test water content after filtration.

3.2.4. Selective Water-oil Separation

A mixture of light oil and water was filtered through either cotton@PDA or KP@PDA membrane pretreated with water. For heavy oil/water separation, the

mixture was filtered through either cotton@PDA or KP@PDA membrane prewetted with corresponding heavy oil. A 20 mL of the oil/water mixture with volume ratio=1:1 was added to the filtration device. The separation is driven by gravity. Liquid flux is calculated by the following equation:²³

$$F = \frac{V}{A \times t} \quad (\text{Equation 3.1})$$

where F (Lm⁻²h⁻¹) is the flux, V is the volume of liquid passing through the membrane, A is working area of the membranes and t is permeated time. The filtration efficiency is measured by following equation:

$$E = \left(1 - \frac{C}{C_0}\right) \times 100\% \quad (\text{Equation 3.2})$$

where v₁ and v₂ are the volumes of filtrate and corresponding liquid before separation, respectively.

3.3. Results and Discussion

3.3.1. Preparation of Dual-superlyophobic Fiber Membranes

We used both the hydrophilic and hydrophobic fibers to study the change in surface composition as well as surface wettability after PDA modification. We observed that the color of the fibers changed from white (cotton) and light gray (kapok) to darkened brown after the surface modification. Moreover, the kapok which floated on water before modification, sank down after modification, revealing a successful modification and the change of surface wettability of cellulose-based fibers (Figure 3.3).

Figure 3.3. (a) Photo images of pristine cotton (white) and cotton@PDA (brown). Both cottons are hydrophilic. (b) Photo images of pristine kapok (light gray) and KP@PDA (brown). Kapok changes to hydrophilic after PDA modification.

It suggested that the polymerization of dopamine with a high concentration increased the surface roughness of the bare pristine fabric substrates.^{185, 186} Figure 3.4 shows that the surface topography of both cotton and kapok before and after modification by PDA changed dramatically. The pristine fabrics consisted of smooth surfaces (Figure 3.4-a,c), whereas after modified with PDA, the surfaces became rough due to deposition of PDA nanoparticles with a mean particles size of 100 nm (Figure 3.4-b,d). We believe that sodium periodate (SPI), which is a strong oxidizing agent, accelerated the polymerization rate, causing aggregation of PDA nanoparticles in a short reaction time.^{125, 148} In contrast, during polymerization with Tris-buffer in the presence of air, the dissolved oxygen polymerized dopamine slowly forming only a thin layer of PDA coating on the fiber surfaces, and hence, made no significant change in the surface roughness of the pristine substrates.^{152, 187}

Figure 3.4. SEM images of cotton and kapok fibers before and after modification with PDA in sodium periodate-acetate buffer. Insets show the morphology of single fiber of cotton and kapok before and after modification with PDA-SPI (the scale bar is 5 μm).

Figure 3.5 shows the FTIR spectra of cotton, kapok, cotton@PDA, and KP@PDA. It showed the two apparent absorption peaks at 1608 and 1510 cm^{-1} corresponding to aromatic C=C resonance vibrations, derived from the catecholic structure of PDA and amine -NH bending vibrations.¹⁸⁸ In addition, it also showed the absorption peak around 1720 cm^{-1} corresponding to the carboxylic group in the modified fibers.^{125, 148} However, all these absorption peaks were not present in both pristine cotton and kapok which contain only cellulose (in cotton) and lignin (in kapok), hence, confirming a successful surface modification of the pristine cotton and kapok with PDA.

Figure 3.5. ATR - FTIR spectrum of (a) cotton (black curve) and cotton@PDA (blue curve), (b) kapok (green curve) and KP@PDA (violet curve).

The compositional change was also investigated by X-ray photoelectron spectroscopy (XPS) analysis. The difference in XPS spectrum of cotton, cotton@PDA, kapok and KP@PDA was shown in Figures 3.6-a and 3.7-a. We observed the peaks of C1s and O1s in raw cotton and kapok, while the peak of N1s appeared in both cotton@PDA and KP@PDA, arising from PDA coating on the fibers.¹³⁹ In the C1s spectrum of kapok, the peaks of C–C/C=C at 284.6 eV and C–O at 285.3 eV indicated cellulose and lignin as the major content in the fibers.¹⁸⁹ It was also consistent with O1s spectrum which had only one peak of C–O at 532.2 eV (Figure 3.6 b-i and b-ii). The C1s peak of KP@PDA was fitted into four peaks of C–C/C=C at 284.5 eV, C–O/C–N at 286.5 eV, C=O at 287.8 eV and O–C=O at 288.9 eV, which were consistent with the O1s spectrum (Figure 3.6 c-i and c-ii).¹⁸⁷ In C1s XPS spectrum of raw cotton, three main peaks were observed of C–C/C=C at 284.6 eV, of C–O at 286.5 eV and of C=O at 287.8 eV whereas the two corresponding peaks were observed in O1s spectrum (Figure 3.7 b-i and b-ii). The three peaks -NH₂ (401.6 eV), -NH- (399.8 eV) and -N=

(398.5 eV) of N1s spectrum were analyzed in both KP@PDA and cotton@PDA (Figure 3.6 c-iii and 3.7 c-iii, respectively). It has been concluded based on the higher intensity of secondary amines that there was conversion from the primary amine group of dopamine to the secondary amine which is presented in indolic compounds,¹⁹⁰ implying a spontaneous polymerization of dopamine to PDA.^{139, 191} It also has been pointed out that the minor primary amine in the structure of PDA is caused by self-assembly of dopamine.¹²³ After surface modification, the XPS peaks of cotton@PDA are similar to those peaks of KP@PDA indicating the same surface components which are derived from the structure of PDA.¹⁹²

Figure 3.6. XPS analysis of pristine kapok (top row) and KP@ PDA (bottom row)

Figure 3.7. XPS analysis of pristine cotton (top row) and cotton@PDA (bottom row)

3.3.2. Surface Wettability of Underwater Superoleophobic and Underoil

Superhydrophobic Fiber Membranes

The surface wettability of cotton, kapok, cotton@PDA, and KP@PDA towards water and oil was shown in Figure 3.8. Pristine cotton displayed superhydrophilic (oleophilic) in air whereas, exhibited superhydrophilic nature underoil with water, showing $CA_W \sim 0^\circ$ and superoleophobic nature underwater with $CA_{O/W} = 161.8 \pm 1^\circ$. After PDA modification, the $CA_{W/O}$ of cotton@PDA increased significantly to $160.4 \pm 1.2^\circ$ showing superoleophobicity, while the $CA_{O/W}$ remained nearly unchanged (Figure 3.8-a). In contrast, kapok fiber was originally hydrophobic in air with $CA_W = 144.5 \pm 0.9^\circ$. Hence, it showed extremely high $CA_{W/O} = 165.1 \pm 3.8^\circ$, indicating the underoil superhydrophobicity and $CA_{O/W} \sim 0^\circ$, indicating the underwater superoleophilicity. Notably, after surface modification of kapok fabric, the CA_W

dropped to $\sim 0^\circ$, while $CA_{O/W}$ raised sharply to $158.1 \pm 0.4^\circ$ and the $CA_{W/O}$ dropped slightly to $161.6 \pm 1.0^\circ$ (Figure 3.8-b).

Figure 3.8. (a-b) Static contact angle (CA) of 3 μL water in air (left), CA of 3 μL water under oil (middle) and contact angle of 5 μL oil under water (right) of raw cotton (top) and cotton@PDA (below) (a), raw kapok (top) and KPs@PDA (below) (b), respectively. (c-d) dynamic interaction of the 3 μL water and 5 μL oil on surface of cotton@PDA (c) and KPs@PDA (d) submerged in oil and water.

The underwater superoleophobic property can allow water to permeate through the membrane and filtered off while retaining the oil on top. In contrast, the underoil superhydrophobic property allows oil to go through the modified membrane while water is retained. We also investigated the dynamic contact procedure to provide a deeper understanding of the underwater oil repellency and underoil water repellency of the cellulose-based fibrous membrane (Figure 3.8-c and d). To test this, droplets of oil (5 μL) and water (3 μL) were introduced on fibers with a preloading-relaxing cycle. The preloading and relaxing procedure can be recycled without dropping of any water or oil droplets. Therefore, we

believe that the wetting states of the fibrous membrane in both oil and water medium shows Cassie–Baxter type behavior where the adhesion force of liquid droplet on the surface of the composite is very low.^{45, 193}

Besides the effect of chemical composition, the wettability of the fibers under oil or water also depends on surface morphology.¹⁹⁴ We investigated the impact of surface morphology on the ability of oil repellency underwater and water repellency underoil. We found that the morphology of deposited PDA nanoparticles strongly depends on the dopamine concentration and reaction time.^{125, 186} Figure 3.9-a and 3.9-b illustrate the dependence of coating morphology of cotton and kapok on concentrations of dopamine, C_{DA} , while the reaction time was kept constant at 2 hours. The surface of both cotton and kapok was covered by a thin layer of PDA when a low C_{DA} was used ($C_{DA} = 0.5 \text{ mg ml}^{-1}$). However, when C_{DA} increased to 1 mg ml^{-1} and 1.5 mg ml^{-1} , nanoparticles were formed on the fiber surfaces, thus enhancing surface roughness. It was further noticed that the coating of PDA nanoparticles was denser when $C_{DA} = 1.5 - 2 \text{ mg ml}^{-1}$ as compared to $C_{DA} = 1 \text{ mg ml}^{-1}$. However, when we further increased C_{DA} to 3 mg ml^{-1} , the surface roughness again decreased in both cotton@PDA and KP@PDA. We believe that either the excess PDA nanoparticles formed during reaction just levels off the valleys of the rough surfaces and smoothens partly the fiber surfaces or the excess PDA nanoparticles were just formed as by products in the reaction without depositing on the fiber surfaces.¹⁸⁶ The result subsequently showed that varying C_{DA} at a fixed reaction time caused a big shift in $CA_{W/O}$ and $CA_{O/W}$ for submerged cotton@PDA and KP@PDA membranes (Figure 3.9-c and 3.9-d). For examples, cotton@PDA fibrous membrane only

displayed dual-superlyophobicity when C_{DA} was higher than 0.5 mg ml^{-1} making both $CA_{W/O}$ and $CA_{O/W}$ above 150° . Whereas, KP@PDA fibrous membrane performed the dual-superlyophobicity only when C_{DA} was higher than 1 mg/ml .

Figure 3.9. SEM images of single fiber of PDA modified cotton (a) and kapok (b). The $CA_{W/O}$, $CA_{O/W}$ of PDA modified cotton (c) and kapok (d), respectively at various dopamine concentration for reaction time 2h.

The morphology of PDA coating, in addition, also depended on reaction time (Figure 3.10). It was noticed that the rough cover was observed on surface of cotton and kapok, respectively, when reacted 0.5 h (Figure 3.10- a and e). When we further increased the reaction time while fixing C_{DA} at 2 mg ml^{-1} , the density/amount of PDA nanoparticles also increased, thus further enhanced the surface roughness (Figure 3.10- b, c, f, g). This phenomenon did not result into much difference to the $CA_{W/O}$ and $CA_{O/W}$ for cotton@PDA and KP@PDA

membranes. Both KP@PDA and cotton@PDA showed $CA_{W/O}$ and $CA_{O/W}$ higher than 150° when reaction time increased from 0.5 hours to 4 hours (Figure 3.10-d and h), indicating less dependency of dual-superlyophobicity on reaction time. Hence, we showed that the dual-superlyophobicity of cotton@PDA and KP@PDA fiber membranes can be achieved by adjusting the dopamine concentrations and/or reaction time.

Figure 3.10. SEM images of the single fiber of PDA modified cotton (a-c) and kapok (e-g) and $CA_{W/O}$, $CA_{O/W}$ of PDA modified cotton (d) and kapok (h), respectively at various reaction time for dopamine concentration at 2 mg ml^{-1} .

Next, we investigated the influence of polymerization rate on dual-superlyophobicity of both cotton@PDA and KP@PDA. In this experiment, we used the oxygen in air (in Tris buffer, pH = 8.5) to replace SPI as the oxidizing agent and the modified fibers of cotton and kapok were denoted as cotton@PDA_{Tris} and KP@PDA_{Tris}, respectively. C_{DA} was maintained at 2 mg ml^{-1} and reaction time was 1 hour. The CA_W , $CA_{W/O}$, $CA_{O/W}$ of cotton@PDA_{Tris} were 0° , $162.52 \pm 2.75^\circ$ and $131.53 \pm 2.45^\circ$, respectively. On the other hand, the CA_W , $CA_{W/O}$, $CA_{O/W}$ of KP@PDA_{Tris} were $135 \pm 5.6^\circ$, $164 \pm 1.8^\circ$ and $123 \pm 2.48^\circ$,

respectively (Figure 3.11). We found that slow polymerization rate of dopamine cannot result dual-superlyophobicity.

	$CA_{w/a}$	$CA_{w/o}$	$CA_{o/w}$
KP@PDA _{Tris}	air Water	Oil Water	Water Oil
Cotton@PDA _{Tris}	air Water	Oil Water	Water Oil

Figure 3.11. Water contact angle in air ($CA_{w/a}$), water contact angle under oil ($CA_{w/o}$) and oil contact angle under water ($CA_{o/w}$) of KP@PDA_{Tris} (top) and cotton@PDA_{Tris} (bottom).

3.3.3. Mechanism of Underoil-water Surface Wettability

The intrusion pressure has been used to describe the wetting state of materials in association with contact angle.¹⁹⁵ Herein, we modeled the water-oil interaction mechanism when the membranes were submerged in water or oil (Figure 3.12).

$$\Delta P = \frac{2\gamma_L}{R} = \frac{-4\gamma_L \cos \theta}{d} \quad (\text{Equation 3.3})$$

where ΔP is intrusion pressure, R is the radius of liquid droplet, d is average distance between single fibers. θ is $CA_{w/o}$ or $CA_{o/w}$. On the assumption that R

and d are unchanged, the intrusion pressure only depends on contact angle of the liquid droplet. From equation 3.3, when $\theta > 90^\circ$, the fibers can prevent the penetration of the liquid droplet due to negative capillary effect. In contrast, when $\theta < 90^\circ$, the liquid can permeate the fibers spontaneously due to capillary effect.^{170, 171, 196} For example, the raw cotton has $CA_{W/O} = 0^\circ < 90^\circ$ (Figure 3.12-a). Thus, it cannot repel water droplet underoil. In contrast, the raw kapok has $CA_{O/W} = 0^\circ < 90^\circ$ (Figure 3.12-d), therefore, it cannot repel oil underwater. However, raw cotton can repel oil underwater (Figure 3.12-b) and raw kapok can repel water underoil (Figure 3.12-c) as in both cases $\theta > 90^\circ$. In case of modified fibers, the cotton@PDA and KP@PDA membranes display the opposite phenomenon. Both fibers have $\theta > 90^\circ$, thus possibly repelling water underoil and oil underwater and they can support pressure under the liquid. Moreover, the lower contact angle ($\theta < 90^\circ$) of cotton@PDA and KP@PDA fibers in air caused a capillary effect ($\Delta P < 0$). Thus, oil and water can penetrate through and wet the as-prepared fibrous membranes. It is noticed that when water (or oil) interacts to cotton@PDA and KP@PDA prewetted by oil (or water), water (or oil) cannot pass through unless we apply larger pressure (ΔP). Hence, from the above analysis, we believe that the prewetted cotton@PDA and KP@PDA membranes are suitable to selectively separate oil and water from oi/water mixtures.

Figure 3.12. Schematic diagram of the wetting mechanism underwater and under oil of cotton before (a, b), kapok (c,d) and after surface modification with PDA nanoparticles (e,f).

As mentioned, Wenzel and Cassie's equations can illustrate the wettability of superwetting/super anti-wetting surfaces.^{105, 197} Here, we apply these equations to obtain deeper understanding on the underwater superoleophobic and underoil superhydrophobic cotton@PDA /KP@PDA fibers. Using Cassie's and Wenzel's equation, the wettability of cotton@PDA and KP@PDA underwater or underoil when the roughness of fibers changes can be clearly explained. The smooth cotton@PDA /KP@PDA fibers can be considered when $C_{DA} = 0.5 \text{ mg ml}^{-1}$ and the rough fibers are taken when C_{DA} is higher. Taking the KP@PDA as an

example, the $CA_{O/W}$ on smooth fiber is only $108.8 \pm 4.84^\circ$. However, $CA_{O/W}$ on a rough fiber increases to $148.56 \pm 0.96^\circ$ ($C_{DA} = 1 \text{ mg ml}^{-1}$), and $150.14 \pm 0.94^\circ$ ($C_{DA} = 3 \text{ mg ml}^{-1}$) and $157.56 \pm 1.58^\circ$ ($C_{DA} = 1.5 \text{ mg ml}^{-1}$), $158.14 \pm 0.58^\circ$ ($C_{DA} = 2 \text{ mg ml}^{-1}$). Nevertheless, only an extreme roughness ($C_{DA} = 1.5 \text{ mg ml}^{-1}$ and 2 mg ml^{-1}) can result a Cassie state, otherwise, the contact angle only presents Wenzel state. To better understand, we sketch the models representing wetting states on different roughness fibers submerged in one liquid (Figure 3.13). Smooth fibers display Young's state in which CA of droplet could be a little higher than 90° (Figure 3.13-a). When the surface roughness is small, Wenzel's model is dominant (Figure 3.13-b). However, Cassie's model is dominant when the roughness raises to the extreme because the liquid 1 intrudes into the solid-liquid 2 interface as roughness increases (Figure 3.13-c). Now we come back to the case of KP@PDA above. When roughness of the fiber increases, the $CA_{O/W}$ also increases. However, the roughness is so small that liquid 1 cannot intrude between the solid-liquid interface, causing a sticky liquid 2 droplet (the CA is normally less than 150°). When the roughness further increases, liquid 1 now can intrude into the interface, enhancing the liquid 2 repellency and causing a slipper droplet (the CA is normally higher than 150°).¹⁹⁸

Figure 3.13. Schematic diagram of under-liquid 1 contact angle of liquid 2 on surface of smooth fiber (a-Young state) and rough surface (b-Wenzel state or c-Cassie state). Liquid 1 and liquid 2 can be either oil or water, depending on surface chemistry of the fibers. The fibers are in the same surface chemistry: cotton@PDA /KP@PDA.

3.3.4. Selective Separation of Water-oil using As-prepared Prewetted Modified Membranes

The water-light oil and water-heavy oil mixtures separation using dual-superlyophobic cotton@PDA and KP@PDA fibers membranes driven by gravity are shown in Figure 3.14. TOL/water and CF/water mixtures were taken to illustrate selective separation of the membranes; other oil/water mixtures separation were tested accordingly. As shown in Figure 3.14-a,b, TOL and CF were effectively separated out of water using cotton@PDA and no visible liquids were observed in the filtrates. The water flux in toluene/water separation was $20059 \pm 457 \text{ Lm}^{-2}\text{h}^{-1}$ and the oil flux in CF/water separation was $22743 \pm 524 \text{ Lm}^{-2}\text{h}^{-1}$. Figure 3.14-c,d shows that the cotton@PDA membrane exhibited purity higher than 99.995% for water removal with oil content ranging from 7.5 ± 3.2 ppm (TMB) to 42.6 ± 8.5 ppm (TOL). The membrane also exhibited purity higher than 99.98% for oil removal process with water content ranging from 48.5 ± 2.4 ppm (CTC) to 102.7 ± 1.5 ppm (CF). The same separation was applied to KP@PDA membrane. As shown in Figure 3.14-e,f, TOL and CF were also effectively separated out of water using KP@PDA. The water flux in TOL/water separation was $4212 \pm 47 \text{ Lm}^{-2}\text{h}^{-1}$ and the oil flux in CF/water separation was $8618 \pm 223 \text{ Lm}^{-2}\text{h}^{-1}$. Figure 3.14-g,h show that the KP@PDA membrane exhibited purity higher than 99.995% for water removal and oil content ranging from 12.9 ± 4.9 ppm (XYL) to 43.7 ± 5.1 ppm (TOL). The membrane also exhibited purity higher than 99.98% for oil removal process with water content ranging from 37.3 ± 1.4 ppm (CTC) to 130.1 ± 2.4 ppm (CF). The above analysis confirmed the excellent ability of cotton@PDA and KP@PDA to selectively

separate oil and water, which is comparable to the dual-superlyophobic membranes that are reported previously (Table 3.1).

Figure 3.14. (a,b) Separation illustration of toluene/water and CF/water. (c) Separation efficiency of mixtures between water, light oils and heavy oils. (d) Oil content and water content analysis after separation using cotton@PDA. (e,f) Separation illustration of toluene/water and CF/water. (g) Separation efficiency of mixtures between water, light oils and heavy oils. (h) Oil content and water content analysis after separation using KP@PDA.

Next, we investigated the re-generation of the biomass membranes. Taking toluene/water mixture as an example, the separation was applied to cotton@PDA and KP@PDA for 10 cycles. As shown in Figure 3.15, the membranes still exhibited excellent separation efficiency of higher than 99.99 %. Moreover, cotton@PDA displayed content of toluene ranging from 42.7 ppm to 93.6 ppm; while KP@PDA displayed content of toluene ranging from 35.5 ppm to 83.9 ppm. Interestingly, the fiber membranes still performed dual-superlyophobicity after 10 cycles separation of water/oil, For example, $CA_{W/O}$ and $CA_{O/W}$ of cotton@PDA were $156.46 \pm 2.56^\circ$ and $157.82 \pm 3.87^\circ$. $CA_{W/O}$ and $CA_{O/W}$ of KP@PDA were $158.87 \pm 1.57^\circ$ and $163.22 \pm 1.35^\circ$.

Figure 3.15. (a) Separation efficiency of water/toluene mixture, (b) oil content measured in filtrate after separation, (c) $CA_{W/O}$, $CA_{O/W}$ after 10 cycles separation using cotton@PDA membrane, (d) Separation efficiency of water/toluene mixture, (b) oil content measured in filtrate after separation, (c) $CA_{W/O}$, $CA_{O/W}$ after 10 cycles separation using KP@PDA membrane.

Figure 3.16. SEM images of (a) cotton@PDA fiber and KP@PDA fiber (b) after 10 cycles separation of oil and water.

After the re-generation, morphology of the fibers was examined. Figure 3.16 shows that the morphology of the cotton@PDA and KP@PDA fibers did not change significantly after separation. High roughness fibers were observed after

10 cycles separation indicates a high durability of the membranes. From the above results, the as-prepared cellulose-based fiber membranes are promising for long-term usage to separate water-oil mixtures selectively.

Materials	Fabrication method	Cost	Separated substances	Flux (Lm ⁻² h ⁻¹)	Efficiency	Ref
Corn straw powder	The con straw powder is mixed with waterborne polyurethane and then spray-coated on cotton fabric	Low	Light oil/water /heavy oil	13680 (water flux)	>98 %	[23]
				32040 (light oil flux)	>98 %	
				47880 (heavy oil flux)	>98 %	
Potato residue	The potato residue powder is mixed with waterborne polyurethane and then spray-coated on stainless steel mesh	Low	Kerosene, petroleum ether, rapeseed oil, toluene, hexane, chloroform, tetrachloroethane and water	25000 (water flux)	>97 %	[171]
				36000 (oil flux)	>98 %	
TiO ₂ nanorods	Thermal deposition of TiO ₂ nanorods on Cu foam	High	Water and diesel	245 000 (oil flux)	>99 %	[183]
				65000 (water flux)	>99 %	
Polysulfone (PSU)	3D printing technique is applied on PSU powder	High	Hexane, petroleum ether, heptane, mineral oil and water	~19000 (both oil and water flux)	>99 %	[184]
SiO ₂ nanoparticles /PDA/PEG	Electrospinning tri-layer of PVDF, hydrophobic SiO ₂ , followed by surface modification of PDA and PEG	High	10% petroleum ether and water	463 (water flux)	>99.99 %	[137]
			10% water and petroleum ether	1900 (oil flux)	>99.99 %	
PDA nanoparticles	One step deposition of Polydopamine nanoparticles on cotton fiber	Low	Toluene/water	20059 (water flux)	>99.95 %	This work
			Water/chloroform	22473 (oil flux)	>99.8 %	
PDA nanoparticles	One step deposition of Polydopamine nanoparticles on natural kapok fiber	Low	Toluene/water	4212 (water flux)	>99.95 %	This work
			Water/chloroform	8618 (oil flux)	>99.8 %	

Table 3.1. The advantages of as-prepared biomass-based membranes to other available membranes.

3.4. Conclusion

In conclusion, we have fabricated the dual-superlyophobic membranes by mussel-inspired surface modification of PDA nanoparticles on the surface of biomass wastes such as cotton fibers and kapok fibers. The preparation was simple and made use of biomass wastes effectively. The membranes exhibited excellent repellency of oil underwater and repellency of water underoil which were not obtained with the modification of PDA thin layer coating. In addition, the dependence of dual-superlyophobicity on surface morphology of PDA coating was also investigated. Oil/water mixtures were selectively separated with a high efficiency, high flux and good regeneration. The simple fabrication, environmentally friendly, and abundant resource of raw materials will allow us to scale up the whole process and use the membranes for real-world separation applications.

We would like to highlight here the consistencies of the raw materials. For example, the kapok fibers are collected from a local garden, while the cotton fibers are purchased from a medical store. We agree with the examiner that this sample collection does not assure the quality of the raw materials. However, the main purpose of this surface modification is to estimate the adhesive property of PDA on any substrate. Indeed, kapok is a natural resource with hydrophobic property. The fibers are widely available in tropical lands such as in Singapore. We would like to compare with hydrophilic fibers, for example, cotton which surface is easily modified. Here we show Figures 3.8a and 3.8b again to clarify the property of raw materials. As shown, the raw cotton cannot repel water

underoil, while the raw kapok cannot repel oil under water. After surface modification with PDA nanoparticles, both cotton and kapok are able to repel water underoil as well as repel oil underwater, revealing the dual-superlyophobicity. This confirms the universal adhesion of PDA on both hydrophilic and hydrophobic substrates and that PDA can tailor wetting behaviour of the surfaces to exhibit unique property. To justify the impact of raw materials on the final outcomes, we characterize diameter of the raw fibers in different batches. Figure 3.17 below shows SEM images of raw cotton and raw kapok fibers collected in three different batches. In each batch, five random fibers are measured their diameter. As shown, diameter of raw cotton ranges from 14.5 μm to 16.5 μm in all three batches, while diameter of raw kapok ranges from 15.5 μm to 23.0 μm in all three batches. The similarity of size distribution of fibers among different batches ensure the outcomes of as-prepared membranes. Although, the as-prepared membranes exhibit excellent separation flux and efficiency, we agree with the examiner that a further study in future work should be carried to investigate the impact of different materials sources to the final outcomes.

Figure 3.17. SEM images of three different batches of raw cotton (top row) and kapok (bottom row)

Chapter 4. Polydopamine-mediated Superlyophobic Coating for Efficient Separation of Immiscible Liquids

4.1. Introduction

Separation of oil/water mixture using wetting materials has been extensively investigated during the last decade.⁵³ There are two main types of wettable materials to separate oil and water: “oil-removing” (hydrophobic) and “water-removing” (hydrophilic).¹⁹⁹ However, the wastes released in industrial processes such as multi-phase liquids extraction or chemical reaction contain more complicated liquids components.^{200, 201} Indeed, the separation of immiscible organic liquids is more difficult than only oil/water. The significantly lower surface tension of organic liquids than water causes oleophilicity to almost any surfaces, which makes the common hydrophobic and hydrophilic materials unable to separate. Recently, only a few membranes with lyophobic/superlyophobic property have been reported to separate immiscible organic liquids mixtures such as nanofibrous membrane,^{70, 196} and copper mesh.¹⁹⁵ It suggests that the membranes display oleophobicity to one liquid and oleophilicity to the other one. With the SE of the membranes falling between the ST of the two liquids, lower ST liquid can pass through, while the higher ST liquid is retained. However, the multistep fabrication and limited option of materials may inhibit the practical application. In addition, to the best of our knowledge, no sorbents have been developed to separate immiscible liquids thus far. Herein, we report a simple approach for the separation of immiscible liquids via both static and continuous strategies using 3D sorbents and 2D membranes. The as-prepared materials exhibited superlyophobicity to high surface tension

(ST) liquids such as formamide or diethylene glycol and superlyophilicity to liquids with ST lower than 30 mN/m such as n-hexadecane.

Figure 4.1. Schematic illustration of the fabrication process PDA-SPI modified materials, followed by further surface modification with ODTS and their application in separation of immiscible liquid.

As illustrated in Figure 4.1, raw materials with both 2D and 3D conformation, hydrophobic and hydrophilic property were modified with PDA nanoparticles. We then used PDA coating as the template to prepare broad range of superlyophobic materials which were fabricated by growing silicone microsheets (SMSs) derived from hydrolysis of octadecyl trichlorosilane (ODTS) on the PDA coated materials. We have demonstrated that the higher

loading of PDA offered more chelating surfaces, on which more SMSs were observed, while surface without PDA treatment only obtained thin silicone layer (SL). The higher surface roughness from SMSs brings new insights into both theoretical understanding and practical application. This work also offers a new strategy besides membrane technology for a general liquid waste treatment process.

4.2. Experimental Section

4.2.1. Materials

Filter papers were purchased from Whatman plc. Melamine sponge, polyurethane foam, polyester fabric, and cotton fabric were bought from a supermarket. Dopamine hydrochloride (DA), sodium periodate (NaIO_4), octadecyl trichlorosilane (ODTS), octyl trichlorosilane (OTS), methyl trichlorosilane (MTS), 1H,1H,2H,2H-perfluorododecyl trichlorosilane (PFDTs), 1H,1H,2H,2H-perfluorooctyl trichlorosilane (PFOTS), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$), acetic acid (CH_3COOH), formamide (FM), glycerol (GLY), ethylene glycol (EG), diethylene glycol (DEG), n-hexadecane (HDC), soybean oil, silicon oil, oleyamine, octadecene were purchased from Sigma Aldrich. Anhydrous sodium acetate, tris (hydroxymethyl) aminomethane hydrochloride (Tris-HCl), technical grade ethanol, n-hexane, acetone, toluene, chloroform were purchased from Fischer Scientific. Carbon tetrachloride (CCl_4) was purchased from S1-LAB PTE. LTD, Singapore. Wasted cooking oil and pump oil were collected after use.

4.2.2. Surface Modification

Whatman filter paper (pore size 3 μm) was immersed in acetate buffer (pH = 5.0) containing different mass ratios of sodium periodate (SPI) and dopamine hydrochloride (DA). The mixture was sealed and stirred in dark for 2 hours for DA:SPI = 1:2 and also for 3 hours in case of DA:SPI = 1:3. After finishing, the paper was taken out and rinsed with water and ethanol gently and dried in an oven at 50 °C overnight before further modification. The polydopamine modified papers were denoted as paper@PDA. Dried filter papers (pristine and modified ones) was immersed in toluene (removed trace water by CaCl_2) containing 1% volume of either ODTS, OTS or MTS, PFDTS or PFOTS in 1 hour. The filter papers were then taken out and immersed in acetone in 10 minutes, followed by washing with ethanol and n-hexane, respectively. The silanized papers were denoted as paper@PDA@C18. Similarly, other substrates were modified by various ratio of PDA:SPI and ODTS following the same procedure. Briefly, filter paper (pore size 10 μm), stainless steel mesh, polyester fabric, cotton fabric, melamine sponge and polyurethane foam were immersed in acetate buffer containing mass ratio of DA:SPI = 1:2. The mixture was sealed and stirred in dark for 2 hours. After finishing, the paper was taken out and rinsed with water and ethanol gently and dried in an oven at 50 °C overnight before further modification. Dried materials were further modified by ODTS with the procedure described above. ODTS modified pristine materials were also prepared similarly without the DA:SPI modification. Modification of substrate materials with PDA in air was conducted by immersing materials in Tris buffer (pH = 8.5) containing

2 mg ml⁻¹ dopamine for 2 hours. The ODTS modification was conducted similarly.

4.2.3. Characterization

Surface morphology of pristine and modified substrates was characterized by field emission scanning electron microscopy (FE-SEM, JSM-6700F) and scanning microscopy (SEM). Surface chemistry was characterized by Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectrometer (XPS). Organic content was characterized by thermal gravimetry analysis (TGA, SDT Q600) under continuous 100 mL/min nitrogen flow at a heating rate of 20 °C/min. The contact angle of water and other liquids were characterized by Dataphysics contact angle system OCA 15ec and Kruss DSA 25 contact angle analyzer.

4.2.4. Oil Absorption Capacity Test

To test the oil absorption capacity (M), the MS@PDA₁@C18 and PU@PDA₁@C18 foams are immersed in various oils for 10 min at room temperature. The foams were then taken out and weighted to obtain the absorbed mass. The capacity was calculated by the following equation.

$$M = \frac{m - m_o}{m_o} \quad \text{(Equation 4.1)}$$

Where m_o and m are weight of the foams before and after absorption of oils, respectively. The foams were rinsed with ethanol to regenerate after each cycle of oil absorption (n-hexane) and dried at 70°C in air. At the same time, the contact

angle of formamide on surface of regenerated foams was also investigated to evaluate the recyclability.

4.2.5. Immiscible Liquid Separation

4.2.5.1. Separation of Immiscible Organic Mixture by Filtration

The as-prepared mesh@PDA₁@C18 and cotton@PDA₁@C18 are fixed between two glass fixtures. The mixture of CCl₄ and water or formamide (4/1, v/v) was poured through these membranes and the separations were driven by gravity. The paper@PDA₁@C18 (pore size 10µm) is fixed in a vacuum driven filtration device. The mixtures of carbontetrachloride and water, formamide (10/1, v/v) were mixed under magnetic stirrer. The separation was driven by a vacuum pump at 100 mbar. The average separation flux was calculated by the following expression.

$$F = \frac{V}{A \times t} \quad \text{(Equation 4.2)}$$

where V is volume of permeable liquid, A is effective area of membrane and t is filtration time measured when no dropping of liquid was observed.

The separation efficiency was evaluated by the following expression.

$$E = \frac{V_1 + V_2}{V_0} \times 100\% \quad \text{(Equation 4.3)}$$

where V₁ is collected volume, V₂ is the volume absorbed by membrane and V₀ is original volume of the passing liquid.

4.2.5.2 Separation of Immiscible Organic Mixture by Absorption

The separation of immiscible liquid mixture is demonstrated by the absorption of light oil and heavy oil out of formamide. n-hexadecane (light oil, colored with oil red O) and CCl₄ (heavy oil, colored with oil red O) were mixed with formamide. MS@PDA₁@C18 and PU@PDA₁@C18 were then used to selectively absorb the oils from mixture. For the n-hexadecane/formamide mixture, the foams floated on surface and quickly absorbed oil. For the CCl₄/formamide mixture, we manually immersed the foams into the formamide to contact with the CCl₄ and the oil was absorbed. The dynamic separation by absorption is demonstrated as following schedule: (1) n-hexadecane (colored by red dye) and formamide was mixed using a high speed stirrer. MS@PDA₁@C18 was then placed into the stirring mixture and taken out after few seconds. The disappearance of red color indicated a completed absorption. (2) A piece of MS@PDA₁@C18 was dropped into toluene/formamide (1/1, v/v). The foam was then taken out and squeezed to remove the absorbed toluene. The separation was repeated until no red color was observed in the formamide batch.

4.3. Results and Discussion

4.3.1. Preparation of paper@PDA and paper@PDA@C18

We started with the 3 μm pore size filter paper to optimize fabricating conditions, other materials were then modified through the optimized process. Figure 4.2 below shows that surface of the filter paper before and after modification with PDA changed significantly.

Figure 4.2. SEM images of filter paper (pore size 3 μm) raw (a) and modified by PDA particles at different dopamine:SPI mass ratios and time: DA:SPI = 1:2, react 2 hours (b), DA:SPI = 1:2, react 2 hours (c), DA:SPI = 1:3, react 3 hours (d).

Compared to the smooth surface of pristine filter paper (Figure 4.2-a), the surface of modified filter papers showed rough surfaces attached due to the deposition of PDA particles. The aggregation of PDA particles was induced by the strong oxidizing agent – sodium periodate (SPI).^{125, 148} Moreover, we found that the morphology of PDA coating strongly depended on the mass ratio between DA and SPI. When 2 mg ml^{-1} dopamine reacted with 4 mg ml^{-1} SPI (i.e., at the mass ratio of DA: SPI = 1:2) for 2 hours (Figure 4.2-b), a homogeneous coating of PDA particles with a mean particles size of 100 nm was observed. On the other hand, when the SPI increased to 6 mg ml^{-1} (i.e., at the mass ratio of DA: SPI = 1:3) (Figure 4.2-c), the coating of PDA was no longer homogeneous. Some bigger particles with a mean particles size of 250 nm as well as some big clusters were observed. The filter papers with PDA modification were denoted as paper@PDA. Next, we investigated the effect of PDA content to the morphology of surface after silanization. As shown, the silanization did not change or damage

the fiber structure. For the pristine filter paper, the surface of fiber remained smooth even after the surface treatment with ODTS (Figure 4.2-d). After ODTS treatment, the surface morphologies of paper@PDA samples changed dramatically. The SMSs were observed to grow on the surface of paper@PDA, leading to the highly rough surfaces after silanization. We denoted the filter paper after ODTS modification as paper@C18 and paper@PDA@C18. ODTS has been used to modify surface of the paper and various substrates which have hydroxyl-terminated solid surface.^{202, 203, 204, 205} As shown, due to its slow hydrolysis, ODTS modification intended to form ordered monolayers on the surface of the substrates via strong interchain van der waals forces.^{52, 193, 206} This explained the SL observed on paper@C18. In contrast, faster hydrolysis and condensation of alkyl silane, such as methyl silane, have been illustrated resulting in 3D aggregated nanostructure on surface of substrates.^{207, 208} Therefore, we believe that the coating of PDA on surface of filter paper before silanization triggers the condensation of silanols derived from ODTS. However, the density of SMSs was not the same on the surface of paper@PDA@C18 samples. For the case of DA: SPI = 1:2 (paper@PDA₁), the SMSs had a high density with well-retained morphology (Figure 4.2-e); while in the case of DA: SPI = 1:3 (paper@PDA₂), SMSs did not cover fully the surface of cellulose fiber (Figure 4.2-f). This difference was probably caused by the amount and morphology of PDA coated on surface of cellulose fiber.

4.3.2. Study of surface components and surface wettability

The presence of PDA coating on the surface of filter paper was examined by thermal gravimetric analysis (TGA). Figure 4.3-a shows the residual weight of pristine and PDA modified filter papers during the TGA process. There was a significant difference in decomposition temperature between pristine filter paper and paper@PDA₁ and paper@PDA₂. The pristine filter paper had an onset of thermal decomposition temperature at around 350 °C, followed by a decrease in residual mass. In contrast, the paper@PDA₁ and paper@PDA₂ had the lower thermal decomposition temperature, around 100 °C less than the unmodified paper. The lower thermal decomposition temperature has been attributed to the depolymerization of catechol groups of PDA.²⁰⁹ In addition, the residual weights of pristine filter paper, paper@PDA₁ and paper@PDA₂ were 6.07 %, 14.41 % and 8.89 %, respectively. The mass residues revealed a considerable amount of PDA particles coated on the surface of filter paper and that amount was affected by the precursor ratio. Higher amount of PDA was observed on paper@PDA₁ compared to paper@PDA₂. Furthermore, the change in chemical components of pristine filter paper and paper@PDA was investigated by ATR-FTIR (Figure 4.3-b). The spectrum shows the apparent absorption peak at 1608 cm⁻¹, which represents the aromatic C=C resonance vibrations from catecholic structure of PDA and the peak at 1510 cm⁻¹, which represents the amine N-H bending vibrations.¹⁸⁸ In addition, the absorption peak around 1720 cm⁻¹, which is assigned to the carboxylic group, was also observed in PDA modified papers.^{125,}
¹⁴⁸ All of the above absorption peaks were not observed in pristine filter paper

which contains only cellulose fibers, revealing a successful coating of PDA on the surface of filter paper. After silanization, a strong double peak was obtained at 2900 and 2800 cm^{-1} , representing the signal of a long alkyl chain, which was also confirmed by asymmetric bending of methyl group at around 1465 cm^{-1} .²¹⁰ Furthermore, the absorption peak at 780 cm^{-1} assigned for Si-O-Si bonding formed after condensation (Figure 4.3-c).²¹¹ All these peaks appeared on the spectrum of both pristine and PDA modified filter paper. This suggests a successful surface hydrophobization using ODTs on surfaces of both cellulose and PDA.

The XPS analysis further confirms the successful surface modification. Taking paper@PDA₁ as an example, Figure 4.3-d shows XPS spectra of the paper before and after PDA decomposition as well as after ODTs surface modification. The spectrum of pristine filter paper was found to be lack of N1s peak and Si2p peak while there was no Si2p peak in the paper@PDA spectrum as well as no N1s peak in the paper@PDA@C18 spectrum. The three components of N1s peak in the paper@PDA spectrum in Figure 4.3-e corresponded to amine groups (R-NH₂, 401.6 eV), substituted amines (R-NH-R, 399.8 eV), and imino groups (=N-R, 398.5 eV).¹³⁹ The higher intensity of substituted amines implied the conversion to secondary amine from the primary amine. This suggested that the oxidation under SPI converted dopamine to indolic compounds and spontaneously polymerized to PDA.¹⁹¹ It has been concluded that the noncovalently self-assembled dopamine caused the minor primary amine in the structure of PDA.¹²³ XPS scanning of the Si 2p region in Figure 4.3-f showed two main peaks at 100.1 eV and 102.2 eV. The peak observed at 100.1 eV

assigned to Si-C bonds²¹² from the structure of alkylsilane in which the alkyl chains and the silicon atoms form covalent bonding. Likewise, the peak at 102.2 eV attributed to Si-O bonds,²¹³ suggesting the hydrolysis of chloro alkylsilane. These evidences confirm the consecutive coating of PDA and ODTS on the surface of filter paper.

Figure 4.3. TGA curve (a) and FT-IR (b) of pristine filter paper, paper@PDA₁ and paper@PDA₂. FT-IR (c), the whole XPS spectrum (d), XPS analysis of N1s (e) and XPS analysis of Si 2p of paper@C18, paper@PDA₁@C18 and paper@PDA₂@C18 (f).

Figure 4.4-a shows static contact angle (CA) of liquids with different surface tensions on the surface of paper@C18, paper@PDA₁@C18 and paper@PDA₂@C18 which were denoted as (a), (b) and (c), respectively. The figure indicated that the difference in PDA coating prior to silanization affected significantly the liquid repellency of filter paper membranes. According to Young's equation,^{214, 215} the contact angle of liquid closely depended on interfacial tensions of the solid-gas-liquid triple phase. In addition, the contact

angles of liquids formed on membrane surface decreased with decreasing liquid surface tension until the liquid spreads out and permeates through the membrane. As shown, the contact angles of water (ST = 72.7 mN/m), glycerol (ST = 62.7 mN/m), formamide (ST = 58.2 mN/m), ethylene glycol (ST = 47.7 mN/m) and diethylene glycol (44.8 mN/m) on surface of (b) which showed the highest mass loading of PDA were $161.8 \pm 2.9^\circ$, $161.1 \pm 2.9^\circ$, $155.4 \pm 1.9^\circ$, $144.6 \pm 1.9^\circ$, $141.2 \pm 0.5^\circ$, respectively. The contact angles of high surface tension liquids on surface of (b) were higher than those on (a) and (c). Taking FM as an example, $CA_{FM(b)} = 155.4 \pm 1.9^\circ > CA_{FM(c)} = 145.7 \pm 2.3^\circ > CA_{FM(a)} = 142.1 \pm 2.6^\circ$. On the other hand, all the papers displayed superlyophilicity to liquids from n-hexadecane (ST = 27.5 mN/m) to n-hexane (ST = 18.4 mN/m). The photo image of liquid droplets, such as water, glycerol, formamide and ethylene glycol, on the surface of the paper@PDA before and after silanization can be seen in Figures 4.4-b and c. With only PDA modification, the paper displayed superlyophilicity, on which all the liquids easily penetrated. After silanization, the liquids retained on the surface of the paper with nearly spherical shape. We believe that the dense growth of SMSs in paper@PDA₁@C18 significantly enhances its lyophobicity surpassing other papers. Therefore, we hypothesize that both amount and morphology of PDA coating affect the morphology of the growth of SMSs, leading to difference in liquid repellency of the papers.

Figure 4.4. (a) Static contact angle of different liquids on the surface of the membrane (a), (b) and (c). (b) Photograph of liquids on surface of paper@PDA. (c) Photograph of liquids on surface of and paper@PDA@C18.

To support our hypothesis, a thin layer of PDA was coated on the filter paper in Tris buffer before silanization (detail is shown in the section 4.2.2) which was denoted as paper@PDA_{Tris} and paper@PDA_{Tris}@C18, respectively (Figure 4.5). The SEM image of paper@PDA_{Tris} (Figure 4.5-a) showed no difference to pristine paper, while signals of catechol groups in PDA were observed on FT-IR spectrum (Figure 4.5-c), suggesting a thin layer of PDA coated on the paper surface. A few SMSs were also observed on paper@PDA_{Tris}@C18 (Figure 4.5-b) and Si-O-Si vibration was obtained at 710 cm⁻¹ on FT-IR spectrum after silanization (Figure 4.5-d). Thus, the lesser amount of PDA coating (Figure 4.5-e) before silanization caused less effectiveness in the growth of SMSs. As shown, paper@PDA_{Tris}@C18 only showed superlyophobicity to water and glycerol. Other high surface tension liquids displayed considerably lower CAs compared to (b) which had the highest amount of PDA coating. For example, CA_{FM} of paper@PDA_{Tris}@C18 was $144.5 \pm 0.8^\circ$ that was significantly lower than $155.4 \pm$

1.9° (Figure 4.5-f). Therefore, using SPI to trigger polymerization of dopamine is more effective in term of surface silanization compared to using Tris-O₂.

Figure 4.5. SEM images of (a) paper@PDA_{Tris} and (b) paper@PDA_{Tris}@C18. (c) TGA analysis, (d) and (e) FT-IR spectrum of paper@PDA_{Tris} (black) and paper@PDA_{Tris}@C18 (red), respectively. Inset of (e) shows the peak of -Si-O-Si-. (f) the static contact angle of various liquids with different surface tension on the surface of paper@PDA_{Tris}@C18.

Methyl silane (MTS) and octyl silane (OTS) modification on paper@PDA₁ were conducted to investigate the impact of alkyl chain length on superlyophobicity. The filter paper modified by these molecules was denoted as paper@PDA₁@C1 for MTS and paper@PDA₁@C8 for OTS. Indeed, the MTS modification of paper@PDA₁ resulted a layer of silicone nanofilament (SNF, Figure 4.6-a), while the thin layer of silicone (SL) was observed on paper@PDA₁ modified by OTS (Figure 4.6-b). The different morphology of the coating layers is caused by the different rate of hydrolysis between short and longer alkyl chain length.^{203, 216} MTS is believed to hydrolyze faster than OTS, causing an aggregation on the substrate. More importantly, both MTS and OTS modification only displayed superrepellency to water and glycerol. The CAs of other high

surface tension liquids such as formamide, ethylene glycol and diethylene glycol dropped significantly. For example, $CA_{\text{FM-ODTS}} = 155.4 \pm 1.9^\circ > CA_{\text{FM-OTS}} = 136.09 \pm 1.22^\circ > CA_{\text{FM-MTS}} = 112.02 \pm 7.97^\circ$. Especially, $CA_{\text{DEG-MTS}} \sim 0^\circ$ for MTS coating (Figure 4.6-c). Despite enhancing liquid repellency, $CA_{\text{DEG-OTS}} = 116.7 \pm 2.1^\circ < CA_{\text{DEG-ODTS}} = 141.2 \pm 0.5^\circ$ (Figure 4.6-d). That means the modification of MTS and OTS on paper@PDA₁ resulted in a superhydrophobic coating. Therefore, ODTS coating, with the longest alkyl chain, is more suitable for superhydrophobic modification.

Figure 4.6. (a) SEM image of filter paper@PDA₁@C1 membrane. The PDA coated filter paper was modified by methyl trichlorosilane. (b) SEM image of filter paper@PDA₁@C8 membrane. The PDA coated filter paper was modified by octyl trichlorosilane. (c) static contact angle and droplet image of different liquids on the surface of the filter paper@PDA₁@C1 membrane. (d) static contact angle and droplet image of different liquids on the surface of the filter paper@PDA₁@C8.

The fluoro-based molecular modifications, such as fluoro thiol or fluoro silane, have been widely applied to fabricate superhydrophobic as well as superamphiphobic surfaces via thin coating layer.^{186, 217, 218} This kind of modification relies on topography of pristine substrate. Nevertheless, no investigation on the impact of morphology of the coating to wettability has been conducted thus far. In this work, surface of paper@PDA₁ was modified with two kinds of fluoro silane owing different chain lengths, PFDTs (C12F) and PFOTS (C8F). The reaction condition was the same with ODTS modification. The SEM image in Figure 4.7-a shows that modification by PFDTs resulted in the formation of fluoro silicone micro-sheets (FSMSs). The FSMS, similar to the SMS, also enhanced surface roughness. On the other hand, the SEM image in Figure 4.7-b shows that modification by PFOTS resulted formation of fluoro silicone layer (FSL). Figure 4.7-c shows the contact angle of liquids ranging from water ($\sigma = 72.7 \text{ mN/m}$) to n-hexane ($\sigma = 18.4 \text{ mN/m}$) on paper@PDA₁@C12F. The paper can repel most of the liquids except n-hexane ($\sigma = 18.4 \text{ mN/m}$). Liquids from water to diethylene glycol (DEG) exhibited CAs $> 150^\circ$. n-hexadecane (HDC) and dichloromethane (DCM), on the other hand, exhibited slightly lower CAs with $CA_{HDC} = 132.24 \pm 1.03^\circ$ and $CA_{DCM} = 124.57 \pm 0.96^\circ$. However, paper@PDA₁@C12F can be considered as superomniphobic or superamphiphobic surface.²¹⁹ Figure 4.7-d shows that paper@PDA₁@C8F poorly repelled the liquids. Liquids from water to DEG exhibited CAs smaller than 150° , while DCM and HEX penetrated quickly. HDC also exhibited significantly low CA which was $95.85 \pm 0.68^\circ$. Therefore, it can be concluded that paper@PDA₁@C8F only exhibits omniphobicity.²²⁰

Figure 4.7. (a) SEM image of $\text{paper@PDA}_1\text{@C}_{12}\text{F}$ membrane. The PDA coated filter paper was modified by methyl trichlorosilane. (b) SEM image of $\text{paper@PDA}_1\text{@C}_8\text{F}$ membrane. The PDA coated filter paper was modified by octyl trichlorosilane. (c) static contact angle and droplet image of different liquids on the surface of the filter paper $\text{paper@PDA}_1\text{@C}_{12}\text{F}$ membrane. (d) static contact angle and droplet image of different liquids on the surface of the $\text{paper@PDA}_1\text{@C}_8\text{F}$.

4.3.3. Mechanism of Surface Wettability

The schematic diagram of wettability via high surface tension liquids of the filter paper before and after PDA modification and further silanization is shown in Figure 4.8. For a simple visualization, the fibers of papers are modeled on the assumption that their cross sections are in round shape, making a regular pore arrangement. The surfaces of pristine filter paper and paper@PDA are hydrophilic, θ_1 and $\theta_2 < 90^\circ$, thus the liquids penetrate through their fibers

immediately (Figure 4.8-a and b). On the contrary, the paper@C18 and paper@PDA@C18 show lyophobicity to high surface tension liquids (Figure 4.8-c and d). The CAs of these liquids on paper@PDA@C18 are higher than on paper@C18 ($\theta_4 > \theta_3$). This is because the roughness enhances the surface wettability.^{195, 221} The rough surface caused by SMSs enhances the underneath air encapsulated, thus improving the liquid repellency.⁴⁴ The critical pressure is expressed by the following equation.⁵⁸

$$\Delta P = \frac{2\gamma_L}{R} - \frac{4\gamma_L \cos \theta}{d} \quad (\text{Figure 4.4})$$

where ΔP represents the critical pressure; γ_L represents the surface tension of liquid; θ represents the contact angle; R represents radius of the liquid droplet and d is the distance between center of the two adjacent cellulose fibers. The critical pressure is associated with the maximum pressure that one membrane can stand under a certain amount of liquid. Larger value of critical pressure reveals more lyophobic behavior of the membrane. From equation 4.4, the critical pressure is related to the contact angle of the liquid. That means, the liquid with $\theta < 90^\circ$ (Figure 4.8-a and b) has chance to penetrate though the paper, resulting in the critical pressure $\Delta P < 0$. In contrast, the liquid with $\theta > 90^\circ$ (Figure 4.8-c and d) cannot pass through the paper, resulting in $\Delta P > 0$. In addition, $\theta_4 > \theta_3$ after ODTs modification, revealing $\Delta P_4 > \Delta P_3$.

Figure 4.8. The scheme illustrates wetting mechanism of a high surface tension liquid droplet on surface of pristine filter paper (a), paper@PDA (b), paper@C18 (c) and paper@PDA@C18 (d). The high surface tension liquid shows lyophilicity on the surface of both pristine paper and paper@PDA with critical pressure $\Delta P < 0$, lyophobicity on the surface of both paper@C18 and paper@PDA@C18 with critical pressure $\Delta P > 0$. The paper@PDA@C18 with decoration of micro-sized sheets enhances surface roughness, thus strengthening the liquid repellency: $\theta_4 > \theta_3$.

4.3.4. Surface Modification of Other Materials

PDA has been shown to versatily coat on various substrates, including hydrophilic and hydrophobic due to its high chelating ability.^{130, 222, 223, 224} Therefore, besides 3 μm pore size filter paper, various substrates including 2D and 3D materials such as 10 μm pore size filter paper, cotton fabric, melamine sponge (hydrophilic) and PU foam, stainless steel mesh, polyester fabric (hydrophobic) were selected. Comparison of SEM images between the pristine and PDA modified materials (Figures 4.9-a to 4.9-f, insets) clearly showed that PDA nanoparticles aggregated densely on skeletons of the structures and therefore increased the hydrophilicity of substrates. After silanization, as shown in Figures 4.9-a₁ to 4.9-f₁, the SMSs with interconnected feature were also

observed on these surfaces, revealing a successful modification of ODTS on surface of PDA coated materials.

Figure 4.9. The facile approach to other materials: SEM images of silanized modification on same filter paper with larger pore size (10 μm - a), hydrophilic melamine sponge (b), hydrophobic polyurethane foam (c), hydrophobic stainless-steel mesh (d), hydrophilic cotton fabric (e) and hydrophobic polyester fabric (f). Insets of figures a-f show higher magnification of PDA modified materials with scale bar.

The contact angle of different liquids on the surface of these materials was also shown (Figure 4.10). The image and value of CA were listed from (a) to (f), according to $\text{paper@PDA}_1\text{@C18}$ (10 μm pore size), $\text{MS@PDA}_1\text{@C18}$, $\text{PU@PDA}_1\text{@C18}$, $\text{Mesh@PDA}_1\text{@C18}$, $\text{Cotton@PDA}_1\text{@C18}$ and $\text{PE@PDA}_1\text{@C18}$, respectively. Except $\text{PE@PDA}_1\text{@C18}$ which only displayed superhydrophobicity, the other as-prepared materials with different geometries displayed superlyophobicity to high ST liquids, ranging from water to ethylene glycol, while showing superlyophilicity to low ST liquids, ranging from n-hexadecane to n-hexane, which have ST lower than 30 mN/m. Notably, although all the materials experienced the same preparing condition, the repellency of high

ST liquids may vary among the materials, due to the difference in surface morphology. Therefore, the CA values of liquids were different between all materials.

Figure 4.10. The contact angle of different liquids on the surface of silanized modification on same filter paper with a larger pore size (a), hydrophilic melamine sponge (b), hydrophobic polyurethane foam (c), hydrophobic stainless- steel mesh (d), hydrophilic cotton fabric (e) and hydrophobic polyester fabric (f).

The visualization of lyophobicity of as-prepared materials was shown in Figure 4.11. The PDA-only modified materials and the PDA@C18 modified materials were placed onto a beaker containing pure formamide solution. Since after modification with PDA, materials became superlyophilic they sunk down below the formamide surface. On the other hand, after one step treatment with ODTs, the materials became superlyophobic. Therefore, they floated on surface of the formamide solution. This phenomenon suggested the good repellency of

the materials to formamide. Thus, both 2D and 3D skeletons of materials are promising to separate immiscible liquid mixtures.

Figure 4.11. Photo images of materials immersed in formamide. Since after modification with PDA materials become superlyophilic they sink down to the bottom (except PU@PDA₁ because of low density). On the contrary, after one step treatment with ODTS, the materials become superlyophobic. Therefore, they float on top of formamide solution.

The surface wettability of ODTS modified pristine substrates was also investigated to evaluate the role of PDA pretreatment, taking the CA_{FM} as an example. Figure 4.12a shows that the silanized materials without PDA nanoparticles treatment had significantly lower CA_{FM} compared to the silanized materials with deposition of PDA nanoparticles. Among them, only cotton@C18 displayed superlyophobic to formamide with $CA_{FM} = 151.49 \pm 1.09^\circ$. However, this value was still lower than CA_{FM} of cotton@PDA₁@C18 which was $153.5 \pm 0.9^\circ$. Expanding to other high surface tension liquids, such as EG and DEG, the

contact angle of these liquids on cotton@C18 were significantly lower than on cotton@PDA₁@C18. For example, $CA_{EG}(\text{cotton@C18}) = 136.47 \pm 2.06^\circ < CA_{EG}(\text{cotton@PDA}_1\text{@C18}) = 152.9 \pm 1.0^\circ$ and $CA_{DEG}(\text{cotton@C18}) = 133.67 \pm 2.07^\circ < CA_{DEG}(\text{cotton@PDA}_1\text{@C18}) = 150.54 \pm 1.38^\circ$ (Figure 4.12-b). This result, again, revealed the advantage of deposition of PDA nanoparticles for further surface modification.

Figure 4.12. (a) The contact angle of 3 μL formamide (FM) on the surface of various substrates after modification by ODTS without pre-coating of PDA. (b) Comparison of contact angle of various high surface tension liquids on surface of cotton@PDA@C18 (black) and cotton@C18 (red).

4.3.5. Separation of Immiscible Liquids by Absorption Strategy

Figure 4.13-a₁ shows the absorption capacity of MS@PDA₁@C18 towards different liquids. It can be seen that the absorption capacity of the sponge ranged from 53 g/g to 120 g/g. The mass before and after absorption was also recorded to evaluate the reusability (Figure 4.13-a₂). Taking n-hexane as an example, the foam (0.0195 g) was squeezed and dried at 70 °C for 10 min after absorption. The mass after 10 cycles absorption was remained at 0.969 g, indicating absorption capacity of 52.2 g/g. The CA_{FM} was also measured to confirm the recyclability of the foam after each absorption cycle (Figure 4.13-a₃). The CA_{FM} remained at

151.3 $\pm$ 0.9° after 10 cycles, revealing a high durability of the foam. The similar absorption test was investigated using PU@PDA₁@C18. The absorption capacity was recorded ranging from 26.9 g/g to 52.5 g/g (Figure 4.13-b₁). The lower capacity of PU@PDA₁@C18 compared to MS@PDA₁@C18 may be caused by the higher solid content of PU (see the SEM images also). The foam also displayed a good regeneration with a remained absorption capacity for n-hexane and CA_{FM} were approximately 27 g/g and 149.3 $\pm$ 1.3°, respectively (Figure 4.13-b₂, b₃).

Figure 4.13. Absorption capacity, the reusability of the foams and contact angle measurement of formamide droplet (3 μ L) on surface of recovered foams tested with (a₁-a₃) MS@PDA₁@C18 and (b₁-b₃) PU@PDA₁@C18.

The high repellency of as-prepared membranes and foams towards high ST liquids and their high permeability towards low ST liquids endows the selective separation of immiscible liquid mixtures. Both static and continuous strategies were applied to separate and purify solvents from other contaminated liquids. Taking HDC/FM and CCl₄/FM as examples of immiscible liquid mixtures, MS@PDA₁@C18 and PU@PDA₁@C18 were used to absorb oils from

formamide. To remove light oil from formamide, the foams were placed on formamide containers. The n-hexadecane could be seen to completely removed within 1 min showing an efficient purification ability (Figure 4.14-a and c). The removal of heavy oil underneath of formamide was shown in figure 4.14-b and d. Using the same porous foams, carbon tetrachloride was quickly absorbed when immersing the foams in formamide. Notably, a mirror surface appeared on the foams because of trapped air. When the oil interacted with the foams, trapped air was then driven out releasing bubbles that moved out of formamide. The fast absorption of heavy oil confirmed the excellent oil removal under high surface tension liquids such as formamide.

Figure 4.14. The separation of HDC/FM and CTC/FM mixture by absorption using MS@PDA₁@C18 (a and b) and PU@PDA₁@C18 (c and d). For the separation of HDC/FM: (i) the mixture of n-hexadecane (dyed with oil red O) and formamide, (ii-iv) the absorption was completed within 1min after adding

the foams. For the separation of CCl_4/FM : (i) the mixture of carbon tetrachloride (dyed with oil red O) and formamide, (ii-iv) the oil was absorbed quickly after the foams was immersed into formamide.

In the static absorption separation, $\text{MS@PDA}_1\text{@C18}$ was observed to absorb oils faster than $\text{PU@PDA}_1\text{@C18}$. Therefore, we choose $\text{MS@PDA}_1\text{@C18}$ to dynamically remove oils from FM. A fast stirring was applied in the mixture of HDC/FM . It can be seen that HDC can be removed quickly even the mixture was in a fast stirring, leaving no color of dye. After the absorption, $\text{MS@PDA}_1\text{@C18}$ floated on the solution that was easy to take out (Figure 4.15-a). Furthermore, multi-cycle absorption-squeezing process also can remove a large amount of toluene in the mixture with formamide (Figure 4.15-b). The oil was colored with organic dye. After several absorption-squeezing cycles, the oil was completely removed out of formamide batch, leaving no obvious color of the dye.

Figure 4.15. (a) removal of n-hexadecane (dyed with oil red O) from formamide under strong stirring. (b) removal of toluene (dyed with oil red O) from formamide by absorption followed by squeezing.

4.3.6. Separation of Immiscible Liquids by Membrane Filtration

The separation of immiscible liquids mixture was also investigated by 2D superlyophobic membranes. We choose the mixture of FM (colored by methylene blue) and CCl_4 to test the separation ability of the mesh@PDA₁@C18. Figure 4.16-a shows that the mixture was quickly separated by the mesh membrane leaving no visible liquid mixture existed in the collected phase. The mesh membrane also successfully separated water/ CHCl_3 mixture as a normal superhydrophobic membrane. Besides, other 2D materials such as cotton@PDA₁@C18 and paper@PDA₁@C18 were also applied to separate both FM/ CCl_4 and water/ CHCl_3 mixtures with the separation efficiency all above 97% (Figure 4.16-b). Moreover, the regeneration of the mesh membrane was confirmed by testing CA_{FM} , filtration flux and efficiency after 10 cycles. As shown in Figure 4.16-c, after 10 cycles, the CA_{FM} only showed a little change from $149.1 \pm 1.5^\circ$ to $146.1 \pm 1.5^\circ$, while the average separation flux was maintained above $7250 \text{ Lm}^{-2}\text{h}^{-1}$ and the separation efficiency remained $\sim 98.5\%$.

Figure 4.16. (a) The separation process of formamide/CCl₄ mixture (formamide was dyed with methylene blue) using mesh@PDA₁@C18. (b) Separation efficiency of water/CHCl₃ and formamide/CCl₄ mixtures using cotton@PDA₁@C18, mesh@PDA₁@C18 and paper@PDA@C18. (c) Separation flux of formamide/CCl₄ after 10 cycles and static contact angle of formamide according to each cycle. Separation efficiency at some representative cycles was also shown.

4.4. Conclusion

In conclusion, we introduced a simple method to fabricate both 2D and 3D superlyophobic materials in the application of immiscible liquids separation. The superlyophobicity was obtained by the growth of silicone microsheets (SMSs) on the PDA modified structures which enhanced the trapped air fraction. As-prepared materials exhibited superlyophobicity to high surface tension liquids such as formamide or diethylene glycol and superlyophilicity to liquids with ST < 30 mN/m. The impact of PDA morphology on the growth of SMS revealed that the deposition of PDA nanoparticles with homogeneous particles size about

100nm triggers the formation of homogeneous SMSs. The separation of immiscible liquids mixture was investigated by both continuous and static strategies. 3D sorbents used in this work offers new strategy besides membrane technology for general liquid purification.

Chapter 5. Hierarchical Graphene-Metal Organic Frameworks Composites: from Superamphiphobic Coatings to Membranes for Separating Immiscible Liquids

5.1. Introduction

Superamphiphobic surface is known to repel both water and oil with CA higher than 150° ,⁵¹ leading to various applications such as self-cleaning, organic liquid transportation or oil droplet manipulation.²²⁵ Recently, hierarchical architectures have been introduced to create superamphiphobicity with excellent water and oil repellency.^{45, 218, 226} In these reports, hierarchical structures are found to trap air much more effectively compared to simply roughed surfaces, thus repelling oil droplets more efficiently.²²⁷ Several types of hierarchically re-entrant structure such as marshmallow-like,²²⁸ mushroom-like and serif T-shape,²²⁹ or overhang structures,²³⁰ have been reported in the success of enhancing air pocket trapped, realizing the repellency of low surface tension (ST) liquid. However, most reported articles are destructive to the substrate because they use chemical etching or plasma treatment.^{45, 218} It have been shown that porous structure which has monoliths interconnection can trap air effectively.²³¹ In addition, the fabrication of porous structure, mostly by ice templating, is simple, energy effective and environmentally friendly.^{232, 233} For example, Li et al.⁴⁸ reported a superamphiphobic coating relying on porous structure generated from PDA coated fumed silica nanoparticles (HiFSNs) building block. The coating can repel oil droplet with surface tension as low as n-decane (ST = 23.9 mN/m) with CA = 154.8° . However, since this paper, no superamphiphobic

surface based on porous structure has been reported thus far. The further discovery of other porous structures which can be used to fabricate superamphiphobicity, thus, is highly demanding.

Owing to its extremely high porosity, hierarchically porous graphene has been wisely employed in both environmental treatment,^{139, 162, 234, 235} and energy.^{236, 237} However, until now porous graphene has only been considered as bulk adsorbents for contamination removal or energy storage devices and has never been used as the surface coating building block. Moreover, graphene has not been employed to fabricate superamphiphobic structure thus far. Herein, we used dopamine and graphene oxide (GO) to fabricate GH-PDA frameworks. In the presence of ionic liquid (IL), GO reduced by dopamine and functionalized by PDA forms porous particles, which can be dispersed in solution without losing the porosity. ZIF-8 nanoparticles grown on PDA were further used to modulate the pore sizes of GH-PDA. Both GH-PDA and GH-PDA-ZIF-8 hybrid structures were then modified by 1H,1H,2H,2H perfluorodecyltriethoxysilane (PFDTs) (Figure 5.1-a). We investigated that ϕ_{air} diminished from 0.97 to 0.8 with the increase in amount of ZIF-8 particles. This reveals that the wettability of the hybrid materials can be tuned from superamphiphobicity to omniphobicity. The tailored wettability allowed certain liquids to penetrate and retained others when coated on Ni foams, leading to separation of immiscible liquids (Figure 5.1-b).

Figure 5.1. Illustration of (a) the fabrication of tailored superamphiphobic 3D silanized GH-PDA-Z framework from GO/DA/IL dispersion followed by loading of MOFs nanocrystals on GH-PDA surface and modification of the resulting surface by silanization. (b) The preparation of filtration membrane by drop casting silanized GH-PDA-Z on Ni foam for the separation of immiscible organic solvent mixture.

5.2. Experimental Section

5.2.1. Materials

Dopamine hydrochloride (98%), 1H,1H,2H,2H perfluorodecyltriethoxysilane (PFDTs) (96%), natural graphite powder, diphosphorous pentoxide (P_2O_5), potassium persulfate ($K_2S_2O_8$), potassium permanganate ($KMnO_4$), 1-butyl-3-methylimidazolium tetrafluoroborate (IL), zinc (II) nitrate hexahydrate ($Zn(NO_3)_2$), 2-methyl imidazole (MID), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), glycerol (Gly), formamide (FM), ethylene glycol (EG) were purchased from Sigma-Aldrich. n-hexadecane (HDC), chloroform (CF), diethylene ether (DEE), petroleum ether (PTE), n-hexane

(HEX), methanol (MeOH), ethanol (EtOH), were purchased from Fisher chemical. Carbon tetrachloride (CTC) was purchased from S1-LAB PTE. LTD, Singapore.

5.2.2. Preparation of GH-PDA colloid

The preparation of graphene oxide (GO) was conducted using natural graphite powder via modified Hummer's method.^{238, 239, 240} After that, the GH-PDA colloid was prepared following the method reported by Y. Zhang et.al with some modifications.²⁴¹ Briefly, 20 mg of GO (10 mg/mL) was diluted to a solution with 2 mg/mL by DI water. The GO suspension was then sonicated using sonicate probe for 2 hours. 10 mg of dopamine was then added to GO solution before the following addition of 50 μ L IL. The mixture was then sonicated to ensure that IL dissolved completely in water and heated in an oven at 90 °C for 12 hours. After the reaction, black solid was collected by filtration under low pressure. The final GH-PDA colloidal powder was obtained after 2 days freeze-dry. GH-PDA was prepared using the same method without adding any ionic liquids and filtration.

5.2.3. Preparation of GH-PDA-ZiF-8 Composite

2 mg of GH-PDA colloidal powder was dispersed in a mixture of MID (60 mM) and $\text{Zn}(\text{NO}_3)_2$ (30 mM) which were dissolved in methanol with different concentrations of graphene. The mixture of GH-PDA colloid and ZIF-8 precursors was mixed overnight under stirring. The composite product was finally centrifuged at 6000 rpm in 10 min and washed several times with methanol.

5.2.4. Surface Modification of GH-PDA and GH-PDA-Z and Coating Procedure

Surface modification was conducted following the work of Chen and co-workers.²⁴² Briefly, 2 mg of GH-PDA colloidal powder was mixed with 50 μL of PFTDS in a small vial. The vial, which was covered by an aluminum paper, was then placed in an oven at 200 °C for 10 min. After naturally cooling to room temperature, silanized GH-PDA was dispersed again in ethanol and then drop casted on substrates (i.e. glass (1.5 cm x 1.5 cm) or Ni foam (1.5 cm x 1.5 cm)). Coated substrates were dried at 50 °C for several days followed by an additional dry at 100 °C for 1 hour. The same procedure was applied for GH-PDA-Z samples.

5.2.5. Filtration of Immiscible Liquid Mixtures

In the first experiment, a simple mixture of carbon tetrachloride and high surface tension solvents such as water, glycerol, formamide and ethylene glycol, which are colored by organic dyes, was poured through a funnel liked silanized GH-PDA-Z₄ coated Ni-foam which was pre-wetted by carbon tetrachloride. In the second experiment, mixtures of low surface tension liquids and formamide were poured through GH-PDA-Z₄ coated Ni-foam. In the third experiment, the mixture of chloroform and formamide was repeatedly filtered through GH-PDA-Z₄ coated Ni-foam for 20 cycles. Control experiments such as filtration using bare Ni foam and silanized GH-PDA-Z₂ coated Ni foam also are conducted at the same condition.

The separation efficiency is calculated by the following expression:¹⁹⁵

$$R(\%) = \frac{V_1 + V_2}{V_o} \times 100\% \quad \text{(Equation 5.1)}$$

Where V_o (L) is the original volume of oil. V_1 and V_2 are the volume of collected oil and the volume absorbed by membrane, respectively.

The filtration flux is calculated by the following expression:

$$F = \frac{V}{A \times t} \quad \text{(Equation 5.2)}$$

where V (L) is the volume of liquid passed through the membrane, A (m²) is the effective area of the membrane and t (h) is the total time that liquids pass through the membrane.

5.2.6. Characterization

Surface morphology of pristine and modified substrates was characterized by field emission scanning electron microscopy (FE-SEM, JSM-6700F). Surface chemistry was characterized by Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). Surface compositions of materials were examined using X-ray photoelectron spectroscopy (XPS). Powder X-ray diffraction (XRD) patterns was obtained on Bruker AXSD2 Advanced X-ray diffractometer with monochromatized Cu Ka radiation ($\lambda = 1.54056 \text{ \AA}$, 40kV and 20mA). Contact angles of liquids were measured using Dataphysics contact angle system OCA 15ec. The Young's contact angle was measured on PFDTs treated glass slide.

5.3. Results and Discussion

5.3.1. Fabrication of graphene/ZIF-8 building block with tailored surface wettability

When we added IL to the colloidal dispersion of GO and DA, the colloidal particles agglomerated into macro-scale clusters and probably an aqueous percolating network containing colloidal suspension of GO and DA surrounded by IL molecules is formed.²⁴³ This is caused due to neutralization of the surface charges of colloidal particles by the ions carrying opposite charge from the IL leading to de-stabilization of colloidal suspension of graphene oxide in water/IL mixture.²⁴⁴ Then, the colloidal mixture was heated overnight at 90 °C when GO was reduced by PDA and consequently, self-assembled into 3D GH-PDA hydrogel particles inside the colloidal agglomerates. GH-PDA colloidal hydrogel was then filtered and freeze-dried to obtain the black powder, which retained its porous structure while dispersing in methanol under mild sonication (Figure 5.2-a and b). Next, we tuned the surface topography of the hierarchically porous GH-PDA colloid by loading various amount of ZIF-8 nanocrystals. ZIF-8 nanoparticles can easily nucleate *in situ* on a thin layer of polydopamine (PDA) due to the metal chelating ability of PDA^{130, 222, 223, 224}. In our study, we observed that ZIF-8 nanoparticles were successfully deposited on the surface of GH-PDA by simple mixing of porous GH-PDA powder and methanol solution of the precursors. We found that the coating density and coated wall thickness of ZIF-8 on 3D porous GH-PDA colloids were highly dependent on the weight percentage of graphene.

Figure 5.2. SEM images of the 3D porous micron-sized GH-PDA powder (a) low and (b) higher magnification. (c - e) SEM images of GH-PDA-Z₁, GH-PDA-Z₂, GH-PDA-Z₃ and GH-PDA-Z₄ corresponding to the initial concentration of GH-PDA colloids at 28.6, 7.15, 2.86 and 1.43 wt%, respectively.

When higher amount of graphene (28.6 wt%) was utilized with respect to ZIF-8, the porous surface of GH-PDA colloids (GH-PDA-Z₁) were not fully coated by ZIF-8 as shown in Figure 5.2-c. When the amount decreased to 7.15 wt%, we observed that the surface of porous GH-PDA colloids (GH-PDA-Z₂) were uniformly coated with a thin conformal layer of ZIF-8 particles (Figure 5.2-d). The coated wall thickness on the porous GH-PDA colloids further increased with decreasing graphene concentration from 2.86 wt% (GH-PDA-Z₃) to 1.43 wt% (GH-PDA-Z₄), leading to successive reduction in pore diameter (Figure 5.2e-f). Moreover, we observed that the micron-sized pores of the GH-PDA colloid were almost fully covered at 1.43 wt% graphene content (Figure 5.2-f). Therefore, when the GH-PDA amount was lowered from 28.6 to 7.15 wt%, the number of nucleation active sites of ZIF-8 on graphene surface increased, leading to uniform thin surface coverage. However, with further increase in the amount of ZIF-8, the

nuclei of ZIF-8 particles started growing more and form multiple layers of ZIF-8 nanocrystals onto the wall of the GH-PDA.

The advantage of using IL to synthesize porous GH-PDA particles is shown in Figure 5.3. Our previous article reported that the reduction of GO by PDA without presentation of IL resulted the cylindrical shaped bulk GH-PDA hydrogel (Figure 5.3-a, right);¹³⁹ while the introduction of IL in this work resulted a porous powder form of GH-PDA (Figure 5.3-a, left). Although SEM images of both the GH-PDA samples showed 3D porous structures (Figure 5.3-b and c), the bulk GH-PDA hydrogel completely lost its 3D porous structure when the hydrogel was re-dispersed in methanol with sonication (Figure 5.3-d). We believe that the 3D porous network of bulk GH-PDA hydrogel was broken down inside its structure under ultrasonic energy, whereas, the 3D open porous structure of GH-PDA formed inside the micron-sized small colloidal clusters remained quite stable via π - π interactions and cation- π bonding between IL and graphitic carbon skeleton.²⁴⁵

Figure 5.3. (a) Optical photograph of porous micron-sized GH-PDA colloidal powder and cylindrical shaped bulk GH-PDA hydrogel. SEM images of solid state of (b) GH-PDA colloid and (c) GH-PDA hydrogel. (d) SEM image of methanol dispersed GH-PDA hydrogel.

Besides the hierarchical topography, the introduction of low surface energy coating is also very important to fabricate super-repellent surfaces. Here we modify the surface of porous GH-PDA and GH-PDA-Z composites by PFDTs, which attached to the catechol groups of PDA via covalent interaction and strongly interacted with ZIF-8 particles.^{48, 242} Figure 5.4 shows the SEM images of GH-PDA and GH-PDA-Z after silanization, named as silanized GH-PDA and silanized GH-PDA-Z. The wall thickness of porous GH-PDA which changed from several ten nanometers to nearly 100 nm and to around 400 nm due to deposition of various amount of ZIF-8, as mentioned above, remained almost the same after silanization. However, the large variation in wall thickness from few nm up to 100 nm for GH-PDA-Z₁ was due to the non-uniform deposition of ZIF-8 nanoparticles on the surface. However, if we compared the microscopic

structure of all the ZIF-8 coated GH-PDA before and after silanization, we found that the molecular coating layer of fluorosilane did not change the macro-scale porosity of graphene skeletons. Hence, we can tailor the surface chemistry of GH-PDA-Z frameworks without significant changing their surface topography.

Figure 5.4. SEM images of 3D porous GH-PDA as well as GH-PDA-Z frameworks after surface modification with fluorosilane. (a, b) low and higher magnification of silanized GH-PDA; (c) silanized GH-PDA-Z₁, (d) silanized GH-PDA-Z₂, (e) silanized GH-PDA-Z₃, (f) silanized GH-PDA-Z₄.

The successful depositions of ZIF-8 and coating of PFDTS on GH-PDA colloid were confirmed by FTIR analysis (Figure 5.5-a). FTIR spectrum of GH-PDA showed the characteristic peaks at 1572 cm^{-1} and 1720 cm^{-1} , corresponding to the respective stretching vibration of C=C and C=O coming from catechol group of PDA.¹³⁹ Moreover, a small peak at 1060 cm^{-1} corresponding to the stretching vibration of B-F (-BF_4) indicated that small amount of IL is still grafted on the graphene sheets even after washing in methanol.²⁴⁵ To show the coating of ZIF-8 particles on the GH-PDA frameworks, we chose an exemplary sample GH-PDA-Z₂ because the ZIF-8 crystals start covering fully from this sample. The observed additional peaks in the spectral region of $500\text{ cm}^{-1} - 1350\text{ cm}^{-1}$ and the

humps in between 1350 cm^{-1} – 1500 cm^{-1} assigned to the respective plane bending and stretching of imidazole ring confirms the successful ZIF-8 deposition on the graphene framework. Moreover, the small peak at 1584 cm^{-1} corresponding to the stretching vibration of C-N from imidazole and peaks for aromatic and aliphatic C-H stretch at 2929 cm^{-1} and 3135 cm^{-1} further confirmed the ZIF-8 coating on GH-PDA.²⁴⁶ Furthermore, a new peak at 1214 cm^{-1} corresponded to the covalent C-F bonds⁴³ as well as the peaks at 778 cm^{-1} and 1075 cm^{-1} corresponded to the bending and stretching vibration of Si-O-Si, respectively,^{152, 247} confirmed the successful modification of GH-PDA and GH-PDA-Z₂ composites by PFDTs. The compositional changes of porous graphene before and after loading with ZIF-8 particles and further modification by PFDTs were characterized by X-ray photoelectron spectroscopy (XPS) as shown in Figure 5.5-b. While the peaks of C1s, N1s and O1s were observed for GH-PDA colloid, a new peak of Zn2p was observed in GH-PDA-Z₂ sample, indicating the presence of ZIF-8 coating on its surface. The XPS spectra of silanized GH-PDA and GH-PDA-Z₂ showed additional peaks of F1s and Si2p, indicating the successful surface modification of graphene frameworks by fluorosilane. However, the Zn2p peak from silanized GH-PDA-Z₂ was not observed as the surface of ZIF-8 coating is now fully covered by the layer of fluorosilane and therefore, not detected in XPS which is a surface-sensitive spectroscopic technique. However, the characteristic spectra for ZIF-8 nanoparticles were well observed in XRD spectrum (Figure 5.5-c). We also investigated the nitrogen-sorption isotherm study (Figure 5.5-d) to evaluate any change in nanoscale porosity of GH-PDA colloids before and after surface modifications. We obtained the BET surface

area of $187.83 \text{ m}^2\text{g}^{-1}$ for GH-PDA colloidal powder. Although this was slightly lower than the surface area of cylindrical bulk GH-PDA hydrogel ($310 \text{ m}^2\text{g}^{-1}$), but it was comparable to those of meso/macropores prepared by sintering,²⁴⁸ or other hydrothermal methods.^{249, 250, 251} After ZIF-8 loading, the BET surface area of GH-PDA-Z₂ increased to $646.36 \text{ m}^2\text{g}^{-1}$ due to the contributions from micropores of ZIF-8 particles and mesopores of graphene.^{43, 252} However, after surface modification by PFDTs, the surface area of both silanized GH-PDA and silanized GH-PDA-Z₂ decreased sharply to $15.60 \text{ m}^2\text{g}^{-1}$ and $24.63 \text{ m}^2\text{g}^{-1}$, respectively. This reduction in surface area was coming from the coating layer of fluorosilane, in which polysiloxane networks are formed due to fast deposition,^{253, 254} filling the nanoscale pores of GH-PDA colloid and ZIF-8 in GH-PDA-Z₂, keeping only the microscale pores to contribute in BET experiment.²⁵⁵ This result further supported the disappearance of Zn2p peak in XPS spectra of silanized GH-PDA-Z₂ samples.

Figure 5.5. (a) FTIR spectra, (b) XPS spectra, (c) XRD spectra (d) BET analysis of GH-PDA, GH-PDA-Z₂, silanized GH-PDA, and GH-PDA-Z₂ colloidal powders. The FT-IR peaks of C=O and C=C are highlight with blue and green colors, respectively, while the characteristic peak positions are indicated with an arrow in (a). The XRD spectrum of silanized GH-PDA is not shown in (c) as no peaks were observed.

The static contact angle of solvents with different surface tensions were measured on silanized GH-PDA and silanized GH-PDA-Z films (Figure 5.6). The Figure indicates that the increase in loading of ZIF-8 worsen liquid repellency. Surfaces from silanized GH-PDA to silanized GH-PDA-Z₃ showed super-repellence for liquids from water to ethylene glycol with CAs >150°. Especially, coating surfaces from silanized GH-PDA to silanized GH-PDA-Z₂ displayed superamphiphobicity with CA_{HDC} > 150°. Whereas, for low surface tension liquids from n-hexadecane to methanol, glass surface coated with

silanized GH-PDA colloid displayed the best ability to repel these solvents with $CA_{MeOH} > 141^\circ$. The repellency of silanized GH-PDA- Z_4 dropped sharply with $CAs < 150^\circ$ to all liquids. The surface only displayed lyophobicity to liquids from water to n-hexadecane. For the liquids with surface tension lower than n-hexadecane, it displayed superlyophilicity. Notably, n-hexane can penetrate through all the surfaces.

Figure 5.6. Static contact angle measurement of different liquid droplets with different surface tensions on surface of (a) silanized GH-PDA, (b) silanized GH-PDA- Z_1 , (c) silanized GH-PDA- Z_2 , (d) silanized GH-PDA- Z_3 and (e) silanized GH-PDA- Z_4 .

Dynamic contact angle measurement further confirmed these results, i.e., measuring the advancing and receding contact angles. We used FM, for this measurement. The 3 μ L of FM was compressed and then released on the surface of samples. We found that surfaces of silanized GH-PDA to silanized GH-PDA- Z_3 show super-repellence for FM with small difference between advancing and receding forces. After compression, the FM droplet was easily released without leaving any trace of FM. On the contrary, the silanized GH-PDA- Z_4 displayed a

large difference between advancing force and receding force. The FM droplet stuck on the surface of silanized GH-PDA-Z₄ and cannot release from the surface (Figure 5.7). This result revealed lesser amount of air entrapment inside the pores of silanized GH-PDA-Z₄ compared to former surfaces (silanized GH-PDA, silanized GH-PDA-Z₁, silanized GH-PDA-Z₂, silanized GH-PDA-Z₃), due to its thicker wall coating.

Figure 5.7. Advancing contact angle (up) and receding contact angle (bottom) of 3 μ L formamide droplet on the surface of silanized GH-PDA, silanized GH-PDA-Z₁, silanized GH-PDA-Z₂, silanized GH-PDA-Z₃, silanized GH-PDA-Z₄ coated glass slide from left to right.

5.3.2. Dependence of Super-repellency on Surface Structure

Unlike “re-entrant” or “T” shaped structures which are uniformly constructed in regular morphologies, porous structure is formed mostly by assembly of 2D materials²⁵⁶ and/or ice-templation²⁵⁷ of cross-linked 2D materials. Therefore, it is more complicated to investigate the effect of structure parameters to surface wettability. Recently, pore height (H) of porous coating structure has been considered as the main factor causing transition from superamphiphobicity to quasi-superamphiphobicity corresponding to Cassie-Baxter to Wenzel transition.⁴⁸ Cassie-Baxter model is known as meta-stable

state.^{258, 259} Thus, it can be changed under certain conditions such as amount of air trapped underneath liquid droplet,^{260, 261} surface tension of deposited liquid¹⁹⁵ or break-in pressure (or intrusion pressure),^{262, 263} Therefore, it is termed as Cassie-Baxter to Wenzel transition.²⁵⁹ Here, we consider the trapped air fraction (ϕ_{air}) to investigate this transition by varying thickness of graphene wall, e.g., changing pore diameter of graphene unit (D) while keeping the same coating height (H). Figure 5.8 illustrates a representation of how the change of wall thickness affects the volume of air trapped leading to the change in surface repellence of liquids droplet.

Figure 5.8. SEM images (top) and schematic illustration (bottom) for the curved three-phase contact lines with side view and top view. Droplet deposited on the (a) thin ($D_1=1/\kappa_1$) and (b) thick microscale pore coating surface ($D_2=1/\kappa_2$).

In the case of a porous structure, ϕ_{air} can be approximately calculated by the following equation and independent to the coating thickness:⁴⁸

$$\phi_{air} = \frac{D}{T + D} \quad \text{(Equation 5.3)}$$

As ZIF-8 particles grow on graphene wall surface, it reduces pore diameter of the graphene (D) as well as increases the wall thickness (T). Therefore, sum of T and D, $(T+D)$, i.e., the average pore size of GH-PDA should stay unchanged and should equal to 2 μm , as can be seen from Figures 5.2 and 5.4. We choose three samples, silanized GH-PDA, silanized GH-PDA-Z₂ and silanized GH-PDA-Z₄ with T approximately equals to 55, 100 and 400 nm, respectively, for the calculation of air fraction of porous structure. D therefore should be 1.945 μm , 1.90 μm and 1.6 μm , respectively. It is clearly seen that $T < D/2$ in all cases, thus, all samples can be considered as microscale porous structure rather than nanoscale porous in which T exactly equal to $D/2$.²⁶⁴ By substituting the values of T and D in equation 5.3, ϕ_{air} for silanized GH-PDA, silanized GH-PDA-Z₂ and silanized GH-PDA-Z₄ are 0.97, 0.95 and 0.80, respectively. Substituting these air fraction values and Young contact angle (71.1°) into equation 2.5, we can calculate the theoretical contact angle values of the liquid droplets. Therefore θ_{EG}^* for silanized GH-PDA, silanized GH-PDA-Z₂ and silanized GH-PDA-Z₄ are found to be 163.8°, 159° and 137°, respectively. θ_{EG}^* for silanized GH-PDA-Z₄ is smaller than 150° implying the transition from Cassie-Baxter state to Wenzel state. These values indicate that the presence of smaller air fraction in silanized GH-PDA-Z₂ and silanized GH-PDA-Z₄ creates less oleophobicity compared to silanized GH-PDA. This is an expected outcome when either nanoscale porosity or microscale porosity is dominant compared to the hierarchical structure.^{226, 265}

To explain the results, Laplace pressure is considered as the driving force, because it causes the contact line to move downward, making the curve at solid/liquid/air interface (Figure 5.8). Laplace pressure, ΔP_{Lap} , is proportional to curvature of liquid (κ) which is inversely proportional to the radius of a curved surface.

$$\Delta P_{Lap} = 2\kappa\gamma \quad \text{(Equation 5.4)}$$

where κ is the curvature at the sagging contact line and is inversely proportional to the radius a of a curved surface ($\kappa=1/a$). When pore diameter on the surface decreases, i.e., wall thickness increases, it will cause an increase in Laplace pressure. This makes the three-phase contact line to slide down from the top side of porous structure and move downward to the bottom causing the penetration of liquid droplet. Therefore, the larger value of Laplace pressure will cause easy penetration of liquid through a porous surface.⁴⁸

5.3.3. From Surface Coating to Separation of Immiscible Liquids Mixture

Porous Ni foam was used to fabricate filtration membrane. The Ni foam was also modified by PFDTS to evaluate any differences after drop casting silanized GH-PDA-Z₄ on it. Figures 5.9-a,b show the morphology of Ni foam before and after PFDTS modification. The SEM images indicated the maintain of surface morphology. However, the CA_{FM} of silanized Ni foam increased significantly, indicating the change of surface chemistry. The coating of silanized GH-PDA-Z₄ simultaneously decreased the SE of Ni foam and increased its surface roughness (Figure 5.9-c). The increase in surface roughness strengthens the repellence of

liquid if the contact angle is higher than the intrinsic value or allows the liquid to penetrate if the contact angle is lower than the intrinsic value.^{266, 267} Therefore, CA_{FM} of silanized GH-PDA- Z_4 coated Ni foam further increased. Figure 5.9-d, in addition, confirms the CAs of other liquids. Generally, silanized GH-PDA- Z_4 coated Ni foam displayed significantly higher CAs of liquids from water to ethylene glycol. Especially, while bare Ni foam and silanized Ni foam exhibited superlyophilicity to n-hexadecane, silanized GH-PDA- Z_4 coated Ni foam exhibited lyophobicity with $CA_{HDC} = 80.5 \pm 1.5^\circ$. All the Ni foam showed superlyophobicity to liquids with lower surface tension than n-hexadecane.

Figure 5.9. SEM image of (a) bare Ni foam, (b) silanized Ni foam, and (c) silanized GH-PDA- Z_4 coated Ni foam. A droplet of 3 μL formamide on top of the respective membranes is shown as insets in (a - c). (d) static contact angle of different surface tension liquid droplets on surface of bare Ni foam, silanized Ni foam and silanized GH-PDA- Z_4 coated Ni foam, respectively.

Apart from the ability to separate the immiscible liquids, the separation efficiency as well as the repeatability of a membrane are highly desirable criteria for practical applications. Therefore, we studied the separation efficiency of the silanized GH-PDA-Z₄ coated Ni foam membrane from the immiscible liquid mixtures. The separation efficiency of CCl₄ from the mixture of high surface tension solvents was found higher than 98 % (Figure 5.10-a). In addition, Figures 5.10-b and c show the separation efficiency of formamide from the mixture with low surface tension solvents and corresponding flux were above 85% and 2500 Lm⁻²h⁻¹. Moreover, to examine the regeneration of the membrane, we used a mixture of formamide and chloroform. After each filtration, the membrane was washed with ethanol and dried in air at 80 °C. It is clear to see that the membrane was good to filter formamide out of chloroform at high efficiency (more than 83 %) and the flux maintained approximately 3000 Lm⁻²h⁻¹ after 20 cycles of filtration (Figure 5.10-d). This result is promising for a long-term application of membrane.

Figure 5.10. (a) separation efficiency of mixture between different polar solvents and carbon tetrachloride. (b) and (c) separation efficiency and calculated flux through the membrane of mixture between formamide and nonpolar solvents. d) re-generation and filtration flux of membrane using formamide and chloroform after 20 cycles.

We further demonstrated that the surface chemistry and surface topography of the membrane are very crucial to successfully separate two immiscible liquids that have small surface tension difference. We used the mixture of CF and FM as an example for this experiment (Figure 5.11).

Figure 5.11. Optical images represent separation of formamide/chloroform mixture with a) bare Ni form, b) silanized GH-PDA- Z_2 coated Ni form and c) silanized GH-PDA- Z_4 coated Ni form. Formamide is colored by methylene blue.

FM was colored with methylene blue and can be seen floating on top of the mixture as the density of chloroform is higher. Bare Ni foam, silanized GH-PDA- Z_2 and silanized GH-PDA- Z_4 coated Ni foam membranes were used for the separation. Where bare Ni foam membrane cannot selectively separate the mixture components and allowed both the liquids to pass through it (Figure 5.11-a₁ to 5.11-a₃), silanized GH-PDA- Z_2 coated Ni foam membrane repelled both the liquids and hence cannot filter the mixture (Figure 5.11-b₁ to 5.11-b₃). In contrast, when silanized GH-PDA- Z_4 coated Ni foam membrane was used, low surface tension chloroform can easily pass through it while comparatively high surface tension formamide remains on top of the membrane (Figure 5.11-c₁ to 5.11-c₃).

Furthermore, filtration of CF and FM mixture using silanized Ni foam was also conducted as another control (Figure 5.12). Due to the high repellency to formamide, silanized Ni foam potentially separates formamide out of chloroform (from figure 5.12-a to 5.12-c). However, when more liquid come to the membrane surface, a part of formamide also penetrate through the membrane (Figure 5.12-d). This is caused by the fact that the smooth surface has lower intrusion pressure than a rough surface, meaning lesser amount of liquid can be filtered using a smooth membrane.¹⁹⁵ Therefore, silanized GH-PDA-Z₄ with higher surface roughness allowed the separation of immiscible liquids more effectively.

Figure 5.12. Optical photographs of separation of chloroform/formamide mixture using silanized Ni foam. First, formamide stays on top and chloroform passes through the membrane. However, when more liquid comes, a part of formamide also penetrates through the membrane due to intrusion pressure.

The CA values of silanized GH-PDA-Z₂ and silanized GH-PDA-Z₄ toward various liquids revealed that both surfaces cannot repel critical low ST liquids such as n-hexane (ST = 18.5 mN/m). Therefore, both the coated Ni foams show

potential to separate n-hexane from high surface tension liquids. In this work, FM and n-hexane (HEX), mixture was used to demonstrate the separation. Interestingly, both the silanized GH-PDA-Z₂ and silanized GH-PDA-Z₄ coated Ni foam membranes showed successful separation of formamide out of n-hexane (Figure 5.13 and Figure 5.14). The strategy may have the potential for the separation of other high surface tension liquids with n-hexane as well.

Figure 5.13. Optical photographs of separation of n-hexane/formamide mixture using silanized GH-PDA-Z₄ coated Ni foam. n-hexane quickly passes through the membrane while formamide stays on top.

Figure 5.14. Optical photographs of separation of n-hexane/formamide mixture using silanized GH-PDA-Z₂ coated Ni foam. n-hexane quickly passes through the membrane while formamide stays on top.

5.4. Conclusion

In summary, the porous GH-PDA particles are successfully prepared in the presence of ionic liquid. The particles represent outstanding properties of PDA layer, in which ZIF-8 nanoparticles and PFDTs molecules can easily deposit and tailor both the surface morphology and surface chemistry of pristine GH-PDA. Such modification can manipulate the surface topography of the composites by controlling the amount of entrapped air underneath, leading to different liquid repellency. The decrease in air fraction resulted conversion from superamphiphobicity to omniphobicity, indicating the transition from Cassie state to Wenzel state. Based on this tailored property, Ni foam coated by the graphene composites can be used to separate the immiscible liquids. To sum up, the comparison between materials developed in this chapter and chapter 4 and

materials reported previously for separation of immiscible organic liquid is mentioned in the table 5.1 below.

Substrates/materials		Fabrication method	Cost	CA(FM)	Application	Ref
Metal mesh	Cu(OH) ₂ nanoneedles	Oxidation of copper mesh, followed by modification of 1H,1H,2H,2H-perfluorodecyl triethoxy silane	Quite low	145.5°	Filtration	[58]
	Electrospun fiber	Electrospinning of polyvinylpyrrolidone, titanium (IV) butoxide (TNTB), orthosilic acid tetraethyl ester (TEOS) mixture followed by pyrolysis and surface modification	High	~120°	Filtration	[70]
	Electrospun fiber	Electrospinning of poly(vinylidene fluoride-co-hexafluoropropylene) and 1H, 1H, 2H,2H-perfluorodecyl Triethoxy silane	High	135.3°	Filtration	[196]
	PDA NPs/SMS	Deposition of PDA nanoparticles followed by the growth of silica microsheets generated from hydrolysis of octadecyltrichloro silane	Low	149.7°	Filtration	Chapter 4
Cotton fabric	PDA NPs/SMS			153.5°	Filtration	Chapter 4
Polyester fabric	PDA NPs/SMS			135.9°	Filtration	Chapter 4
Melamine sponge	PDA NPs/SMS			154.1°	Absorption	Chapter 4
PU sponge	PDA NPs/SMS			149.7°	Absorption	Chapter 4
Filter paper	PDA NPs/SMS			153.2°	Filtration	Chapter 4
Ni foam	GH-PDA-Z ₄	Drop-casting of silane modified GH-PDA/MOFs	Quite high	140.5°	Filtration	Chapter 5

Table 5.1. The comparison between materials developed in chapters 4 and 5 and the previous materials reported in literature review for immiscible liquid separation.

Chapter 6. Conclusions and Future Research

6.1. Conclusions

In this thesis, we have presented three novel super-wetting material systems derived from polydopamine (PDA) modification for the effective separation of immiscible liquids. The surface treatment by highly adhesive PDA imparted a series of properties such as physical attaching, metal-ion chelating or (in air) amphiphilic property, which is involved in the strong adhesion of PDA molecules. The coating of PDA on various materials also allowed for designing novel structures with tailored wettability on which liquids with different surface tension can selectively penetrate. The strategies introduced in this thesis provide an effective method to solve the problems related to liquid remediation.

Surface property	Name of materials	Application	Advantages	Disadvantages	Ref
Dual-superlyophobicity	cotton@PDA KP@PDA	Selective filtration of oil and water	-Cost effectiveness, High separation flux of both oil and water and high efficiency - The fabrication is fast and simple with only one step deposition of PDA nanoparticles on the fibers	- The biomass fibers are collected without proper quality assurance - The fouling of highly viscous oils such as crude oil can cause decrease in the separation flux	Chapter 3
Superlyophobicity	paper@PDA@C18 Mesh@PDA@C18 Cotton@PDA@C18 PE@PDA@C18	Filtration of immiscible organic liquids	-Excellent ability to filter low surface tension liquids from the higher immiscible ones -Source of raw materials is not a problem due to the	-The fabrication still requires the use of strong oxidation agent to deposit PDA nanoparticles - Organic	Chapter 4

			adhesion of PDA	solvents such as toluene are required to grow the silicone microsheets (SMS)	
	MS@PDA@C18 PU@PDA@C18	Absorption of low surface tension liquids	-Excellent absorption capacity towards low surface tension liquids - The separation by absorption is not limited to oil/water and can separate almost any immiscible organic liquids		
Superamphiphobicity Omniphobicity	Silanized GH-PDA-Z	Filtration of immiscible liquids	-The silanized GH-PDA-Z can be applied into both coatings and filtration separation. - The separation of immiscible liquids can be selective by tailoring surface wettability of the graphene/MOFs composites between superamphiphobicity and omniphobicity	-The relatively high cost of graphene can render the practical application of the membranes. - The omniphobic membrane is unable to separate oils with surface tension around 30 mN/m such as n-hexadecane from higher surface tension liquids	Chapter 5

Table 6.1. Advantages and disadvantages of as-prepared materials in this thesis compared to the other available ones which are developed from the same raw materials and/or substrates.

First, we demonstrated a facial approach to design dual-superlyophobic membranes by using cotton and kapok biomass fibers functionalized with PDA nanoparticles. Surface roughness imparted by PDA nanoparticles endowed cotton@PDA and KP@PDA with simultaneous underwater superoleophobicity and underoil superhydrophobicity. The interesting property allows for retaining oil when the membranes are infused with water, while the membranes can retain water when they were infused with oil. When the mixtures of oil and water are

applied, the robust coating of PDA nanoparticles give rise to membranes with selective separation of oil and water in high efficiency, high flux, and good regeneration.

Second, we developed various superlyophobic materials that can repel liquids with surface tension higher than 30 mN/m, and thus not only limited to water ($ST = 72$ mN/m). The versatile adhesion of PDA makes it possible to modify both hydrophobic and hydrophilic materials. The PDA functionalized materials were then modified by silicone micro-sheets (SMSs) derived from hydrolysis of octadecyltrichloro silane (ODTS-C18). In contrast, a thin layer of silicone (SL) was observed on the surface of materials without PDA modification. The growth of SMSs enhanced surface roughness of materials, leading to more effective repellency of as-prepared surfaces towards high surface tension liquids such as formamide or ethylene glycol, which have significantly lower surface tension than water. The as-prepared materials have shown great ability to separate immiscible liquids by both absorption and membrane filtration.

Third, we synthesized porous GH-PDA colloid with the assistance of ionic liquids. The self-polymerization of dopamine into PDA not only functionalized graphene oxide but also reduced GO. Surface morphology of the porous graphene was tailored by the decomposition of ZIF-8 nanoparticles. The GH-PDA and GH-PDA-ZIF-8 composites were modified with fluoro-silanes to further tailor the surface energy. The ZIF-8 loading on GH-PDA resulted in different wettability of the composites. The surface wettability evolving from superamphiphobicity to omniphobicity allows for controlling liquid repellency, which enables selective

liquid penetration through the composites. The Ni foam was coated with the as-prepared composites to separate mixtures of different immiscible liquids.

One of the interesting properties of PDA is its ability to coat on various surfaces regardless to size or shape of pristine materials. Thus, the surface coating using PDA is scalable.²⁶⁸ In this thesis, all the raw materials and substrates, including kapok fiber, cotton fiber, polyurethane sponge, melamine sponge, cotton fabric, polyester fabric, stainless steel mesh, filter paper are inexpensive. To scale up the filtration materials, we only need to use a larger size of raw materials and container, remaining unchanged the fabrication conditions. The scaled-up materials, thus, can treat larger volume of immiscible liquids. However, the relatively high cost of graphene may cause the difficulty in scaling up of the graphene/MOFs composite.

6.2. Future Research

In this thesis, functional coating forms the fundamental basis of fabricating materials with tailorable wettability. Although these materials displayed the ability to separate immiscible liquids, there are still many other applications that the PDA-based wetting materials can be used. In this section, I will discuss possible applications of the PDA-based hybrid materials as well as some expansions of new materials.

Future research may follow these strategies:

1. In chapter 3 of dual-superlyophobic membranes for selective separation of oil and water, the raw materials are not consistently collected. The kapok fibers

were collected from a local garden. This does not assure the quality of the raw materials. Although, the as-prepared membranes exhibit excellent ability to selectively separate oil and water a further study should be conducted to justify the effect of materials source to the final outcomes. In future work, I hope a proper quality of raw materials can improve the outcome of the membranes.

2. Currently, the PDA-based wetting materials are applied to separate simple mixtures of immiscible liquids, and the separation relies on existing substrates. PDA only plays the role as a coating layer. Hence, self-standing PDA membrane with controlled pore sizes is an interesting device for the separation of not only simple mixture but also emulsion. Porous PDA has been reported for the fabrication of Lithium battery.²⁶⁹ We can apply the same principle to make self-standing porous PDA membrane for both mixture and emulsion separation of immiscible liquids.

3. In the two systems of this thesis, I have shown that the surface energy of the membranes should be controlled so that it is located between surface energy values of immiscible liquids. In this case, the lower surface energy liquid can penetrate, while the higher surface energy liquid is retained. Moreover, the surface of the membranes is usually manipulated by covalent modification. However, it is very difficult to control the surface energy of membrane for the separation of immiscible liquids that have critical low surface energy difference such as ethylene glycol (EG, $SE = 47.7 \text{ mJm}^{-2}$) and diiodomethane (DIM, $SE = 50.7 \text{ mJm}^{-2}$). Fowkes et al. have reported that SE consists of two individual components: dispersive SE (DSE) and polar SE (PSE).^{270, 271} In some cases, the

dispersive interfacial attraction force and polar interfacial attraction force can be treated independently. On the other hand, $PSE_{EG} = 16 \text{ mJm}^{-2}$ is higher than $PSE_{DIM} = 1.8 \text{ mJm}^{-2}$. Therefore, the fabrication of membranes that utilize polar-polar interaction is promising for the separation of small difference SE immiscible liquids.

4. The use of tailored wetting materials in this thesis focuses on liquid-liquid separation. However, the controlled wetting materials are believed to have more applications. In particular, the chemical versatility of PDA provides different types of surface modification. Therefore, the PDA-based hybrid wetting materials can be applied to other aspects of environmental protection. For example, our previous work showed that PDA can direct the growth of hyperbranched Au plasmonic blackbodies (AuPBs) which showed broad-spectrum absorbance in the first near-infrared (NIR-I) and the second near-infrared (NIR-II).¹⁴⁵ Moreover, Au@PDA nanoparticles have shown excellent catalytic activity. Therefore, the multifunctional wetting materials can be fabricated for the integrated applications in nanocatalysis, liquid-liquid separation and water harvesting driven by sunlight.

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List of Publications

1. **Van Cuong Mai**, Paramita Das, Goei Ronn, Jiajing Zhou, Zheng Fang, Teik Thye Lim, and Hongwei Duan, Hierarchical Graphene-Metal Organic Frameworks: from Superamphiphobic Coatings to Membranes for Separating Immiscible Liquids, [in preparation](#)
2. **Van Cuong Mai**, Paramita Das, Jiajing Zhou, Teik Thye Lim, and Hongwei Duan, Biomass-Derived Dual-superlyophobic Membranes for Selective Oil/water Separation, [in preparation](#)
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4. Ling Bai, **Van Cuong Mai**, Yun Lim, Shuai Hou, Helmuth Möhwald, and Hongwei Duan, Large-scale non-iridescent structural color printing enabled by infiltration driven non-equilibrium colloidal assembly, [Adv. Mater. 2018, 30, 1705667](#).
5. Paramita Das, **Van Cuong Mai** and Hongwei Duan, Highly Flexible Bioinspired Ternary Nanocomposites based on Carboxymethyl Cellulose/Nanoclay/Graphene Oxide, [Submitted](#)
6. Ling Bai, Yuheng He, Jiajing Zhou, Yun Lim, **Van Cuong Mai**, Yonghao Chen, Shuai Hou, Yue Zhao, Jun Zhang and Hongwei Duan, Scalable Production of Responsive Amorphous Photonic Structures by Colloidal Metal–Organic Frameworks, [Submitted](#)

7. Ling Bai, Yuheng He, Jiajing Zhou, Yun Lim, **Van Cuong Mai**, Yonghao Chen, Shuai Hou, Yue Zhao, Jun Zhang and Hongwei Duan, Responsive Amorphous Photonic Structures of Spherical/Polyhedral Colloidal Metal–Organic Frameworks, [Adv. Optical Mater.](#) **2019**, 1900522.
8. Shuai Hou, Surendra H. Mahadevegowda, **Van Cuong Mai**, Mary B. Chan-Park, and Hongwei Duan, Glycosylated Copper Sulfide Nanocrystals for Targeted Photokilling of Bacteria in Near Infrared II Window, [Submitted](#)
9. Jiun-Ming Li, Po-Hsiung Chang, Lei Li, Yiyuan Liu, Van Bo Nguyen, Chiang Juay Teo, Boo Cheong Khoo, **Van Cuong Mai**, Hongwei Duan, Crumpling Behavior of Graphene Oxide in Jet A-1 Vapor in Air and Its Effects on Combustion Process, [Book Chapter, 31th International Symposium on Shock Waves 1](#). pp 269-277. DOI: 10.1007/978-3-319-91020-8_30