Preparation of novel special wettable materials for water remediation

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**NANYANG
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UNIVERSITY**

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**PREPARATION OF NOVEL SPECIAL WETTABLE
MATERIALS FOR WATER REMEDIATION**

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**Interdisciplinary Graduate School
Nanyang Environment and Water Research Institute**

2017

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**Interdisciplinary Graduate School
Nanyang Environment and Water Research Institute**

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2017

Statement of Originality

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

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Abstract

Materials with special wettability have attracted tremendous research attention in recent decades in many fields of applications, such as energy storage and conversion, medicine and healthcare, nanoparticle synthesis and environment remediation. Particularly, the special wettable material has been regarded as one of the most promising materials for water remediation and purification, due to its controllable affinity towards water and various water contaminants. Thanks to the extensive research effort, significant progress has been achieved in the fundamental understanding of the surface wetting phenomenon, the synthesis of special wettable materials, and the potential applications in various fields. The practical implementation of such materials requires the development of novel materials from low-cost precursors through sustainable preparation methods, which unfortunately has not been sufficiently explored and researched.

In this thesis, I will present my research works on two novel low-cost and sustainable special wettable materials, and demonstrate their promising application in oily water remediation. The mainly adopted material development strategy is to convert waste materials into functional special wettable materials.

In the first project, a novel hydrophobic and oleophilic carbon aerogel is developed using waste pomelo peels as raw materials. The resulted carbon aerogels possess a three-dimensional interconnected porous structure with light density. The carbon aerogels are used as absorbents to selectively absorb water-immiscible oils and organics from oil/water mixtures. The low-cost and sustainable preparation approach and the high oil absorption capacity make the carbon aerogel a promising material for cleaning up oil spills.

In the second project, a novel inorganic superhydrophilic and underwater superoleophobic mesh is developed using waste soda-lime glass as starting material. Due to the high surface tension and surface roughness, the resulted mesh shows high affinity toward water in air, and extremely low affinity toward oils under water. Therefore, it can selectively and continuously separate oil/water mixtures through filtration by allowing water permeation while blocking oils. In addition, the as-developed inorganic mesh shows the excellent stability against various harsh environments and the multifunctional water remediation characteristics, making it highly promising for practical water remediation applications.

Figure Captions

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Abbreviations

3D	Three-Dimensional
CA	Contact Angle
CNT	Carbon Nanotube
DI	Deionized
EDS	Energy Dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
ICP-OES	Inductively Coupled Plasma with Optical Emission Spectrometer
HRTEM	High Resolution Transmission Electron Microscopy
MB	Methylene Blue
OCA	Oil Contact Angle
PDDA	polydiallyldimethylammonium
PFO	perfluorooctanoate
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SEI	Secondary Electron Images
SNM	Silica-based Nanowires-coated Mesh
SS	Stainless Steel
TEM	Transmission Electron Microscopy
UWOCA	Underwater Oil Contact Angle
WCA	Water Contact Angle
XRD	X-ray Diffraction

Chapter 1

Introduction

This chapter gives a brief overview of the thesis. The research background and the research topic are presented which contextualize the thesis. Then, the scope and objectives of this thesis are described based on the problem statement. With a brief description of each individual research work that will be presented in details in following chapters, the research outcomes and conclusions of this Ph.D. thesis are summarized.

1.1 Problem Statement

1.1.1 Clean Water Scarcity

Water is the vitally important natural resource to all forms of life on the Earth. For human beings, clean and safe water determines not only the public health, but also the development of human civilization. However, water scarcity is currently one of the major global challenges (Figure 1.1).^[1] The total amount of fresh water is insufficient. Although 70% of the Earth surface is covered by water, the portion of fresh water only takes about 2%. However, not all fresh water is available to human, as 90% of the fresh water stays as ice which is frozen and locked in glaciers. Currently, over 1.2 billion people live without a proper supply of clean water, and such problem is expected to be further deteriorated by the continuously growing water demand.^[2] The global water usage is projected to further increase by over 50 percent within the next 30 to 40 years. Unfortunately, large amount of clean water is still wasted due to the improper water usage habits, especially in agricultural activities.^[3, 4]

Due to the over-paced industrialization process and expansion of human population, the clean water shortage is further aggravated by pollutions from industrial and domestic wastewater discharge. Among various water contaminants, oils and organic solvents are one of the major concerns. Many modern industries produce oily water, such as oil and gas, metallurgy, pharmaceutical and cosmetics industries, whose oily wastewater needs to be purified before discharge. Besides the oily water resulting from the daily industrial and domestic effluent discharges, the precious sea water resources and marine habitat are also vulnerable to anthropogenic disasters, such as massive oil spills.^[5, 6] Therefore, oily water remediation by

efficiently separating oil/water mixtures has become a very practically important topic in both research and industry sectors.

Figure 1.1 Global challenge of water scarcity comes from four aspects, i.e. fresh water shortage, water pollution, water wastage, and anthropogenic disasters.

1.1.2 Special Wettable Materials for Oily Water Remediation

Many new materials and technologies for water remediation have been developed by researchers, aiming for the higher efficiency, lower cost and more sustainable approach.^[7, 8] Materials with special surface wettability have recently attracted increasing research attention as promising materials for water remediation.^[9, 10] Particularly for oil/water separation, special wettable materials which have the opposite surface affinity toward water and oils are developed and studied.^[11-13] Two types of special wettable materials can be used in selective oil/water separation, i.e. hydrophobic and oleophilic materials which remove oil from water, and

hydrophilic and oleophobic materials which remove water from oil. Although significant breakthrough has been achieved, there are still several problems that hinder the practical implementation of these special wettable materials, such as expensive precursors and raw materials, complicated synthesis process, and toxic chemicals and by-products. Therefore, it is still highly desired for the further development of novel special wettable materials with low-cost precursors through environmentally friendly approaches. Furthermore, the accumulation of solid waste invades the precious and limited land spaces for human and animals to live on. Effective solid waste management has become an important research topic. Some previous research demonstrated the preliminary concept and possibility of converting solid waste into functional materials, in order to reduce the fabrication cost of functional materials and mitigate the solid waste pollution simultaneously. However, this research direction is still at an initial stage without proper exploration, which requires more research efforts.

1.2 Objectives and Scope

Based on the problem statement and research gaps mentioned above, the main objective of this thesis is to explore the preparation of low-cost and sustainable special wettable materials by using common waste materials as raw materials. The basic material development strategy in this thesis is proposed to be a “waste-to-treasure” philosophy. The scope of this thesis includes two general aspects, i.e. to achieve the synergistic effect between the materials surface chemistry and the surface architecture by proper waste conversion methods, and to study the potential applications of the developed materials in selective oil/water separation. The specific research scopes are described as follows:

First, biomass is used as raw material to prepare the hydrophobic and oleophilic

carbon aerogel. The biomass chosen here is the waste pomelo peel, which naturally possesses highly porous structure. The non-oxidative pyrolysis technique is used to carbonize the waste pomelo peel, yielding the porous hydrophobic and oleophilic carbon aerogel. Then, the as-developed carbon aerogel is evaluated as a potential oil absorbent for selective oil absorption from water, which serves as a promising candidate in oil spills cleaning up.

Second, an inorganic superhydrophilic and underwater superoleophobic mesh is developed using waste soda-lime glass as raw material. The high surface tension and the rough surface architecture are achieved simultaneously by the hydrothermal method, which converts the waste glass into the functional material. Water can selectively permeate through the mesh while oils are blocked, resulting in the selective oil/water separation. In addition, the stability of the as-developed mesh under various harsh environment is also studied. Finally, a multifunctional water remediation approach is explored, by which metal ions and water-soluble organic dyes can be removed simultaneously during the oil/water separation process.

1.3 Dissertation Overview

This thesis addresses the current research gap in the sustainable preparation of special wettable materials and the waste re-utilization by two representative types of waste materials. The conversions from organic biomass waste and inorganic waste into functional materials are demonstrated. The usages of these sustainable and low-cost special wettable materials in water remediation, especially in oil/water separation, are demonstrated with proof-of-concept applications using absorption approach and filtration approach.

Chapter 1 provides an overview of the research background of this thesis,

rationalizes the research topic, identifies the research gaps and outlines the research goals and scope.

Chapter 2 provides a comprehensive literature review about the current research progress on the synthesis of special wettable materials and their potential applications in oil/water separation.

Chapter 3 presents the methodology involved in the thesis to prepare, characterize, and utilize the special wettable materials. The rationales for the methods and materials selection are discussed, and the proof-of-concept applications are demonstrated.

Chapter 4 presents the research about the conversion of a biomass material, i.e. waste pomelo peel, into a three-dimensional (3D) porous hydrophobic and oleophilic carbon aerogel. The pyrolysis technique is used to carbonize the biomass in a non-oxidative environment. The carbon aerogel is used as the high efficiency oil absorbent, which shows high oil absorption capacity and excellent reusability.

Chapter 5 presents a novel superhydrophilic and underwater superoleophobic mesh that is developed using waste soda-lime glass as the starting material. The resulted mesh can selectively allow water to permeate while block oils. The as-developed mesh also shows the excellent stability against many harsh working conditions, as well as the multifunctional water remediation ability.

Chapter 6 provides a conclusion of the entire thesis by showing the new knowledge that has been developed from this thesis. The reconnaissance studies which can be conducted in the future are also elaborated.

1.4 Findings and Outcomes/Originality

In this thesis, I demonstrate that two different types of waste materials, i.e. organic biomass and inorganic glass waste, can be converted into functional materials by two different methods, leading to two novel special wettable materials:

First, I successfully converted the biomass into a novel carbon aerogel. From the research, I found that the 3D porous structure of the biomass aerogel was well maintained after the pyrolysis process, directly leading to a 3D carbon aerogel. The cellulose-based biomass was the key for the preservation of the 3D structure skeleton.

Second, I successfully converted the waste soda lime glass into a superhydrophilic and underwater superoleophobic mesh. From this research, I demonstrated that the high surface energy and rough surface textures were the keys to construct underwater superoleophobic surface. I also demonstrated the concept of multifunctional water remediation, and proved the excellent stability of the mesh.

For each type of waste, I proved that the combination of the surface energy and the surface roughness was the key to construct special wettable surface. For different type of waste, the corresponding conversion method should be properly selected, in order to well match the intrinsic characteristics of the waste.

This thesis broadens the knowledge on the synthetic methodology for the special wettable materials. In addition, this thesis also contributes new insights into the smart and novel methods for waste management and re-utilization.

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Chapter 2

Literature Review

This chapter provides a review of the recent development in the preparation of special wettable materials and their application in water remediation, especially oil/water separation. First, the fundamental theory of wetting and superwetting behaviours on solid surfaces is introduced. Then, materials with different types of special wettability are reviewed and summarized, including hydrophobic and oleophilic materials, hydrophilic and oleophobic materials, and materials with responsive/switchable wettability. Finally, the questions related to the thesis based on literatures are also discussed.

2.1 Basic Theory on Wetting and Superwetting Behaviours on Solid Surface

Wetting is the phenomenon which occurs at the liquid-solid interface when the two phases are brought into contact. The wetting of the liquid is determined by two forces, i.e. adhesive force which causes the liquid to spread across the solid surface, and cohesive force which maintains the liquid in the ball-like shape to minimize its surface energy.^[1] The wetting behaviours are commonly characterized by contact angle (CA) measurement. The contact angle is measured between the tangent lines of the liquid-air interface and the solid-liquid interface at the point where the two interfaces meet. It is determined by the classic Young's equation:

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

where γ_{SV} is the interfacial energy between the solid phase and the vapour phase, γ_{LV} is the interfacial energy between the liquid phase and the vapour phase, and γ_{SL} is the interfacial energy between the solid phase and the liquid phase. Figure 2.1 shows the schematic illustration of the three phases and the position of the contact angle.

Figure 2.1 Schematic illustration of the contact angle of a liquid sit on a smooth solid surface.

Water is the most commonly used liquid to characterize the surface wetting behaviour. Based on the classic Young's equation, when a droplet of water is brought into contact with a surface, if the water contact angle (WCA) is smaller than 90° , the surface is defined as hydrophilic; if the contact angle is larger than 90° , the surface is defined as hydrophobic. This is, however, a purely mathematical approach. As the further development in the fundamental understanding on the physical and chemical state of water molecules, new theories are also proposed that define new watersheds between a hydrophilic surface and a hydrophobic surface, e.g. 65° or 62.7° .^[2] Although these new theories have brought new insights into the wetting behaviours, contradictions and disputes still exist, which call for future in-depth studies. In this thesis, I will follow the classic theory by defining the surface hydrophilicity/hydrophobicity using the watershed of 90° . It is therefore logic to further define that the oil contact angle (OCA) watershed between an oleophobic surface and an oleophilic surface is 90° for any type of oils, which is also generally acceptable in the pervasive literatures.

The surface chemistry, or more specifically the surface energy is the primary factor that determines the wetting behaviour of the solid surface. For example, a solid substrate with surface energy higher than that of water exhibits hydrophilicity and oleophilicity (since most oils have lower surface energy than that of water); while a solid substrate with surface energy higher than oils and lower than water exhibits hydrophobicity and oleophilicity. The theory elaborated above is based on an ideal surface, which means a perfectly flat and chemically homogenous surface (Figure 2.2a). In practical situations, both surface chemistry and surface roughness play the critical roles in determining the wetting behaviour, i.e. when the solid surface is rough, the wetting behaviours of the liquid will be affected. The surface roughness is the second critical factor that determines the wetting behaviour of a solid substrate. To study such wetting phenomena on the rough surface, two models were

proposed and used to describe the wetting of a liquid droplet on a rough solid surface.

The Wenzel Model predicts the CA of a liquid droplet on a rough surface to be:

$$\cos \theta^* = R \cos \theta \quad \text{(Equation 2.2)}$$

where θ^* is the apparent contact angle, or measured contact angle of the liquid on the rough surface, and θ is the intrinsic contact angle, which is defined as the contact angle of the liquid on the perfectly smooth surface of the same chemical composition. R is the so-called roughness factor, which is calculated as the ratio between the real surface area of the surface to the apparent surface area. For a rough surface, as the roughness factor will always greater than 1, the Wenzel Model predicts that the roughness of the surface will enhance both the wetting and the antiwetting behaviours of the flat surface. This means that when θ is less than 90° , θ^* decreases with surface roughness, i.e. the surface appears to be more hydrophilic; And when θ is larger than 90° , θ^* increases with surface roughness, i.e. the surface appears to be more hydrophobic. In Wenzel Model, the liquid droplet completely wets the cavities of the rough surface, and the solid-liquid-vapour three phase line is continuous, a situation under which the droplet is called being at the Wenzel state (Figure 2.2b). The Wenzel state represents the thermodynamically equilibrium state (or absolute minimum energy state) for a completely wetted solid surface, where the total free energy is minimum. The droplet experiences pinning effect, and does not move on the surface easily.

The second model for the wetting behaviours on rough surface is the Cassie-Baxter Model, in which the liquid droplet on the rough surface is supported by both solid materials as well as the air trapped within the cavities (Figure 2.2c). The apparent

contact angle of a droplet that is measured on rough surface in the Cassie state is given by the equation:

$$\cos \theta^* = f \cos \theta + (1 - f) \cos \theta_{LV} \quad (\text{Equation 2.3})$$

where f is the fraction of the rough surface of the solid which is in contact with the liquid droplet, and θ_{LV} is the intrinsic CA between the air and the liquid. It is generally assumed that the θ_{LV} is 180° . As such, the equation 2.3 can be simplified to:

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

In Cassie-Baxter Model, the solid-liquid-vapour three phase line is discontinuous, and the droplet is said to be at the meta-stable state, i.e. Cassie state. The Cassie state represents the lowest energy state in an open-air regime.

Figure 2.2 Schematic illustration of a liquid droplet sits on a) a flat surface, b) a rough surface at Wenzel state, and c) a rough surface at Cassie state.

Generally, solid surface with liquid contact angle larger than 150° is defined as a superantiwetting surface. For example, superhydrophobic surface refers to surface with WCA larger than 150° , and superoleophobic surface refers to a surface with

OCA larger than 150° . However, the water droplet can still behave differently depending on whether the water droplet is in Wenzel state or Cassie state. The water droplet in Wenzel state will experience high adhesion force with the solid surface, as the water droplet fully filled into the micro/nano cavities. In contrast, the water droplet in Cassie state will show minimum adhesion with the solid surface, as the air trapped inside the cavities will support the droplet. The Cassie state is believed to be more energetically favoured than Wenzel state for situations involving extremely rough surfaces or surfaces with extremely low surface energy. However, the surface roughness makes it possible to have several local minimum energy states (i.e. intermediate meta-stable states). The Cassie state can transit into Wenzel state (or intermediate states) under various external disturbances, either irreversibly or reversibly depending on the actual surface architectures. By the Cassie-Baxter Model, it is theoretically possible to fabricate a superhydrophobic and superoleophobic surface on any surface with a properly designed surface architecture. For example, a superhydrophobic and superoleophobic surface can be created at an intrinsically highly hydrophilic material (i.e. SiO_2 wafer) by solely manipulating the surface architecture.^[3] The superhydrophilic (or superoleophilic) surface has not been defined precisely. Although debates exist, it is generally acceptable that the superhydrophilic surface (or superoleophilic surface) is a surface with WCA (or OCA) smaller than 5° .^[2]

2.2 Special Wettable Materials for Oil/Water Separation

Oil/water separation is one of the major topics in water remediation. Oil/water mixtures are encountered not only at massive oil spill and leakage accidents, but also in the daily industrial effluent. Special wettable material displays distinctly opposite wetting status towards oil and water. Therefore, taking advantage of such special wettable materials in the oil/water separation application is expected to be

beneficial. The first example of utilizing the special wettable materials for oil/water separation was in 2004, in which a superhydrophobic and superoleophilic mesh made from polytetrafluoroethylene was used to selectively permeate oil and block water. Since then, tremendous research effort has been put into this emerging research field, and many new materials have been developed. In the following text, I will give a literature review on the special wettable materials for oil/water separation, which are divided into three categories, i.e. hydrophobic and oleophilic materials, hydrophilic and oleophobic materials, and materials with switchable wettability.

2.2.1 Hydrophobic and Oleophilic Materials

Hydrophobic and oleophilic materials are the mostly researched materials so far that can be used to separate oil/water mixtures, by selectively removing oils from water. Therefore, this type of material is categorized as the “oil cleaning” material. In this section, I will give a comprehensive summary and discussion of the current research status in “oil-removing” materials. Generally, two different separation approaches are followed when researchers utilize “oil-removing” materials, i.e. absorption and filtration.

During the absorption process, the oils and water-immiscible organic solvents in the water adhere onto the surface and subsequently fill into the inner pores of the materials, while water is repelled by the hydrophobic surface of the materials. The most straightforward approach to fabricate hydrophobic absorbents is to coat the common absorbents with low surface energy materials, e.g. alky polymers, fluorine containing polymers and carbon-based nanomaterials. Recently, a few magnetic oil absorbents were fabricated by coating various hydrophobic polymers onto the iron oxide particles to form core-shell structures.^[4-11] For example,

Fe_3O_4 @polydopamine@Ag hybrid nanoparticles were fabricated.^[5] Polydopamine and Ag nanoparticles contributed to the rough surface on iron oxide particles. After the surface modification with 1H, 1H, 2H, 2H-perfluorodecanethiol, the surface of the hybrid nanoparticles became superhydrophobic (Figure 2.3a). When used in oil/water separation, the hybrid nanoparticles could selectively absorb hexane from water surface. After the absorption process, the hybrid nanoparticles together with the entrapped hexane could be conveniently collected and recycled using a magnet (Figure 2.3b).

Figure 2.3 a) Schematic illustration of the synthesis procedure for superhydrophobic Fe_3O_4 @polydopamine@Ag nanoparticles. b) Digital photos showing the oil/water separation process and collection process with a magnet.^[5] Copyright 2015, Wiley-VCH.

In another example, by self-assembling a monolayer of hydrophobic alkanethiol on the surface of a self-propelling device,^[12] the hydrophobically modified device could self-direct toward oil droplets due to the hydrophobic interaction between the device and oil droplets, and selectively collect and transport oil droplets under the

water (Figure 2.4).

Figure 2.4 Optical microscope images of the device moving towards (left), collecting (middle), and transporting (right) the oil droplets. Inset: Scheme of the hydrophobic polymer grafted self-propelling device.^[12] Copyright 2012, American Chemical Society.

The powdery absorbents generally have very limited oil absorption capacity, as they do not have sufficient pore volume to store the oils. Furthermore, the tiny size makes the handling of the materials during practical application very difficult, due to the inevitable remnants of the absorbents left in the water. Therefore, three-dimensional (3D) porous absorbents are more promising, such as sponges, foams, aerogels, etc. Hydrophobic (superhydrophobic) absorbents were prepared by directly coating hydrophobic polymers onto the skeleton of commercial available polymeric sponges such as polyurethane sponges and melamine sponges.^[13-24] Shuai et al. prepared polydimethylsiloxane-TiO₂ coated polyurethane sponge.^[22] With only polydimethylsiloxane coating, the WCA increased from 109° to 140° due to reduced surface energy. By adding TiO₂ nanoparticles into the polydimethylsiloxane coating layer, the WCA of the polydimethylsiloxane-TiO₂ coated polyurethane sponge further increased to 154°, becoming superhydrophobic, due to the creation of surface roughness (Figure 2.5).

Figure 2.5 SEM images of a) the pristine unmodified polyurethane sponge, and b) the polydimethylsiloxane-TiO₂ coated polyurethane sponge. c) Effect of the TiO₂ concentration in the coating layer on the WCA.^[22] Copyright 2015, Elsevier B.V.

Ge et al. prepared a hydrophobic and oleophilic absorbent by coating SiO₂/polydimethylsiloxane onto commercial sponge, and connected the as-prepared sponge with a pump, obtaining a self-regulating device (Figure 2.6).^[24] The as-made prototype device could continuously absorb and transport oils from the water surface to the oil collecting tank. With such a device, the absorption capacity limit of the absorbent was overcome, i.e. using a small piece of hydrophobic absorbent, large amount of oils were collected without any water.

Figure 2.6 a) Schematic illustration of the self-regulating device by connecting a

pump with hydrophobic absorbent for oil spill remediation. b) Photographs showing the continuous absorption and transportation of oil (red color) from water surface (blue color) using the prototype device.^[24] Copyright 2014, Wiley-VCH.

Carbon-based materials attract substantial research attention for various applications. The intrinsic hydrophobicity of the graphitic carbons, arising from the low energy of sp^2 C-C bond, makes them attractive materials for selectively absorbing oil from oil/water mixtures. As typical examples, the highly crystalline sp^2 carbon nanomaterials, such as carbon nanotube (CNT) and graphene, have been proved as excellent hydrophobic materials for oil/water separation, either as surface modification agents or freestanding carbon aerogels.^[25-41]

Several freestanding 3D porous CNT sponges and graphene sponges have been fabricated as hydrophobic absorbents to selectively remove oils from water.^[25, 26, 42-58] Notably, Sun et al. fabricated a CNT-graphene composite aerogel through the “sol-cryo” method, which integrated the high surface area of graphene sheets and the strong mechanical property of CNTs.^[58] The composite aerogel possessed a low density around 0.16 mg cm^{-3} that was even lighter than the density of air, and a high porosity around 99.9%. Due to the intrinsic hydrophobicity of the CNT and graphene, as well as the ultra-high porosity, the composite aerogel showed a dramatically high oil absorption capacity, which was 900 times greater than its own weight.

Figure 2.7 a) Photo showing a CNT-graphene composite aerogel standing on a

green foxtail (*Setaria viridis*) without deforming it. b) SEM image of the wall of the composite aerogel consisting of graphene sheet and CNT. c) Absorption capacities of the aerogel for different oils and organic solvents against their densities. 1: hexane, 2: ethanol, 3: crude oil, 4: toluene, 5: motor oil, 6: vegetable oil, 7: 1,4-dioxane, 8: 1-butyl-3-methylimidazolium tetrafluoroborate, 9: chloroform, and 10: phenixin.

The viscosity of the oil determines the oil absorption rate. In oil spills, the crude oil usually possesses a very high viscosity, which significantly reduces the absorption rate and the absorption efficiency of the hydrophobic absorbents. Taking advantage of the Joule-heating property of the reduced graphene oxide, Ge et al. reported a reduced graphene oxide coated sponge, which generated heat under the electric voltage. The local temperature increase at the oil/absorbent interface in-situ reduced the viscosity of the crude oil, and therefore speeded up the oil absorption rate. The time required for the oil absorption reduced by 94.6% using the reduced graphene oxide coated sponge if the voltage was applied (Figure 2.8).

Figure 2.8 Photos showing the continuous oil absorption using the reduced graphene oxide coated sponge for viscous crude oil a) without applying a voltage and b) with a voltage.^[59] Copyright 2017, Nature Publishing Group.

Although promising, the highly crystalline sp^2 carbon materials still face difficulties such as high cost and complicated synthetic process. Alternative carbon-based hydrophobic absorbents which are low-cost and easy to prepare are also researched. Carbon-rich polymers and natural biomass with 3D porous structures can be carbonized into carbon aerogels through a non-oxidative pyrolysis process.^[60-69] Wu et al. demonstrated the pyrolysis of bacteria cellulose into a carbon nanofiber aerogel.^[65] After the pyrolysis process, the fibrous shape of the bacteria cellulose remained, and the carbon aerogel showed good surface hydrophobicity. Detailed characterizations were performed to understand the surface hydrophobicity of the carbon nanofibers under different pyrolysis temperatures. Fourier transform infrared spectroscopy (FTIR) indicated that the degree of decomposition of the hydrophilic functional groups, such as C–O, C=O, –OH, increased with the pyrolysis temperatures from 700 °C to 1300 °C. Furthermore, X-ray Diffraction (XRD) characterizations indicated that with the increase in pyrolysis temperature, the crystallinity of the carbon materials also improved, i.e. from an amorphous state to a partial graphitization state. As a result, the WCAs increased with the pyrolysis temperatures (Figure 2.9). This study suggested that although the carbon material was not perfectly crystalline, it still possessed hydrophobic surface, which could be used to selectively absorb oils. Other studies using different carbonaceous precursors, such as cotton, paper, and polymers suggested that a pyrolysis temperature below 1000 °C was sufficient to obtain hydrophobic carbon aerogels with good oil absorption performance.^[66-77]

Figure 2.9 a) XRD patterns, b) FTIR spectra and c) contact angle measurements of the bacteria cellulose and the carbon nanofibers prepared under different pyrolysis temperatures.^[65] Copyright 2013, Wiley-VCH.

In order to enable the ability to design and control the internal structure of the absorbents, polymerization has been utilized as a bottom-up approach to prepare novel 3D polymeric architectures with controllable and tunable pore structures.^[78-89] For example, high internal phase emulsion (HIPE) polymerization process was utilized to fabricate highly porous hydrophobic absorbents from hydrophobic monomers.^[90-92] Du et al. fabricated conjugated microporous polymer (CMP) aerogels with hierarchical porous structures with both meso- and macropores.^[93, 94] The CMP aerogel could selectively absorb oil from oil/water mixture due to its intrinsic hydrophobicity.

The capillary force is responsible for the spontaneous absorption of the oil into the pores with hydrophobic walls, and the voids provide the space for the storage of the oils. Therefore, there are two important parameters of hydrophobic absorbents that determine oil absorption capacity.^[95-97] The first parameter is the porosity of the absorbent, which is positively related to volume of oil that can be stored. However, it should be noted that the absorption capacity is usually expressed in mass percentage, rather than volume percentage in most literatures, probably

because the measurement of mass is much easier than the measurement of volume during the experiment. Therefore, even though the porosities of two absorbents with different materials are same, the absorbent made from lighter material intrinsic density shows higher absorption capacity. The other parameter that influences the oil absorption is the surface hydrophobicity. If the surface is less hydrophobic, water is relatively easier to break into the pores of the absorbent, which decreases the amount of oils that can be absorbed, and lost the oil selectively. Therefore, the highly hydrophobic and superhydrophobic surface, which completely repels water, is very important. The surface hydrophobicity can be improved by the rational design of the hierarchical surface textures.

Filtration is the other approach for oil/water separation. During the filtration process using superhydrophobic and superoleophilic filters, oils selectively permeate through the filter, but water is stopped by the filter. The superhydrophobic filters have been prepared on various substrates, such as metal meshes, fabrics and polymer membranes. Feng et al. fabricated the first superhydrophobic mesh for oil/water separation in 2004, in which a rough polytetrafluoroethylene layer was coated onto the fibers of the stainless steel mesh (Figure 2.10).^[98] The polytetrafluoroethylene-coated steel mesh was superhydrophobic with a WCA about 156° and superoleophilic with an OCA nearly 0° . Similarly, other low surface energy polymers were also used as coating layers onto metallic substrates by dip-coating method or spray-coating method.^[99-102]

Nanoparticles such as SiO_2 and TiO_2 were sometimes blended into polymer solutions as co-coating agents to increase the surface roughness, which improved the surface superhydrophobicity. However, the uniform distribution of nanoparticles across the substrate was difficult to realize. In order to achieve a uniform and controllable surface roughness, metal oxides crystals were in-situ

synthesized on metal substrates through chemical reactions.^[103-105] For example, Chang et al. grew ZnO nanocrystals on stainless steel mesh via hydrothermal reaction. By controlling the reaction time, ZnO crystals with different morphologies were obtained, and the optimized WCA and OCA after grafted with stearic acid were 160° and 0°, respectively.^[104]

Figure 2.10 SEM images of the superhydrophobic rough polytetrafluoroethylene layer-coated stainless steel mesh.^[98] Copyright 2004, Wiley-VCH.

An easier method to fabricate surface textures on metal substrates was through direct oxidation of the metal substrate by immersing in oxidizing solutions, or by thermal oxidation.^[106-110] For example, a superhydrophobic and superoleophilic Cu-based mesh was fabricated through the simple thermal oxidation method and subsequently grafted with hydrophobic palmitic acid (PA).^[110] After the oxidation, the smooth surface of the parent Cu fibers became very rough due to the formation of CuO crystals. Interestingly, the authors proposed an innovative strategy to utilize the mesh that was different from the traditional filtration process, by folding the mesh into a box. The box could float on the water surface and automatically allowed oil to infiltrate into the box but completely repelled water due to its superhydrophobicity (Figure 2.11). After the oil collection, the oil within the box could be easily sucked out for reuse, and the device was regenerated. Other similar

designs for such self-driven selective oil collection were also reported based on other superhydrophobic metal meshes.^[99, 111] These simple but creative designs may enable in-situ cleanup of oil spill over the sea.

Figure 2.11 Photographs showing the process of self-driven selective collection of toluene (dyed with Sudan Black B) from water surface using the superhydrophobic Cu-based mesh box.^[110] Copyright 2014, American Chemical Society.

Fabrics and textiles have also been used as flexible substrates for the fabrication of superhydrophobic and superoleophilic filters by surface modification with hydrophobic polymers.^[112, 113] One advantage of the textile is that the functional groups (e.g. -OH) naturally presenting on the surface of textiles can be used to covalently bond with the coating polymers through chemical reactions, which improves the adhesion of the coating layers.^[114-116] Wang et al. fabricated a polydopamine/SiO₂ coated cotton textile, which was inspired by the strong bio-adhesion of polydopamine. The textiles could maintain the superhydrophobicity even after 90 cycles of oil/water separation, long-time ultrasonic treatment, and acid and alkaline treatment, suggesting a very robust hydrophobic coating.^[115] Ahn et al. reported the robust hydrophobic surface modification through the esterification reaction between hydroxyl groups on the cellulose textile surface and stearic acid.^[116] To increase the surface roughness, inorganic nano- and micro-crystals were introduced on textiles fibers.^[117-121] For example, various metal oxides nanoparticles such as FeO, NiO, etc. were coated onto fabrics via in-situ wet chemical growth.^[118]

Although metal meshes and textiles have shown attractive performance in selective oil/water separation, these filters, in general, can only be used to separate layered oil/water mixtures. They can hardly separate oil/water emulsions due to relatively large size of the pores of the substrates, which are usually much bigger than the emulsified oil droplets. In light of this, polymeric membranes, which have smaller and controllable pores, show the unique advantages in separating oil/water emulsions. By the controllable creation of surface roughness on the traditional hydrophobic membranes, or grafting additional hydrophobic polymers, the filtration efficiency of the membranes were significantly improved. Zhang et al. fabricated a superhydrophobic and superoleophilic polyvinylidene fluoride membrane via an inert solvent-induced phase-inversion process.^[122] By introducing ammonia water during the membrane fabrication process, localized microphase separation of the polymer occurred, resulting in the formation of polyvinylidene fluoride clusters (Figure 2.12). This eventually led to a membrane with interconnected microspheres with rough surface (Figure 2.12). The as-prepared membrane showed a WCA of 158° and OCA less than 1° , suggesting its superhydrophobicity and superoleophilicity. This membrane, for the first time, could effectively separate different types of water-in-oil emulsions, such as micro-sized emulsions and nano-size emulsions, with or without surfactants.

Figure 2.12 a) Schematic illustration of the fabrication of the superhydrophobic and superoleophilic polyvinylidene fluoride membrane with the ammonia-assisted phase-inversion process. b, c) SEM images of the polyvinylidene fluoride

membrane. d) Photos of water-in-oil emulsions before and after the separation using polyvinylidene fluoride membrane.^[122] Copyright 2013, Wiley-VCH.

2.2.2 Hydrophilic and Oleophobic Materials

Absorbents and filters based on hydrophobic and oleophilic materials have been extensively reported with promising results in selective oil/water separation. However, there are a few problems associated with the hydrophobic and oleophilic materials. First, the high affinity towards oil makes the surface of the material easily fouled by oil due to the oleophilicity. The oil fouling may destroy the fine surface architectures, reduce the hydrophobicity, and lower the separation efficiency. Furthermore, during the filtration process where hydrophobic and oleophilic filters are used, a layer of water will settle down below the oil as water has a higher density than that of most oils. The water layer between the hydrophobic filters and the oil layer will stop the continuous filtration process.^[123] Therefore, filters based on hydrophilic and oleophobic materials, which can selectively permeate water and repel oils, are more desirable for practical oil/water separation applications.

As mentioned, the surface tension is the primary factor that determines the wettability of a material. High surface tension materials are desired for better hydrophilicity. However, if the surface tension is high, the material should also exhibit even higher affinity toward oils, because water generally has higher surface tension than most oils, i.e. the material is also oleophilic. Therefore, it is theoretically impossible to have a material that exhibits hydrophilicity and oleophobicity at the same time.

In order to achieve a hydrophilic and oleophobic surface, one method is to synthesize block co-polymers which consist of hydrophilic components and

oleophobic components, and coat them onto substrate materials. A generally accepted mechanism is that the oleophobic components of the polymer locate at the solid/air interface in a relatively mobile state, rendering the surface with oleophobicity and hydrophobicity at the initial moment. Upon contacting with water, the repulsive interaction between the water and oleophobic components and the attractive interactions with hydrophilic components induce the rearrangement of the polymer chains, so that the hydrophilic moieties locate at the solid/liquid interface. As a result, the local spots of the material surface in contact with water becomes hydrophilic. In contrast, upon contacting with oils, such polymer chain rearrangement will not occur, and the surface remains oleophobic.^[124-127] In this way, a time-dependent hydrophilic and oleophobic surface is realized. For example, Zhou et al. reported a superhydrophilic and superoleophobic coating recipe, in which a polymer is synthesized from hydrophilic poly(diallyldimethylammonium chloride) (PDDA) and oleophobic sodium perfluorooctanoate (PFO), and blended with SiO₂ nanoparticles for creation of roughness (Figure 2.13).^[126] The PDDA-PFO/SiO₂ coating material can be applied on various substrates, e.g. metals, glasses, etc., turning their surfaces into superhydrophilic and superoleophobic. When water and oil are just dropped onto the coated surface, both droplets remain spherical, suggesting the amphiphobicity of the material. However, after 9 minutes, the water spreads out due to the water induced molecular rearrangement, but the oil droplet remains standing.

Figure 2.13 a) Chemical reaction for the synthesis of PDDA-PFO block co-polymer. b) Photos of a water and a hexadecane droplet (dyed red) on the PDDA-PFO/SiO₂ coated substrate at 0 min and 9 min. c) WCA and OCA measurements on the PDDA-PFO/SiO₂ coated surface against time.^[126] Copyright 2012, Royal Society of Chemistry.

The block co-polymers for the superhydrophilic and superoleophobic coatings are generally complex and only limited number of such polymers have been reported. More recently, another innovative and simple approach to achieve the selective water permeation has been reported, i.e. superhydrophilic and underwater superoleophobic materials. Theoretically, materials that are superhydrophilic in air will become superoleophobic when under the water. When the superhydrophilic surface is immersed into water, water molecules will be tightly trapped around the hierarchical surface architectures, forming a water layer. Subsequently, when oil contacts with the surface, the water layer will function as a preventive layer against

the oil wetting, because it is energetically unfavorable for the oil to replace the trapped water molecules. As such, the materials appear to be superoleophobic under the water (Figure 2.14a). To characterize such property, the underwater oil contact angle (UWOCA) is measured.

Figure 2.14 a) Schematic illustration of a rough superhydrophilic surface becomes underwater superoleophobic due to the water layer trapped around the surface architecture. b) SEM image of $\text{Cu}(\text{OH})_2$ nanowires covered Cu mesh. Inset: high-magnification side-view SEM image of the $\text{Cu}(\text{OH})_2$ nanowires array. c) Photos showing the WCA and UWOCA on the as-prepared Cu mesh.^[128] Copyright 2013, Wiley-VCH.

A superhydrophilic surface can be made by creating surface roughness on a substrate with high surface tension. Various materials, such as hydrophilic polymers, metal oxides, zeolite, etc. have been coated onto metal substrates to make

superhydrophilic and underwater superoleophobic filters.^[128-132] For example, Zhang et al. prepared a $\text{Cu}(\text{OH})_2$ nanowires coated Cu mesh by the in-situ chemical oxidization of the Cu mesh in the concentrated $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and NaOH solution (Figure 2.14b, c).^[128] Due to the high surface energy of $\text{Cu}(\text{OH})_2$ crystals and the high roughness formed by the $\text{Cu}(\text{OH})_2$ nanowire array, the as-prepared mesh was superhydrophilic in air with $\text{WCA} \sim 0^\circ$, and superoleophobic under the water with $\text{UWOCA} \sim 155^\circ$. Hydrogel is one type of polymeric materials with high water capture ability, which is similar with the high surface tension materials under the water. Therefore, hydrogels have also been utilized as coating materials onto porous substrates, yielding the superhydrophilic and underwater superoleophobic property.^[133-135]

The polymer membrane is still the mostly applied technology for water purification in the industry due to its relatively mature fabrication techniques. The oil-fouling of polymer membranes is one of the major problems that limit the separation efficiency and the membrane life-time. Thus, superoleophobic membranes are especially desired for the fouling prevention. So far, superhydrophilic and underwater superoleophobic polymer membranes are usually fabricated by coating a second layer of hydrophilic polymer.^[136-139] For example, inspired by the fouling resistive property of mussels, Xiang et al. fabricated underwater superoleophobic polyvinylidene fluoride membrane by polydopamine coating, which significantly improved the membrane fouling resistance.^[138] For an intrinsically hydrophilic membrane, the underwater superoleophobicity was simply achieved by the physical creation of surface roughness on the membrane. For example, Gao et al. fabricated a dual-scaled underwater superoleophobic membrane simply by punching holes on the commercial nitrocellulose membranes, which generated micro-sizes pores on the nanoporous membranes matrix.^[140]

Figure 2.15 SEM images of the dual-scaled nitrocellulose membrane. a) Low magnification SEM image showing the punched micro-sized pores. b) High magnification SEM image showing the intrinsic nano-sized pores of the membrane matrix.^[140] Copyright 2014, Wiley-VCH.

2.2.3 Responsive Materials/Materials with Switchable Wettability

Responsive materials can switch the surface wettability upon external stimulus. Therefore, they can selectively permeate water or oil depending on the external environment. In other words, the responsive material acts as a ‘valve’, which controls the “on/off” state of the water path or oil path. The responsive wettable materials enable the controllable oil/water separation.

Generally, the responsive wettable materials are obtained by coating responsive polymers on substrates. The pH responsive coatings are the mostly reported materials. For example, polymers with carboxylic acid groups and amine groups are responsive toward the surrounding pH values, and they switch the wettability by the protonation/deprotonation process. For polymers with carboxylic acid

groups, the polymer become deprotonated under basic environment, which lead to the decrease in the WCA due to the high surface energy; the polymer remains relatively hydrophobic under acid and neutral environment, because the polymer is in protonated state.^[141-147] Figure 2.16 shows the WCA of a surface coated by the mixed polymers of $\text{HS}(\text{CH}_2)_9\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{10}\text{COOH}$ tested under various pH, which agrees with the discussion above. The direction of the pH response is opposite for the polymers with amine group, i.e. relatively hydrophobic under basic environment and relatively hydrophilic under acid environment.^[148, 149] Since the surface roughness can enhance the wettability, switching between superhydrophobic and superhydrophilic states can be realized by coating these polymers onto the rough substrates.

Figure 2.16 WCA measurements of the $\text{HS}(\text{CH}_2)_9\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{10}\text{COOH}$ mixed polymers coated substrate under various pH environment.^[144] Copyright 2014, Royal Society of Chemistry

Similar with pH responsive polymers, metal ions can also induce the polarity and conformational change of some polymers and realize the ion-induced wettability switch. For example, Wei et al. demonstrated a Hg^{2+} responsive mesh coated with

linear poly(acrylic acid) which had the ability to chelate with Hg^{2+} .^[150] Without the presence of Hg^{2+} , the polymer was polar and negatively charged, exhibiting hydrophilicity. When Hg^{2+} was introduced, the polymers chelated with the Hg^{2+} and formed mercury polyacrylate which was nonpolar and neutral, and the mesh became hydrophobic. With the increase in the concentration of Hg^{2+} , the mesh became more oleophilic.

Compare with metal substrates, textiles are more suitable substrates for coating of pH and chemical responsive materials, as metals can be corroded under strong acid and basic conditions or presence of other corroding species.^[148, 151, 152] Lin et al. prepared an ammonia-responsive polyester fabric, which was intrinsically superamphiphobic, but switched to superhydrophilic and superoleophobic upon exposure to ammonia vapor. The coating solution was made from the mixture of heptadecafluorononanoic acid-modified TiO_2 and SiO_2 nanoparticles.^[152] In the presence of ammonia water, the titanium carboxylate coordination bonding was broken by the formation of ammonia carboxylate ions, which increased the surface energy of the coating and decreased the surface tension of water droplet. Therefore, the surface changed to superhydrophilic locally. As a proof of concept, they demonstrated the controllable selective oil/water separation triggered by ammonia vapor (Figure 2.17).

Figure 2.17 a) The time profiles of WCA and OCA measurements on the heptadecafluorononanoic acid-TiO₂/SiO₂ coated fabric after the exposure to ammonia. b) Photos showing the selective oil/water separation by the as-prepared fabric by the ammonia vapor trigger.^[152] Copyright 2015, Wiley-VCH

Materials and polymers that respond to other stimulus and change their wettability have also been reported, such as temperature, light, electric voltage, etc.^[71, 153-156] For example, Kwon et al. prepared an voltage responsive polymer membrane.^[156] The WCA changed from 115° to 56° after a high voltage was applied, while the OCA was not affected.

2.3 Questions to Answer Based on Literature

From the reviewed literatures, one can see that great progress has been achieved in the research field of special wettable materials for oil/water separation. Various novel materials, including both organic and inorganic materials, with special wettable properties have been fabricated from a wide range of methods. However, there are still unexplored research directions.

First, in order to promote the practical implementation of the special wettable materials, the raw materials cost should be as low as possible. Currently, many raw materials used for the fabrication of special wettable materials are still considered highly expensive. For example, for hydrophobic and oleophilic materials, graphene and CNT have shown excellent performance. Unfortunately, the fabrication cost of graphene and CNT is still too high to be practically industrialized. For the hydrophilic and oleophobic polymer coatings, the highly specialized polymers, as well as the complex synthesis routes, also make them nearly impossible to be applied for practical oil/water separation application. Unfortunately, the water

remediation or the water purification is not an industry of high profitability. As clean water is the most important resource for all kinds of domestic and industrial activities, the governments around the world always set price ceiling to the water price to ensure that the poor people can still afford to use water. This inevitably reduces the profit of producing clean water, making the cost of new technology implementation as the first priority of consideration. Therefore, in order to practically implement the special wettable materials, new and novel materials with lower raw materials cost should be developed. Waste materials are excellent candidates as low cost raw materials. However, the development of special wettable materials from waste still remains largely unexplored.

Second, the fabrication of the special wettable materials should be environmentally friendly. The consumption of both water and energy should be minimized during the material synthesis. The solvents, chemicals and the by-products should bring as minimum impact to the environment as possible. Unfortunately, many high performance special wettable materials reported so far still involve highly toxic chemicals. For example, the fabrication of graphene oxide, which is one of the most importance precursors for hydrophobic and oleophobic graphene absorbents and filters, requires highly oxidative chemicals during the preparation process, and consumes huge amount of water to purify the products. Fluorine-containing polymers have been widely used as low surface energy coatings to fabricate hydrophobic and oleophilic materials. However, the release of fluorine is highly toxic to the environment, and many major industrial sectors have already declined the usage of any fluorine-containing polymer product. Therefore, novel synthesis approaches that use and generate minimum or no toxic chemicals are highly desired.

Third, in order for the special wettable material to be applied under practical conditions, the stability of the materials should be high against various harsh

environment. For example, for oil and gas industries, where selective oil/water separation is extremely important, the material should be able to maintain the wettability against high temperature. For oil spill remediation, the material should be able to withstand seawater with high salinity. However, many special wettable materials lose their property under such practical harsh environment. For example, for some metal oxide/hydroxide-based superhydrophilic materials, their surface architectures will be destroyed under strong acidic solution. For polymeric hydrogels based materials, they cannot maintain their superwetting behaviors after being heated. Therefore, novel special wettable materials that are impervious toward harsh working conditions are highly desired.

2.4 PhD in Context of Literature

In this thesis, the main research focus is to explore the preparation of novel special wettable materials by utilizing common waste as raw materials through facile and environmentally friendly methods, and to study their application in oil/water separation. Several contributions from my thesis to the research field are listed below:

First, I demonstrated the successful conversion of a common biomass (pomelo peel) into a novel hydrophobic carbon aerogel. The natural 3D porous structure of the pomelo peels was well maintained after the carbonization process through non-oxidative pyrolysis. The as-prepared hydrophobic carbon aerogel was able to selectively absorb oils and water-immiscible organic solvents from the surface of water and at the bottom of water. The use of the biomass as raw materials greatly reduced the cost of hydrophobic carbon aerogel fabrication.

Second, I demonstrated the successful conversion of waste soda lime glass into a novel superhydrophilic and underwater superoleophobic mesh. From this research,

I demonstrated the smart combination of the high surface energy of silica materials with the rough surface textures created during the conversion process. I also proved that the waste glass-derived superhydrophilic mesh was able to stably perform under a wide range of harsh environment. Furthermore, a novel multifunctional oil/water separation concept was also demonstrated by the simultaneous adsorption of water-soluble contaminants.

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Chapter 3

Experimental Methodology

In this chapter, the rationale for the methods and materials selection in each research work is discussed. The chemicals and the detailed experimental procedures for preparation of each special wettable materials are presented. The techniques and equipment used for materials and samples characterizations are elaborated. Finally, the conduct of proof-of-concept applications in water remediation using the as-developed special wettable materials is introduced.

3.1 Rationale for Materials Selection

As discussed in the previous chapters, surface energy is the primary factor that influences the wetting behaviour of the solid material. Therefore, in order to create a hydrophobic and oleophilic surface, low surface energy materials should be used. Although fluoropolymers generally possess very low surface energy, they are believed to be harmful to the environment. Therefore, environmentally friendly materials are desired for my research projects. The carbon-based material is believed as one type of low surface energy materials due to the low polarity of C-C bonds and C-H bonds, with good environmental compatibility. Recent research demonstrates that several carbon-based foams or aerogels show hydrophobic and oleophilic property regardless their crystal structure, i.e. either graphitic carbon or amorphous carbon.^[1-6] Cellulose-based materials are used as precursors to produce carbon-based materials via several methods, such as hydrothermal method and pyrolysis method, since they can be converted into carbon with relatively high yield at high temperature.^[7-9] Therefore, in my first project, I chose a natural biomass, i.e. pomelo peel, as the raw material as the carbonization precursor because it contains substantial amount of cellulose. Pomelo peel is an ideal candidate for fabrication of carbon aerogel as it naturally possesses a highly porous structure, which provides large pore volume for the oil absorption and storage. In addition, comparing with the previously reported cellulose-based precursors, the pomelo peel is one type of food waste, which shows no value by itself. Therefore, by choosing the pomelo peel as raw material, not only the cost of the final functional carbon aerogel can be reduced, but also a smart way of waste re-utilization is demonstrated.

In the second project, waste soda lime glass was chosen as precursor to fabricate the superhydrophilic and underwater superoleophobic mesh. From the surface energy point of view, a high surface energy material is required to create the

superhydrophilic surface if proper surface textures can be created. Silica (SiO_2) is one type of common hydrophilic materials with minimum environmental toxicity. After grafting hydroxyl groups onto the silica surface, the surface interacts strongly with water molecules due to the hydrogen bonding. The major structure framework of the soda lime glass is amorphous silica, with other alkaline metal ions, such as Na^+ , Ca^{2+} , etc. as interstitial ions within the voids to balance the charge.^[10-12] Previous research has demonstrated that amorphous silica could be easily etched in the alkaline solution.^[13-15] Therefore, I proposed that the soda-lime glass can be in-situ grafted with hydroxyl groups and etched into rough architectures using hydrothermal method in a single process. In this way, I converted the waste soda lime glass into the superhydrophilic material.

3.2 Materials and Synthetic Methods

3.2.1 Materials

Hydrochloric acid (HCl, 37%), Sodium hydroxide (NaOH, 99.99%), Dimethyl ketone (DMK), N,N-Dimethylformamide (DMF, 99.8%), Trichloromethane (TCM or chloroform, 99.8%), Hexane (99%), Sodium chloride (NaCl, 99.5%), Copper Chloride (CuCl_2 , 99%), Silver nitrate (AgNO_3 , 99%), Mercury chloride (HgCl_2 , 99%), Lead nitrate ($\text{Pb}(\text{NO}_3)_2$, 99%), Cadmium chloride (CdCl_2 , 99%), Oil red O (75%), Methylene blue (82%) and Pump oil were purchased from Sigma Aldrich. Ethanol (99%) and Toluene was purchased from Merck. Tetrahydrofuran (THF) was purchased from Tedia. N-methyl-2-pyrrolidone (NMP, 99.5%) was a product from Alfa Aesar. Pomelo, stainless steel (SS) meshes, glass slides, petri dishes, glass cups, petroleum, and canola oil were purchased from local stores. The deionized (DI) water was purified using Milli-Q System (Millipore, Billerica, MA, USA). All materials and chemicals were used as received without further

purification.

3.2.2 Preparation of Hydrophobic Carbon Aerogel

Waste pomelo peels were gathered after the consumption of pomelo. After cutting off the outermost rind layer, the pomelo peels were cut into small cubes with length around 1 cm to 2 cm. Then, the pomelo peel cubes were soaked into 1000 mL hydrochloric acid (10 wt %) and left under mild stirring for 12 h. The cubes were then soaked into deionized (DI) water under mild stirring for 1 hour to remove the absorbed acid. The DI water soaking process was repeated for 3 times until the pH of the soaking water became 7. Then, the pomelo peel cubes together with the water inside were subjected to freeze-drying at a pressure of 0.023 mbar for 3 days to remove the water without destroying their porous structure, yielding the biomass aerogels. Next, the biomass aerogels were transferred into a tubular furnace for pyrolysis. In order to remove the oxygen trapped inside the tube and the biomass aerogel, the furnace tube was evacuated using a pump and purged with argon gas. The evacuation and purging process was repeated for 3 times in order to make sure minimum oxygen content was left inside. Then, the furnace was heated up to 800 °C with a heating rate of 5 °C min⁻¹ and dwelled at 800 °C for 2 h with continuous argon flow. The argon pressure inside the tube was maintained at 1 atmosphere during the pyrolysis. Finally, the furnace was naturally cooled down to room temperature, and the carbon aerogels were retrieved.

3.2.3 Preparation of Superhydrophilic and Underwater Superoleophobic SNMs

Optical microscope glass slides (Sail Brand; Containing about 73% SiO₂, 14% Na₂O, 10% CaO, and other metal oxides) were cleaned by deionized (DI) water and

ethanol, and dried completely. Then, the cleaned glass slides were ground into glass powder using ball milling machine at 400 rpm for 2 hours (Pulverisette 7, Fritsch, Germany). The glass powder was collected after the grinding for future usage.

To prepare the silica-based nanowires-coated meshes (SNM), the resulting glass powder (0.05 g) was dispersed into 1 mL ethanol to make a suspension. Then, the glass suspension was carefully coated onto a piece of stainless steel (SS) mesh with size about 2 cm $\times$ 2 cm using a common painting brush, after which the glass powder-coated mesh was completely dried in an oven at 80 °C. The coating and drying process was repeated until the 1 mL glass powder suspension was completely used up. Then, the glass powder-coated SS mesh was placed in a 20 mL Teflon container with 10 mL DI water and sealed in a stainless steel autoclave. The autoclave was placed in an oven heated to 180 °C for various predetermined time ranging from 0 hour to 24 hours. Finally, the autoclave was naturally cooled to room temperature, and the resulted mesh was taken out for further characterizations and oil/water separation application. SNM-100 and SNM-500 were fabricated through the same procedures described above using 100-mesh and 500-mesh, respectively. Other types of waste soda-lime glass were also used to prepare the SNMs using the similar procedures, by changing the starting materials to a household cup and a lab petri dish.

In order to prepare SNM', the as-obtained glass powder (0.5 g) from the ball milling process was dispersed into 1 mL ethanol to form a paste. Then, the paste was carefully coated onto a piece of SS 500-mesh with size about 2 cm $\times$ 2 cm, and completely dried in an oven at 80 °C. The coating and drying process was repeated until the 1 mL paste was completely used up, after which the holes on the SS 500-mesh frame were no longer observable. Then, the glass powder-coated mesh was subjected to the same hydrothermal process as described above. After naturally

cooled down, SNM' was obtained.

3.3 Characterizations

3.3.1 Scanning Electron Microscopy (SEM)

All SEM images were taken with a field emission scanning electron microscope (FESEM, JEOL JSM-7600F) coupled with an energy dispersive X-ray spectroscopy (EDS) detector. When recording SEM images, the accelerating voltage was set at 5 keV, the probe current was set at 7 μ A, and the stage distance was set at 6 cm. When acquiring the EDS spectra, the accelerating voltage was set at 20 keV, the probe current was set at 10 μ A, and the working distance was fixed at 15 cm.

SEM is a powerful and convenient electron microscope for obtaining the morphological and topographical features of materials. The information is obtained by scanning the sample materials with an electron beam which is emitted from the electron gun. During the electron beam scanning, the incident electrons interact with the atoms of the sample materials, producing various signals that can be captured by different detectors and processed into the information displayed on the computer. Secondary electrons are generated when the incident electrons directly knock out the electrons of the sample atoms. The secondary electrons that are emitted from the sample contain information about the topology of the materials, and are collected to reveal the sample morphology. When the incident electrons knock out the electrons at the inner shells of the sample atoms, the electrons at the outer shells will jump to the electron vacancies at the inner shell in order to lower the energy of the atoms. During such electron jumping process, X-rays are emitted to compensate the excess energy, keeping the energy conservation. As for each

element, the energy gaps between the inner shells and outer shells are different and unique, the X-ray emitted therefore tell the information about the chemical composition of the sample materials.

In this thesis, SEM was used to characterize the morphologies, surface architectures, and chemical compositions of the carbon aerogels and SNMs. To prepare the samples for imaging, the samples were fixed onto the sample stage of the electron microscope. For bulk sample such as carbon aerogel, the sample was cut into tiny species and directly pasted onto conductive carbon tape. For powder samples, the sample was dispersed into DI water or ethanol to form a uniform dilute suspension. Then, about 10 μL of the suspension was drop casted onto a clean Si wafer, and dried completely. The Si wafer was then pasted onto the carbon tape. For insulating materials or materials with low electron conductivity, the samples were coated with a thin layer of Pt to make them conductive, in order to prevent the electron accumulation on the surface of the sample, a phenomenon called charging. The coating was performed on a Pt sputtering coater (JEOL, JFC-1600) for about 30 s. The Pt coating was not performed on samples for EDS measurement, in order to avoid the unnecessary signals of Pt.

3.3.2 Transmission Electron Microscopy (TEM)

TEM characterizations were performed on JEOL JEM 2100F instrument at an accelerating voltage of 200 kV.

TEM is a powerful instrument that characterizes the morphology, crystal structure and chemical composition of materials. Similar with SEM, various signals are generated as a result of the interaction between the electron beam and the sample. However, the electron beam in TEM is in much higher energy, and able to penetrate

through the samples. Therefore, the resolution of the TEM image is much higher than that of the SEM image. With correction of the spherical aberration, the resolution of the TEM image can achieve at sub-nanometer scale, i.e. the high-resolution TEM images (HRTEM). HRTEM can provide information on the samples crystallinity. When the high-energy parallel electron beams pass through the thin sample, the transmitted electrons will be diffracted to certain angles according to the local atomic arrangement of the sample materials, forming a specific pattern, i.e. selected area diffraction pattern (SAED). SAED is used to obtain the information about the sample crystallinity. Generally, patterns with defined sets of spots are produced from single crystalline materials, patterns with a series of diffraction rings are produced from polycrystalline materials, and no diffraction pattern is produced from amorphous materials.

In this thesis, carbon aerogels and silica-based nanofibers were characterized by TEM. The samples were first sonicated within DI water to exfoliate them into tiny and thin species. Then, about 2 μL of solution was dropped onto copper grids and dried completely. The copper grid was fixed on the sample holder and inserted into the column of the TEM.

3.3.3 X-ray Diffraction (XRD)

The XRD spectra were recorded with a Bruker D8 diffractometer (German) using $\text{Cu K}\alpha$ ($\lambda=1.54178 \text{ \AA}$) X-ray source. The scanning was performed from 10° to 80° with a sampling interval of 0.05° and a dwell time of 1 s. XRD is a non-destructive analytical technique used to analyse the crystallographic information of materials.

In the thesis, the XRD characterization was used to identify the crystal structure of the carbon aerogels and the silica-based nanowires.

3.3.4 Contact Angle (CA)

CAs were measured using an OCA15 machine (Data-physics, Germany). The volume of all type of liquid droplets used was set to 3 μL , and the dosing speed was set at 1 $\mu\text{L s}^{-1}$. The measurement was performed based on the sessile drop method.

CA measurement is the most commonly applied technique for evaluating the wetting behaviour between a solid surface and liquids. It can also be applied to measure the interfacial tension between the two phases. In a typical instrument setup, the sample for measurement is put between a light source and a camera in one straight line (Figure 3.1). The shadow image of the droplet on the sample substrate will be received by the camera and processed by computer to measure the contact angle. In a typical sessile drop method, the software evaluates the grey scale values of the recorded image and detects the base line (contact between droplet and solid) and the drop outline. Then, the contact angle is measured by applying tangent at the intersection of the drop outline and the baseline (Figure 3.1).

Figure 3.1 Schematic illustration of instrument setup for contact angle measurements.

In this thesis, the WCAs and OCAs of the carbon aerogels and SNMs were directly measured on the sample stage by dropping water droplet or various oil droplets onto the sample surfaces. In order to measure the underwater oil contact angle (UWOCAs) of the SNM, a highly optically transparent quartz cell was filled up

with DI water, and put onto the sample stage. Then, the SNM was immersed into the quartz cell and fixed horizontally. For oils and organic solvents with lower density than water, a special upwards bended dosing needle was used with the tip of the needle inserted right below the downside of the SNM (Figure 3.2). For organic solvents with higher density than water, a normal dosing needle was used with the needle tip right above upside of the SNM. All the procedures described above were carried out with extremely care to avoid creating air bubbles. For each sample, three measurements at different positions were performed and the average value was used for the value of UWOCA.

Figure 3.2 Schematic illustration of the measurement of UWOCAs for oils and organics with lower density than water.

To measure the underwater oil sliding angle, a chloroform droplet (3 μL) was dropped onto the SNM under the water, after which the sample stage of the instrument was tilted at a rate of $0.3^\circ/\text{s}$. The angle at which the chloroform droplet rolled off from the SNM surface was recorded as the underwater oil sliding angle.

3.4 Proof-of-concept Application

3.4.1 Preparation of Oil/Water Mixtures

The layered oil/water mixtures were prepared by gently adding 10 – 20 mL oil into

10 – 20 mL DI water. The oil-in-water emulsions were prepared by mechanically mixing the DI water and oils in a volume ratio of 10:1 (i.e. ~9 vol% of oil) using an emulsifying mixer. Under ambient condition, the resulting oil-in-water emulsions were stable for 1 day without demulsification. Several oil/water mixtures were prepared by using different oils and organic solvents, i.e. petroleum, canola oil, pump oil, hexane, and chloroform.

3.4.2 Oil/Water Separation

For oil absorption using the carbon aerogels, hexane was added into a beaker containing certain amount of water. Then, the carbon aerogel was directly put onto the surface of the liquid mixture to allow the automatic absorption process. For absorption of chloroform, about 2 mL chloroform was carefully dropped into a beaker containing certain amount of water. Then, the carbon aerogel was slowly pushed into the water to contact with the chloroform droplet.

For oil/water separation using SNM filters, one piece of the as-prepared special wettable filter was horizontally fixed between the ends of two identical glass funnels, which were connected by a clamp. The filter was pre-wetted by 100 μ L of DI water, after which the layered oil/water mixture (20 mL) was poured into the upper funnel. The separation process was solely driven by the gravity. The separated water was collected and the residual oil content was measured. The filtration efficiency was calculated using the following equation:

$$R (\%) = (1 - C_a/C_b) \times 100 \quad \text{(Equation 3.1)}$$

where C_b and C_a were the oil contents in water before and after the separation, respectively. The separation of oil-in-water emulsions was carried out following the

same experiment procedures using SNM'.

For the test of the removal of organic dyes and heavy metal ions from water during the oil/water separation process using SNM', methylene blue (MB) contaminated layered oil/water mixture was prepared by gently adding 10 mL hexane (dyed with oil red O) into 10 mL pre-prepared MB aqueous solution (2 ppm). Heavy metal ion (HMI) contaminated layered oil/water mixture was prepared by gently adding 10 mL hexane into 10 mL pre-prepared HMI aqueous solution (100 ppm). The HMIs used here were Pb^{2+} , Hg^{+} , Ag^{+} , Cd^{2+} , and Cu^{2+} . Then, the as-prepared contaminated layered oil/water mixtures were poured into the upper funnel of the experimental set-up for oil/water separation. The permeated water was collected, in which the concentrations of MB were measured by UV-visible spectroscopy, and that of various HMIs were measured by inductively coupled plasma with optical emission spectrometer (ICP-OES).

3.4.3 Stability Tests of NFMs against Harsh Environments

The organic solvent resistance of the NFMs was evaluated by immersing the NFMs into 15 mL of different organic solvents, i.e. THF, NMP, DMF, DMK, and TCM, for 24 h. Then, the NFMs were taken out and rinsed with ethanol and water to remove the surface-adsorbed solvents, after which their UWOCAs were measured immediately. The high temperature stability was evaluated by annealing the SNMs at different elevated temperatures (i.e. from 100 °C to 600 °C) in a furnace for 2 h. After naturally cooled down to room temperature, their UWOCAs were measured. The acidic and basic solutions were prepared by diluting 1 M HCl solution and 1 M NaOH solution to the desired pH values, respectively. 1 M NaCl solution (pH 7) was used to simulate seawater for the salinity testing. The NFMs were first immersed into 15 mL of the aforementioned acidic, basic and high salinity solutions

for 5 days, and their UWOCAs were measured after they were rinsed with DI water. The UWOCAs of NFMs in acidic, basic and the high salinity water were measured in 1 M HCl solution, 1 M NaOH solution and 1 M NaCl solution, respectively.

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Chapter 4*

Preparation of Three-Dimensional Porous Hydrophobic and Oleophilic Carbon Aerogels from Pomelo Peels as Efficient Absorbents for Oil Spill Remediation

In this chapter, the synthesis of a novel three-dimensional porous carbon aerogel and its potential application in oil absorption are presented. Waste pomelo peel is used as the starting material and is carbonized through pyrolysis method with its porous structure maintained. The as-prepared carbon aerogel shows hydrophobicity and oleophilicity. As a proof-of-concept application, the carbon aerogel is used as a selective absorbent to remove oils and organic solvents from water. Moreover, the carbon aerogel also shows good recyclability.

4.1 Introduction

As the global energy demand continues to grow, the intensified exploitation of the crude oil has inevitably led to oil spill accidents and oil leakage over the seas during the oil drilling and oil transportation. In the past few decades, a number of massive oil spill disasters happened around the world.^[1, 2] Marine resources are quite vulnerable to such anthropogenic disasters. The massive introduction of crude oils into the aquatic environment not only killed the surrounding marine lives, but also caused long-term harmful impacts on the entire ecosystem.^[3] For example, the Exxon Valdez massive oil spill accident brought fatal damage to nearly 300,000 living species in the habitat, and the long-term ecological impact still lasts.^[4]

Traditional methods for remediating the oil spills, such as oil decomposition with chemical or biological dispersants, direct burning, vacuum suction, etc., have shown many disadvantages, such as the toxic chemical residues, emission of by-products and intensive energy consumption.^[5, 6] Therefore, new technologies and materials are highly needed for the remediating the oil spills.

Recently, several low-cost and environmentally friendly materials, such as agricultural by-products, have been evaluated as potential oil absorbents for oil spill cleaning.^[7, 8] However, the results are not satisfactory due to the low absorption capacity. Furthermore, as the surface of the absorbents shows high affinity towards both oils and water, water can be absorbed by these absorbents simultaneously during the oil uptake, which further decreases the absorption efficiency. More importantly, selective removal of oil from water is highly desired in order to reclaim the precious oil resources. Thus, the development of advanced materials that separate oil/water mixture in a selective, efficient and eco-friendly manner has become an urgent agenda and has drawn tremendous research effort.

Absorbents with hydrophobic and oleophilic surface have been studied for oil spill remediation in recent years, due to their opposite affinity towards oil and water, which allows them to uptake only oil, but repel water, achieving the selective oil/water separation. Among various materials, carbon-based absorbents with three-dimensional (3D) porous structure, such as foams, sponges and aerogels, have received tremendous research attention, due to their intrinsic hydrophobicity, chemical stability, low density and high absorption capacity.^[9] For example, CNT- and graphene-based sponges and aerogels, prepared by various methods such as chemical vapour deposition method, hydrothermal method and self-assembly method, show high absorption capacity towards many oils and organic solvents.^[10-16] Unfortunately, the dangerous precursors, toxic by-products, expensive process and complex equipment involved still greatly hinder them towards the practical applications. Therefore, it is highly required to develop novel low-cost 3D carbon aerogels via environmentally friendly methods and low-cost precursors.

Biomass has been explored as a potential sustainable source for the preparation of various carbon-based nanostructures, due to its relatively low cost, richness in carbon element and nontoxicity to the environment. Recently, several carbon-based aerogels have been fabricated from a number of cellulose-based biomass, such as cotton, bacterial cellulose, etc.^[17, 18] Although these biomass-derived carbon aerogels have shown excellent performance in selective absorption of various organic solvents and oils, the precursors, e.g. raw cotton and bacterial cellulose, serve great value by themselves. Cotton can be used to produce many kinds of textiles, which can be used in many industries, e.g. cloths. Bacterial cellulose serves as a raw material in food industry. Therefore, the economic benefit of converting the natural cotton or bacterial cellulose into carbon aerogels remains unclear. Waste cellulose-containing biomass is expected to be a better choice, because of the extremely low cost and the environmental benefit of recycling it. Our group has

previously demonstrated the conversion of waste paper into a carbon pulp. However, the quality of the waste paper source has huge effect on the product, which make it unsuitable for practical applications. Therefore, it is still highly desired to prepare novel carbon aerogels from a source of truly low-valued biowaste.

4.2 Results and Discussion

In this Chapter, I will present my research on the preparation of a novel 3D porous hydrophobic carbon aerogel using the peels of the Citrus Maxima (commonly known as pomelo) as starting materials. The pomelo is one kind of popular fruits that is traditionally favoured by Asian people. Most pomelos possess very thick peels consisting of the outer rind layer and the thick and spongy pith layer which function as the cushion for the fruit against external impact. The SEM image of the pith layer of a typical pomelo peel shows a well-constructed 3D porous network, with pore sizes around a few hundreds of micrometers (Figure 4.1a). The EDS spectrum shows the pith mainly contains C and O elements, as well as minor amount of several mineral elements, such as Ca, K and Mg (Figure 4.1b).

The preparation process for carbon aerogels was described in Chapter 3 in details. The HCl soaking process removed the extra mineral elements before the pyrolysis process, since the presence of metal ions could induce the etching of the carbon products and make the final carbon aerogels hydrophilic. The freeze-drying technique completely dried the spongy pith layer without collapsing the 3D porous structure due to the capillary force when water vaporized. After the soaking and freeze-drying process (Step 1), a freestanding 3D porous biomass aerogel was obtained. Finally, the biomass aerogel was carbonized into the carbon aerogel through pyrolysis process (Step 2) under inert gas environment (Figure 4.1c).

Figure 4.1 a) Photo of a typical pomelo, possessing a thick and spongy pith. b) SEM image of the pith layer. Inset: EDS analysis of the pith. c) Schematic illustration of the preparation process of carbon aerogels using pomelo peels as starting materials.

After the pyrolysis process, the yellowish biomass aerogel turns into black. The size of the carbon aerogel is also smaller than the parent biomass aerogel. For a typical biomass aerogel with length about 3 cm, the dimension of the obtained carbon aerogel after the pyrolysis process shrink to about 2.5 cm, with the width and height also reduced by the similar percentage (Figure 4.2a, b). SEM image shows that the carbon aerogel possesses a 3D interconnected porous structure that is similar with the parent pith and biomass aerogel (Figure 4.2c). The pore sizes range from around several tens of micrometers to hundreds of micrometers. High magnification SEM image shows that the thickness of the pore walls are around 1 to 2 micrometers. Surprisingly, the cross-sections of the pore walls clearly reveal

that another type of tubular-shaped pores are also formed inside the pore walls. Thus, the resulted carbon aerogels possess a unique bicontinuous porous structure (Figure 4.2d). EDS analysis indicates that the pore walls are composed of mainly C elements and trace amount of O element.

Figure 4.2 a) Photo of a piece of typical biomass aerogel. b) Photo of the carbon aerogel fabricated using the biomass aerogel in (a). c) SEM image of the carbon aerogel. d) High magnification SEM image of the carbon aerogel. Inset: EDS spectrum of the carbon aerogel.

The thermal gravitational analysis (TGA) is used to study the carbonization process during the pyrolysis. Figure 4.3a shows that there are mainly three decomposition stages during the ramping of the temperature. The first stage of weight loss before 100 °C is attributed to the evaporation of the moisture adsorbed on the biomass

aerogel. The second weigh loss stage ranges from 160 °C to 330 °C, with a very steep slope. This might attributed to the further loss of water content within the pith structure, and the decomposition of the volatile organic components. The third stage of weight loss is between 330 °C and 780 °C, which is characterized by a less steep slope, which might be attributed to the further decomposition and the gradual loss of oxygen-containing functional groups. Finally, the remaining weight of the carbon aerogel remains constant upon further increasing the temperature up to 900 °C, indicating that the decomposition and carbonization process is completed. Based on the TGA analysis, the pyrolysis temperature for the fabrication of the carbon aerogels is set at 800 °C. The final weight of the carbon aerogel is only 3% of that of the starting biomass aerogel. The carbon aerogel has a very low density. Figure 4.3b shows the mass of a typical carbon aerogel with volume about 0.5 cm³ is 33.6 mg, suggesting the density of the carbon aerogel is only around 0.07 g cm⁻³.

Figure 4.3 a) TGA curve of the pyrolysis process of biomass aerogel. b) Photo showing the mass measurement of a typical as-prepared carbon aerogel.

TEM image shows that the walls of the aerogel is made from stacking of many thin

carbon sheets (Figure 4.4a). Some tubular shaped structures can be observed within the carbon wall, which might be the carbonized products of the veins of the pomelo peels. The thickness of the carbon wall is not uniform, as revealed by the contrast variation across the carbon wall piece. The SAED characterization show no diffraction spots or rings, indicating that the carbon wall is amorphous. The XRD results further confirm that the carbon aerogel has an amorphous structure, with weak and broad peaks for graphitic carbon. This is clearly different from the biomass aerogel which has a crystalline cellulose structure (Figure 4.4b).

Figure 4.4 a) TEM image of the wall of the carbon aerogel. Inset: the corresponding SAED pattern. b) XRD characterizations of the biomass aerogel and the carbon aerogel.

The biomass aerogel is hydrophilic and can be easily wetted by water. For example, one water droplet dyed with methylene blue (MB) is rapidly absorbed into the biomass aerogel and left a blue stain on its surface. (Figure 4.5a). In contrast, the water droplet will stand on the surface of the carbon aerogel without being absorbed, indicating that the as-obtained carbon aerogel is hydrophobic (Figure 4.5b). Moreover, when the carbon aerogel is forced to be immersed into water by a pair of tweezers, an effect of mirror reflection can be observed around the surface of the

carbon aerogel (Figure 4.5c). This is due to the formation of the liquid/gas interface between the air entrapped within the carbon aerogel and the water outside. This phenomenon further proves the hydrophobicity of the as-obtained carbon aerogel and its ability to repel water. Contact angle measurements are performed to further quantitatively study the hydrophobicity of the carbon aerogel. Figure 4.5d and e shows that the WCA of carbon aerogel is around 106° , while the hexane is completely absorbed by the carbon aerogel, which results in an OCA of 0° . The CA measurements confirm that the as-prepared carbon aerogel is highly hydrophobic and oleophilic.

Figure 4.5 Photos showing a) a water droplet absorbed by biomass aerogel and b) water droplets standing on the carbon aerogel. c) Photo showing the mirror reflection around the carbon aerogel when being immersed into water. d) WCA measurement and e) OCA measurement on the carbon aerogel.

In order to further understand the change of the surface wetting property, FTIR was used to characterize the chemical components of the aerogels before and after the pyrolysis. As shown in Figure 4.6, the FTIR spectrum of the biomass aerogel reveals many absorptions peaks, which correspond to the oxygen-containing functional groups, such as C=O, C-O, and -OH.^[17] These polar oxygen-containing

functional groups will promote the interaction with water molecules, making the biomass aerogel surface hydrophilic. In contrast, the FTIR spectrum of the carbon aerogel obtained after the pyrolysis shows almost no absorption peak, indicating the oxygen-containing functional groups are removed, making the surface hydrophobic.

Notably, the HCl soaking step is crucial for obtaining the hydrophobic carbon aerogel. Without the HCl treatment, the mineral elements in the pith will form oxides or ions after pyrolysis, increasing the surface energy of the carbon aerogel, which makes the carbon aerogel hydrophilic (Figure 4.7).

Figure 4.6 FTIR spectrums of the biomass aerogel and the carbon aerogel.

Figure 4.7 WCA measurement of carbon aerogel without the HCl treatment.

The combination of the highly porous internal structure with the hydrophobic surface of the as-prepared carbon aerogel make it suitable for selectively absorbing oils and water-immiscible organic solvents from water. Figures 4.8a and b show the absorption processes of carbon aerogels towards two kinds of organic solvents with different densities. When the carbon aerogel is put onto a hexane layer (dyed with oil red O) floating on the water surface, the hexane is absorbed into the carbon aerogel within 15 s, with no more red coloured liquid observable, indicating the completely absorption of hexane. The carbon aerogel still floats on the water surface after fully absorbed the hexane, and does not release any hexane back to water even for an extended period of time, indicating the ability to hold hexane strongly within its pores. This is particularly important for the facile removal of oil spills and chemical leakage over the sea and rivers. Furthermore, the carbon aerogel can also absorb organic solvents with higher density than water. For example, a chloroform (dyed with oil red O) droplet (~ 1 mL) sitting at the bottom of water is quickly absorbed by the carbon aerogel. It can be clearly observed that when the carbon aerogel is first immersed into the water, the water cannot penetrate into the porous structure of the aerogel and a mirror reflection is observed. However, as

soon as the carbon aerogel contacts with the chloroform droplet, the chloroform is instantly absorbed into the carbon aerogel, while the air bubble are pushed out of the aerogel.

In order to quantitatively study the absorption capacity of the carbon aerogel, I measured the weight gain, which is defined as the weight of absorbed substance per unit weight of the dry carbon aerogel, for different oils and organic solvents, and compared them with the biomass aerogels. The carbon aerogel shows an increased absorption capacity for all of the tested organic liquids compared with biomass aerogels. In general, the carbon aerogel can uptake these liquids at 30 to 62 times of its own weight, which are roughly 2 to 3 times higher than those for biomass aerogels (Figure 4.8c). It can be noticed that the absorption capacity is positively related the density of the organic liquids. The absorption capacity for the pomelo peels derived carbon aerogels is higher than many low-cost or advanced oil absorbents reported in previous literatures, such as sawdust (3-6 times),^[19] winter melon-derived carbon aerogel (15-50 times),^[20] polypyrrole-based sponge (20-30 times),^[21] conjugated microporous polymers (5-25 times),^[22] marshmallow-like macroporous gels (6-15 times),^[23] and kapok (30-61 times).^[24] Although the absorption capacity of the as-prepared carbon aerogel is lower than that of some graphene and CNT-based aerogels such as ultra-flyweight graphene-CNT composite aerogels,^[16] spongy graphene,^[14] etc., the raw material cost of the carbon aerogel here is much lower since waste material, i.e. waste pomelo peel, is used. Therefore, the as-developed pomelo-derived carbon aerogel is considered to be a cost-effective absorbent for the oils and organic solvents spill remediation.

Figure 4.8 a) Photos showing the absorption process of hexane by a carbon aerogel. b) Photos showing the absorption process of chloroform by a carbon aerogel. c) Absorption capacities of the carbon aerogel and biomass aerogel for various oils and organic solvents.

Importantly, the as-developed carbon aerogel also shows excellent recyclability. Due to the chemical and thermal stability of the carbon aerogel, the oils and organic

solvents absorbed into the carbon aerogel can be directly burnt away. As shown in Figure 4.9, a carbon aerogel which is fully absorbed with hexane is light up by fire. After about one minute, the hexane is completely burned out, while the carbon aerogel still remains its integrity. After 5 regeneration cycles through burning, the absorption capacity towards hexane still keeps at nearly 100 %. The combustion method provide a very convenient way to regenerate the carbon aerogel if the absorbed oil is no longer wanted. Distillation is another effective method to regenerate the absorbents, while allows to collect the oil and solvent for recycling purpose. However, many prevailing commercial polymer-based absorbents, such as polyethylene absorbents, cannot be regenerated using distillation method, since the high temperature used to evaporative the oils can destroy the porous structure of the polymer absorbents. Here, I demonstrated that our carbon aerogel could be regenerated 5 times without any observable decrease in the absorption capacity through distillation. This is very important because the spilled crude oil is precious resources that worth recycling.

Figure 4.9 a) Photos of the regeneration of a carbon aerogel which is fully absorbed

with hexane through direct combustion. b) The absorption capacity of carbon aerogel for five cycles of regeneration through directing burning. c) The absorption capacity of carbon aerogel for 5 cycles of regeneration through distillation.

Conclusion

In this Chapter, I have successfully demonstrated the conversion of the pomelo peel, which is a typical biowaste, into novel hydrophobic and oleophilic carbon aerogels through pyrolysis method. The resulted carbon aerogel possesses a unique bicontinuous porous internal structure with pore size around a few hundred micrometers. Due to the high porosity and the hydrophobicity, the resulted carbon aerogel can selectively absorb various oils and water-immiscible organic solvents with high absorption capacity. In addition, the carbon aerogel shows excellent recyclability and can be regenerated for at least 5 times using the distillation and the combustion methods. Importantly, the low-cost and abundantly available source make the carbon aerogel a very cost-effective and promising for material candidate in industrial applications.

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Chapter 5*

Preparation of Stable Superhydrophilic and Underwater Superoleophobic Silica-Based Nanofiber-Coated Meshes from Waste Soda-Lime Glass for Multifunctional Oil/Water Separation

In this chapter, the preparation of silica-based nanofiber-coated meshes (SNMs) from waste glass through a green synthesis strategy is presented. The as-developed SNM is superhydrophilic in air and superoleophobic under water. Importantly, the SNM can maintain the superwetting property in various harsh environments. In addition, the SNM also shows a multifunctional water remediation property.

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5.1 Introduction

In recent years, the deteriorating problem of water contamination resulted from industrial oily wastewater discharge and oil spill accidents has called for more research efforts in special wettable materials for selective oil/water separation.^[1-4] For example, the superhydrophobic and superoleophilic material (including both filters and absorbents) is the first type of special wettable material utilized for the selective oil/water separation and receives quite extensive research attention.^[5-11] However, the high oleophilicity makes such type of material easily fouled by oils. Moreover, in a typical filtration process, a layer of water will form between the superhydrophobic filter and the oil layer, because water has a higher density than oils. The water layer stops the continuous oil permeation. Due to these drawbacks of the superhydrophobic and superoleophilic material, other types of special wettable material are also recently explored, especially those with high affinity towards water and low affinity towards oil.

Inspired by the underwater oil-repellent property of the fish scale and the seashell, researchers recently invent materials that are superhydrophilic in air and become superoleophobic under water, resulting from the combined effect of the high surface energy and the suitable surface roughness.^[12-14] Due to the superhydrophilicity, water molecules will be tightly trapped onto the rough surface of the material, forming a thin water layer. Such water layer is repulsive against the wetting by oil droplets, and thus prevent the oil permeation. The underwater oil-repellence property effectively prevents the oil fouling and promotes the continuous water permeation during the filtration process. Therefore, the superhydrophilic and underwater superoleophobic material is regarded as the most promising material for selective oil/water separation.

To date, the superhydrophilic and underwater superoleophobic material has been prepared from both organic and inorganic materials. For example, Xue et al. fabricated the hydrophilic polyacrylamide (PAM) hydrogel-coated mesh with underwater superoleophobicity and low underwater oil adhesion, which could selectively separate layered oil/water mixtures with high efficiency.^[15] Zhang et al. prepared the inorganic nanowire-hired membrane by growing $\text{Cu}(\text{OH})_2$ nanowires on the Cu mesh via surface oxidation in the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution.^[16] The as-prepared inorganic membrane was superhydrophilic in air and superoleophobic under water, and showed excellent performance in selective oil/water separation. However, the preparation of superhydrophilic and underwater superoleophobic materials so far still involves complicated procedures, expensive reagents, and toxic chemicals.^[17] Moreover, the developed materials are not stable under harsh working conditions. For example, the inorganic metal oxide/hydroxide-based materials become ineffective under the acidic environment, and the polymer-based materials cannot withstand high temperature. Therefore, it is still urgently desired to develop novel superhydrophilic and underwater superoleophobic material that is low-cost, environmentally friendly, and impervious to harsh working conditions for the practical oil/water separation application.

In this Chapter, I will present my research about a low-cost superhydrophilic and underwater superoleophobic silica-based nanowires-coated mesh (SNM) that is derived from waste soda-lime glass, through an environmentally friendly approach using water as the sole reagent. The as-prepared SNM shows excellent performance in selectively separating a wide range of oil/water mixtures, including both layered oil/water mixtures and oil-in-water emulsions. More importantly, the SNM can retain its superwetting property under various harsh environments, including corrosive organic solvents, high temperature, extreme pH conditions and high salinity. In addition, the SNM also shows multifunctional water remediation

property by simultaneously removing the organic dyes and heavy metal ions from the water phase during the oil/water separation process.

Soda-lime glass is the most common type of silica-based glass that is extensively used as construction and household material (e.g. window, cups, containers, etc.). It has become a significant portion of municipal solid waste after being disposed. It is estimated that more than 46 million tons of waste soda lime glass are disposed every year, occupying the precious land space, yet no satisfying solution is available to handle such waste.^[18] By converting the solid waste (i.e. waste glass) into the valuable functional material, my as-developed method also mitigates the severe problem of land pollution caused by the accumulation of solid waste.

5.2 Results and Discussion

The preparation process for the superhydrophilic and underwater superoleophobic SNMs from soda-lime glass is schematically illustrated in Figure 5.1. The detailed preparation procedures were described in Chapter 3. Briefly, soda-lime glass slides were first ground into glass powder by the ball milling process, which was then dispersed in ethanol and carefully “painted” onto a stainless steel (SS) mesh. Then, the glass powder-coated SS mesh was hydrothermally treated in a Teflon-lined autoclave at 180 °C to yield the superhydrophilic and underwater superoleophobic SNM.

Figure 5.1 Schematic illustration of the preparation route for the superhydrophilic and underwater superoleophobic SNM using waste glass as the starting material.

SEM image of a pristine SS mesh (100-mesh) shows that the surface of the steel fibres is clean and smooth (Figure 5.2a). In contrast, SEM images of an as-prepared SNM on the 100-mesh substrate (denoted as SNM-100) show that the steel fibres are uniformly wrapped by a coating layer with microscaled pores and roughness (Figure 5.2b, c). The EDS elemental mapping further indicates the uniform coating of silica-based nanowires across the entire SS frame (Figure 5.2a, b insets). Higher magnification SEM images reveal that the rough surface architecture is constructed from numerous nanowires with size of tens of micrometers in length and sub-100 nanometer to several hundred nanometers in width, which are intertwined together to form a highly porous network (Figure 5.2d)

TEM image of the coating layer also clearly reveals the intertwined nanowires (Figure 5.3a). Furthermore, the higher magnification TEM image reveals that the nanowires are made of bundles of ultra-small nanofibers (Figure 5.3b). The SAED pattern shows no diffraction spot or ring, indicating the resulting silica-based nanowires are amorphous (Figure 5.3b inset).

Figure 5.2 SEM image of the a) pristine SS mesh and b) SNM-100. Insets: EDS mapping of Fe and Si element, respectively. c-d) High magnification SEM images of the SNM-100.

Figure 5.3 TEM images of the silica-based nanowires. Inset of b): SEAD pattern.

Using the same procedures, the SNM can also be prepared on other SS meshes with different mesh numbers. Figure 5.4 shows the SEM images of an SNM prepared using 500-mesh as substrate (denoted as SNM-500), which also reveal the uniform coating of the characteristic highly intertwined nanowires across the entire SS frame.

Figure 5.4 SEM images of the SNM-500 under different magnifications.

In order to further reveal the formation process of the silica-based nanowires, the time-dependent hydrothermal treatment process is studied, and the corresponding SEM images of the resulting meshes are shown in Figure 5.5. The raw glass powder obtained from the ball milling process consists of irregular-shaped granules with size ranging from hundreds of nanometers to few micrometers (Figure 5.5a). High magnification SEM image indicates the surface of the individual glass granule is relatively smooth. After 2 hours of hydrothermal treatment, the glass granules remain discrete, with some of the granules sinter together to form larger ones (Figure 5.5b). High magnification SEM image shows that the surface of the glass granules, however, becomes much rougher compared with that of the raw glass powder. After 6 hours of hydrothermal treatment, some nanowires are formed on

the top of and between the granules (Figure 5.5c). With the further hydrothermal treatment to 10 hours, all the granules are converted into nanowires that are intertwined together forming a highly porous network. No more discrete granule is observable (Figure 5.5d). Further extending the hydrothermal treatment up to 24 hours will destroy the porous network formed by nanowires. Higher magnification SEM image indicates that the collapse of the porous network might be due to the fusion and aggregation of the nanowires (Figure 5.5e). XRD pattern shows no characteristic peak for the formed nanowires and raw glass powders, which proves that the nanowires remain in the amorphous structure after the hydrothermal process (Figure 5.5f).

The morphological changes of various silica-based glass under different hydrothermal conditions were reported in literatures, with different mechanisms being proposed.^[19-25] For example, Liu et al. proposed the mechanism for the formation of a flake-like coating on glass slide to be a four-step reaction, including ion exchange, etching, phase separation and leaching.^[24] Independently, Sun et al. proposed another “corrosion-ion immigrating-recondensation” mechanism for the formation of porous glass shell on glass beads.^[25]

Figure 5.5 a-e) SEM images illustrating the morphological evolution of the glass coating layer on SS mesh with different hydrothermal treatment time. a) 0h, b) 2h, c) 6h, d) 10h, e) 24h. f) XRD characterization of the nanowires and the raw glass powder.

Although the exact mechanism was not clearly understood, both studies agreed that the morphological change of soda-lime glass was initiated by the glass hydration

process. Briefly, the hydrogen atoms from bulk water became sufficiently mobile and reactive under high temperature, which diffused into the highly amorphous framework of the glass, replacing the sodium ions, i.e. $\equiv\text{Si-O-Na} + \text{H}_2\text{O} \rightarrow \equiv\text{Si-OH} + \text{Na}^+ + \text{OH}^-$.^[26] Subsequently, the hydroxyl ions left in the bulk water etched the Si-O-Si bonds of the glass framework. In my project, EDS characterization of the raw glass powder and the resulted nanowires indicates the dramatic decrease in the sodium content, which agrees with previous studies (Figure 5.6a). Element analysis using inductively coupled plasma optical emission spectrometry (ICP-OES) of the DI water used in the hydrothermal process also indicates a dramatic increase in the sodium concentration after the hydrothermal process (Figure 5.6b). In addition, the DI water used in a typical reaction has a pH value about 6.47 due to the slight dissolution of CO_2 from atmosphere, whereas the pH value of the water after hydrothermal treatment is around 10.65. These results confirm the occurrence of glass hydration process.

Figure 5.6 a) EDX results of the raw glass and the nanowires after hydrothermal process, showing the decrease in sodium content after the hydrothermal treatment. b) ICP characterization of the water before and after the hydrothermal treatment of glass, indicating the sodium diffuse out from the glass matrix into the surrounding water environment.

Importantly, the as-developed method is also suitable for other sources of waste glass. For example, SNM can also be obtained from two other different waste glass products, i.e. household glass cups and laboratory petri dishes (Figure 5.7). This implies that my method is general applicable for various waste glass sources, which is highly significant for practical applications.

Figure 5.7 a) SEM and b) high-magnification SEM images of an SNM prepared from a household glass cup. Inset in (b): photo of the glass cup used for preparation of SNM (scale bar = 1 cm). c) SEM and d) high-magnification SEM images of an SNM prepared from a laboratory petri dish. Inset in (d): photo of the petri dish used for preparation of the SNM (scale bar = 1 cm).

The surface superwetting behaviour is the synergistic result from both surface

chemistry and surface architecture. Due to the intrinsically highly hydrophilic property of the silica-based glass and the multi-scaled rough architectures of the resulting porous nanowires network, the as-prepared SNM shows the desired superwetting property. SNM-100 is used for the detailed characterizations of the wetting property. The water droplet can quickly spread across the mesh surface exhibiting a WCA of 0° in air, which indicates its superhydrophilicity (Figure 5.8a). When the mesh is immersed into water, a chloroform droplet can stand on the mesh in the spherical shape with a UWOCA of $\sim 153^\circ$, which indicates its underwater superoleophobicity (Figure 5.8b). These results are distinctly different from the pristine SS mesh without the coating of silica-based nanowires. The pristine SS mesh has a hydrophobic surface in air (WCA of $\sim 120^\circ$), and shows no superoleophobic property under water (UWOCA of $\sim 105^\circ$) (Figure 5.8c, d).

Figure 5.8 a) WCA measurement of SNM-100 in air. b) UWOCA measurement of SNM-100. c) WCA measurement of pristine SS mesh in air. d) UWOCA measurement of pristine SS mesh.

In addition, the as-prepared SNM also shows extremely low underwater oil adhesion. The chloroform droplet can easily roll off the mesh surface even with extremely small tilting angle of less than 5° (Figure 5.9a). The low oil adhesion is further qualitatively characterized by the established oil-contacting method.^[14] A chloroform droplet (5 μL) is suspended on the needle tip, which is then made to contact and subsequently leave the SNM. The oil droplet shows no observable shape change when leaving the SNM, indicating the extremely low oil adhesion (Figure 5.9b). In distinct contrast, for the pristine SS mesh, the chloroform droplet cannot roll off the surface even at a high tilting angle of 50° , and it experiences dramatic shape change upon leaving the pristine SS mesh due to the strong adhesion force with the mesh. The droplet finally adheres onto the mesh (Figure 5.9c, d). These results confirm that I have successfully prepared superhydrophilic and underwater superoleophobic SNM with extremely low underwater oil adhesion.

Figure 5.9 a) Photo showing a chloroform droplet (3 μL) rolling off the SNM at an underwater oil sliding angle of less than 5° . b) Photos showing the process for the underwater oil-contacting characterization of the SNM. The chloroform droplet (5 μL) is suspended on the tip of a needle, and the SNM is moving towards (left),

contacting (middle) and leaving (right) the suspended droplet. The shape of the chloroform droplet does not change in the whole process. c) Photo showing a chloroform droplet (3 μL) adhering on the pristine SS mesh without rolling off at a tilting angle of 50° . d) Photos showing the process for the underwater oil-contacting characterization of the pristine SS mesh. The SS mesh is moving towards (left), contacting (middle) and leaving (right) the suspended droplet. The chloroform droplet experiences dramatic shape change in the process.

The as-prepared superhydrophilic and underwater superoleophobic SNM shows excellent performance in selective oil/water separation. The detailed experiment procedure and set-up was described in Chapter 3. As a typical example of oil/water separation using SNM-100, when the layered mixture of hexane and water (24 mL, volume ratio 1:2) is poured onto the SNM-100 which is pre-wetted by water, the oil is blocked and retained within the upper glass funnel, while water freely passes through the SNM at a very high flux, solely driven by the gravity (Figure 5.10a-c). The entire separation process can be finished within 15 s, corresponding to a water flux approximately $70,000 \text{ L h}^{-1} \text{ m}^{-2}$.

Figure 5.10 Photos showing the entire process of separating a layered oil/water mixture (for clarify, oil and water were dyed with oil red O and MB, respectively) using the SNM-100.

As known, one challenge for most of the superhydrophilic and underwater superoleophobic meshes in oil/water separation is that they are unable to separate oil-in-water emulsions. The size of oil droplets, which is usually less than tens of micrometers, are much smaller than that of the holes of mesh which is around tens of micrometers to several millimeters. Here, by simply increasing the loading amount of the glass powder onto the mesh, I am able to prepare a filter with all the frame holes completely covered by the porous nanowires network (denoted as SNM'). SEM image of the resulting SNM' shows that there is no observable hole across the entire mesh frame (Figure 5.11a). Higher magnification SEM images show that the mesh only consists of small pores formed by the intertwined nanowires, with pore diameters ranging from a few hundred nanometers to about 1 micrometer (Figure 5.11b, c). The water passes through the SNM' only through

these small pores, and the oil droplets can be effectively blocked and separated from the oil-in-water emulsions. After the filtration process using SNM', the milky oil-in-water emulsion (10 vol%) becomes transparent and colourless, indicating the successful separation of the oil/water emulsion. Optical microscope images of the emulsion before and after the filtration further reveal that the oil droplets of sub-ten micrometers in the emulsion are completely absent in the filtrate (Figure 5.11d, e).

Figure 5.11 a-c) SEM images of SNM' under different magnifications. d, e) Optical microscope images of the oil-in-water emulsion before (d) and after (e) separation by the SNM'. Insets in (d, e): photos of the emulsion before (d) and after (e) the filtration process.

In order to quantitatively study the oil/water separation efficiency, a number of different oils and organic solvents, namely petroleum, canola oil, pump oil, hexane and chloroform, are used to prepare the oil/water mixtures including both layered mixtures and oil-in-water emulsions. Layered mixtures are separated using SNM-100, while oil-in-water emulsions are separated using SNM'. The residual oil contents in the filtrate water are then measured with an oil content analyser. The

results show that for all layered oil/water mixtures, the residual oil contents are less than 20 ppm (Figure 5.12a). For oil-in-water emulsions, the residual oil contents in the filtrate water are around 60 ppm. These results indicate that for all the tested oil/water mixtures, the separation efficiency are higher than 99%. To study the reusability of the as-prepared SNM, the oil/water separation process is repeated 5 times using the canola oil-based layered oil/water mixtures and oil-in-water emulsions. Due to the extremely high oil-repellency and low oil adhesion, the oil left on the surface of the SNM after each separation process can be easily rinsed off by water. Therefore, the high separation efficiency can be maintained after 5 cycles of usage (Figure 5.12b).

Figure 5.12 a) The residual oil content in the filtrated water for a series of layered oil/water mixtures and oil-in-water emulsions separated by SNM-100 and SNM', respectively. b) The oil content in the filtrated water for 5 filtration cycles of canola-based layered oil/water mixtures and oil-in-water emulsions using SNM-100 and SNM', respectively.

Till now, most of superhydrophilic and underwater superoleophobic materials are fabricated from either polymers or metal oxides/hydroxides, which are usually unable to retain their superwetting properties in harsh environment. For example, the surface morphologies of polymer-based superhydrophilic and underwater

superoleophobic materials easily deform at elevated temperature as well as upon exposure to various organic solvents.^[27-30] For inorganic oxides/hydroxides-based materials (e.g. ZnO, Cu(OH)₂, NiO, etc.), their surface architectures can be destroyed under strong acidic condition.^[16, 31-37] However, harsh environments, such as extremely pH solutions, high salinity water, high temperature and corrosive organic solvents, are quite commonly encountered in practical oil/water separation applications. Importantly, the as-prepared SNMs here show excellent stability against many harsh conditions. Figure 5.13a shows that the as-prepared SNM can keep its underwater superoleophobicity with UWOCAs above 150° after being immersed in various organic solvents for 24 hours, indicating its excellent stability against various organic solvents. Figure 5.13b shows that the as-prepared SNM can sustain the underwater superoleophobicity after being heated at high temperature up to 400 °C. The excellent high temperature stability, as well as the solvent resistant ability, are the key advantages over polymer-based materials. The UWOCA drops below 150° upon further increasing the annealing temperature. SEM image of the SNM after being annealed at 600 °C shows that the highly porous intertwined nanowires network is destroyed. Large aggregates with relatively smooth surface are observed, which might be resulted from the fusion of the nanowires at high temperature (Figure 5.14).

Figure 5.13 Stability of the SNMs under various harsh environments. a) Measured UWOCAs of SNMs after being immersed in various organic solvents for 24 h (THF: tetrahydrofuran, NMP: N-methyl-2-pyrrolidone, DMF: N, N-dimethylformamide, DMK: dimethyl ketone, and TCM: trichloromethane, i.e. chloroform). Insets: photos of underwater chloroform droplets (3 μ L) standing on SNMs after being immersed in various organic solvents for 24 h. b) Measured UWOCAs of SNMs after being annealed at various temperatures. c) UWOCA measurements and residual oil content in the filtered water after immersing the SNMs in solutions with various pH values and high salinity. d) Residual oil content in the filtered water obtained after 5 experimental cycles with SNMs treated under different harsh conditions.

Figure 5.14 SEM image of the SNM after being annealed at 600 °C for 2 hours.

Moreover, the SNM also shows excellent stability against acidic, basic and high salinity conditions. Figure 5.13c shows that after being immersed in solutions with various pH values and high salinity for 5 days (note that the test at pH 7 was carried out in high salinity water, i.e. 1 M NaCl solution), the SNM remains underwater superoleophobicity and high oil/water separation efficiency. Furthermore, after SNMs are immersed into HCl (1 M), NaOH (1 M) and NaCl (1 M) solutions, respectively, all the measured UWOCAs are still higher than 150° keeping the underwater superoleophobicity (Figure 5.15). These results further prove the excellent pH and salinity stability of the SNM. The reusability after the treatment under three different harsh conditions (i.e. THF treatment, 400 °C annealing and 0.1 M HCl treatment) are also tested. Results show that the SNM still maintains the excellent reusability after being treated in all different harsh conditions (Figure 5.13d). The excellent harsh-environment resistance makes the as-prepared SNM significantly promising toward the practical oil/water separation applications.

Figure 5.15 Photos showing the underwater chloroform droplets (3 μ L) standing on SNMs immersed in a) HCl (1 M) solution, b) NaCl (1 M) solution and c) NaOH (1 M) solution, respectively.

Interestingly, multifunctional water remediation can also be achieved using SNM'. Due to the small pores of SNM', the water flux is reduced, providing longer contact time between the permeating water and the nanowires coating layer. Due to the negative surface potential, the nanowires can effectively adsorb positively charged water contaminants during the filtration process. For example, methylene blue (MB) is a positively charged water-soluble dye that is commonly used in the textile and colouring industries. The presence of MB in the natural water bodies causes several adverse effects on human health, which is highly undesirable and needed to be removed before discharge.^[38] The SNM' can achieve the simultaneous oil/water separation and removal of MB from the water with a single filtration step. The MB dyed water (2 ppm) becomes colourless after passing through the SNM', while the oil is retained within the upper glass tube (Figure 5.16a, b). UV-visible spectra of the feed and filtrate water show that the characteristic absorption peak of MB at 655 nm completely disappears after the filtration process, further proving the removal of the MB (Figure 5.16c). In addition, the used SNM' becomes blue after the filtration process, indicating the MB is adsorbed onto the SNM' (Figure 5.16c, inset). Heavy metal ions (HMIs) are another type of common pollutants from

industrial wastewater, which cause many deadly diseases.^[39] The SNM' can also simultaneously reduce the amount of HMIs presented in the water. Figure 5.16d shows that after single filtration process, the concentrations of various highly toxic HMIs presented in the water phase of the oil/water mixtures are significantly reduced. The HMIs removal mechanism is proposed to be a combination of electrostatic adsorption and ion exchange process.^[23, 40]

Figure 5.16 Multifunctional water remediation characteristics of NFMs. a, b) Photos showing the simultaneous removal of MB from water during the oil/water separation process by SNM'. c) UV-vis spectra of the water before and after the filtration process, i.e. the feed water and filtered water, respectively. Inset: photo of

the SNM' after the filtration process. d) Concentrations of various HMIs in the water before and after the oil/water separation process.

5.3 Conclusion

In conclusion, I demonstrated in this Chapter a low-cost and environmentally friendly method to prepare superhydrophilic and underwater superoleophobic SNMs from waste glass. The as-prepared SNMs showed superior performance in selectively separating both layered and emulsified oil/water mixtures with high efficiency. More importantly, the SNMs exhibited excellent stability against many harsh environments, making it a promising candidate towards oil/water separation under practical conditions. The SNMs also exhibited multifunctional water remediation property. In addition, by converting solid waste into valuable functional materials, my research also provided new strategy in mitigating the land pollutions.

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Chapter 6

Conclusions and Future Work

The chapter concludes the thesis and discusses the originality and contributions of the research to the related research field. The unsolved problems, unanswered questions and the suggested future research directions are also discussed and recommended.

6.1 Conclusion and Originality

In this thesis, I presented two novel special wettable materials developed during my Ph.D. study for the selective oil/water separation within the topic of water remediation. The ultimate goal of this thesis was to develop low-cost special wettable materials, and the core focus and strategy was the smart utilization and conversion of various waste into the functional materials with special surface wettability. By the combination of surface roughness with the surface tension of the recycled waste, value-added materials with different surface wettability were developed to remediating oily water through various ways by taking advantage of some intrinsic characteristics of the recycled water.

First, a 3D porous hydrophobic absorbent was developed using the waste pomelo peel as raw material. The intrinsic microporous structure of the pomelo peel was perfectly utilized, which was transformed into the porous carbon aerogel after the pyrolysis process. Compare with other carbon aerogels reported in the previous literatures, the fabrication process was greatly simplified as no additional pore-making process was needed. In addition, this was also one of the very few works that converted practical waste from real life into functional materials. The waste pomelo peels derived carbon aerogels were used to selectively absorb oils and organic solvents at both the surface and the bottom of water. The absorption capacity was also comparable to other carbon aerogels. Due to the extremely low cost of the raw materials, the absorption capacity normalized to cost was expected to be highly competitive.

Second, a superhydrophilic and underwater superoleophobic mesh was developed using waste soda lime glass as raw material. Taking advantage of the fact that soda-lime glass could be etched into porous structure under hydrothermal condition, I

coated the glass onto commercial stainless steel mesh to create a rough surface. Since the major component of the soda-lime glass was silica, which was a material with intrinsically high surface tension, I obtained a very low-cost superhydrophilic and underwater superoleophobic mesh by the synergistic effect of the high energy surface and rough architectures. In addition, the silica was stable against organic solvents, acid, and salinity, the as-developed mesh could be used under a wide range of harsh environment. This research demonstrated, for the first time, the fabrication of the superhydrophilic and underwater superoleophobic material from not only a low-cost, but also a wasted inorganic raw material. The as-developed mesh was able to separate both layered oil/water mixtures and oil-in-water emulsions, by simply controlling the loading amount of glass. This research also contributed significantly in the research field of special wettable material development, as well as the waste management.

Overall, both projects presented in this thesis are original and contribute new knowledge to the related research field with some new insights. I believe all the materials developed here are highly promising for the practical industrial usage. In addition, the thesis also reveals the importance of the interdisciplinary research for solving the current global water challenges.

6.2 Unsolved Questions and Future Research Directions

Although new and important works have been demonstrated in this thesis, there are still many questions, both fundamental and practical, remaining unanswered. These unexplored areas of knowledge will lead to several exciting and important research directions. In this section, I will briefly provide a discussion of the possible future works for the related research field.

The wettability of the solid surface is a long-known phenomenon. However, only within the recent decade does the extensive research brings new developments and insights into this field. Although new theories and knowledge about the wettability, especially the superwettability, have been proposed, the fundamental rules and understandings into this field still require further research efforts. Particularly for the special wettable materials for oily water remediation, there are still basic fundamental questions remaining unanswered. First, the exact dynamic interaction between oil/water mixtures and the special wettable materials has not been clearly revealed. For a superhydrophobic surface, the surface energy becomes higher after the interaction with oils, and therefore might become less hydrophobic. During the oil/water separation process, how water reacts to such change in the surface energy is not known. One particular interesting and important question is that how the tiny liquid droplet interact with the solid surface during the separation of oil/water emulsions. For example, during the separation of oil-in-water emulsion using either superhydrophobic materials or superhydrophilic materials, how the micrometer or nanometer sized oil droplets behave when contact with the solid surface is unknown, e.g. whether the oil droplet experience local demulsification or remains as individual droplet. This might requires more advanced equipment to in-situ observe the local oil/water separation process at micro- and even nano-scale.

Second, although it is a well-known fact that the surface roughness could enhance the wettability, the exact influences of different shapes and sizes of the surface architectures are less documented. Taking the creation of superhydrophobic surface as an example, in most of the literatures, the general belief is that a rougher surface should have better effect on increasing the WCA. Unfortunately, the exact definition of “rough” is unknown. For two surfaces with the same chemical component, one is with micro-sized architectures in high area packing density, and the other one has a two-tier micro- and nano-sized architectures in low area packing

density, which one of the two surfaces is considered to be rougher and with higher WCA? In the classic Wenzel model, the roughness factor R is defined as the ratio of the true surface area over the apparent surface area. However, as area packing density of the surface architecture continues to increase, the surface tends to become “flat” again at the extreme situation, although the roughness factor R might be extremely high. My belief is that there should be a threshold for each type of surface architecture, over which the enhancing effect of the wettability will decrease, and there should be a limit WCA for each type of surface architectures. These unsolved questions require further fundamental calculation and modelling studies.

Beside these fundamental questions, other research works should also be explored from the materials and application point of view. First, although there are many methods, both physical and chemical, to create special wettable materials, few has shown the potential for large scale fabrication. Simpler and more robust techniques are needed. At the same time, engineering designs and efforts are also highly needed to enlarge the fabrication scale of the existing techniques. Second, the performance of the special wettable materials under the practical working conditions for extended working time is less explored. The real oily wastewater from various industries might be rather complex, with multiple substances, such as solid particles and surfactants. These substance might destroy the surface architectures, and change the surface energy of the special wettable materials, making them lost their oil/water separation ability. Therefore, materials with high wear-resistance and contaminants tolerance should be developed. Third, the development of multifunctional materials that could simultaneously separate oil/water mixtures and perform other functions is an interesting research direction.

In this thesis, I have shown that various types of waste are potential raw materials

for preparation of functional materials with special wettability. As one kind of biomass, the waste pomelo peels do not bring about harmful impact to the environment, as they can be naturally degraded without leaving toxic by-products. It is therefore of higher significance if non-biodegradable and toxic waste could be utilized to fabricate special wettable materials. Synthetic polymers, such as polyethylene, polypropylene, polystyrene, etc. are extensively used in both industrial and domestic sectors on daily basis. They are non-biodegradable and their presence in the environment causes negative impact to animals, microorganisms, and human. Some of the polymers are very difficult to handle, e.g. waste polystyrene, polyvinyl chloride, etc., as the burning temperature in common incineration plants are not sufficient to fully decompose these polymers into CO_2 , and thus releases toxic aromatic or chlorine-containing gaseous by-products. Therefore, more research can be done to explore the effective approach to convert waste polymer products into functional materials. Many common polymers are intrinsically slightly hydrophobic, which provide the material basis to convert them into superhydrophobic materials by creating rough textures.

Finally, the oil/water separation is only one of the applications that special wettable materials show promising results. There are more exciting research directions in terms of applications, such as self-cleaning, directional liquid transportation, anti-icing, anti-fogging, drag deduction, etc. that worth exploring.

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