MODIFICATION OF COPPER MESH TO ACHIEVE SUPERHYDROPHOBIC SURFACE

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MODIFICATION OF COPPER MESH TO ACHIEVE SUPERHYDROPHOBIC SURFACE

by

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LIST OF SYMBOLS

Symbol	Description	Unit
WCA	Water contact angle	°
WSA	Water sliding angle	°

LIST OF ABBREVIATIONS

Symbol	Description
$(NH_4)_2S_2O_8$	Ammonium persulfate
AFM	Atomic Force Microscopy
$AgNO_3$	Argentum nitrate
Al_2O_3	Aluminium oxide
AP	Aluminium phosphate
A-PU	Acrylate-terminated polyurethane
C	Carbon
Cu	Copper
CrO_3	Chromium trioxide
$Cu(OH)_2$	Copper(II) hydroxide
$Cu(OH)_2$-CS	Copper(II) hydroxide on copper substrate
$Cu(OH)_2$-SSS	Copper(II) hydroxide on stainless steel substrate
Cu_2O	Copper oxide
$CuCl_2$	Copper(II) chloride
CuO	Copper(II) oxide
$CuSO_{4.5}H_2O$	Copper sulfate pentahydrate
Cu-SSS	Copper on stainless steel substrate
DDT	Dodecanethiol
DI	Deionized water
DDVAC	N,N-dimethyl-dodecyl-(4-vinylbenzyl) ammonium chloride
EDX	Energy dispersive X-ray spectroscopy
FAS	Fluoroalkylsilane

FTIR	Fourier-transform infrared spectroscopy
H_2SO_4	Sulfuric acid
H_3BTC	1,3,5-benzenetricarboxylic acid
H_3PO_4	Phosphoric acid
HCl	Hydrochloric acid
HPAM	polyacrylamide
ISTP	In-situ thermal polymerization
$K_2S_2O_8$	Potassium persulfate
MOF	Metal organic framework
$NaBH_4$	Sodium borohydride
$NaNO_3$	Sodium nitrate
NaOH	Sodium hydroxide
O	Oxygen
ODT	Octadecanethiol
PC	Polycarbonate
PDA	Polydopamine
PDMS	Polydimethylsiloxane
PE/EVA	Polyethylene/ethylene vinyl acetate
P(MMA-SMA-MAPOSS)	POSS hybrid acrylic polymer
POSS	Polyhedral oligomeric silsesquioxane
POTS	1H,1H,2H,2H-perfluorooctyltriethoxysilane
PSP	Precipitated silica particle
S	Sulfur
SAC	Silicon-acrylic copolymer

SCM	Copper hydroxide coated mesh
SEM	Scanning electron microscopy
SPM	Superhydrophobic polymer material
SSM	Stainless steel mesh
TCMS	Trichloromethylsilane
VTES	Vinyltriethoxysilane
$ZnSO_4$	Zinc sulfate

PENGUBAHSUAIAN JARINGAN KUPRUM UNTUK MENCAPAI PERMUKAAN YANG SUPERHIDROFOBIK

ABSTRAK

Pengubahsuaian jaringan kuprum untuk mencapai permukaan superhidrofobik telah dibentangkan dalam tesis ini. Jaringan kuprum superhidrofobik telah disintesis dengan merendam jaringan kuprum dalam larutan akueus yang mengandungi ammonium persulfate ($(NH_4)_2S_2O_8$) dan natrium hidroksida (NaOH), diikuti dengan rawatan asid stearik, bahan tenaga permukaan rendah yang tidak toksik, murah dan mudah didapati. Kesan gabungan struktur mikro-nano kuprum(II) hidroksida ($Cu(OH)_2$) kasar dan salutan dengan molekul asid stearik tenaga permukaan rendah disifatkan kepada permukaan jaringan kuprum superhidrofobik yang terhasil. Pengubahsuaian dijalankan untuk mengkaji kesan kepekatan ammonium persulfat, kepekatan asid stearik dan nombor jaringan kuprum. Didapati bahawa jaringan yang diubah suai dengan nombor mesh 500 dan 2000 mempamerkan superhidrophobik, dengan sudut sentuhan air 162.7° dan 159°, masing-masing untuk kepekatan 0.5 M $(NH_4)_2S_2O_8$. Selain itu, permukaan jejarum nano $Cu(OH)_2$ yang diubah suai dengan kepekatan asid stearik 0.006 M menunjukkan sudut sentuhan air 152.7° yang mengesahkan ciri-ciri superhidrofobik. Kepekatan asid stearik yang lebih tinggi menyebabkan hablur stearat termendap pada permukaan jaringan. Sampel yang disediakan telah dianalisiskan dengan menggunakan teknik mikroskopi elektron pengimbas (SEM), spektroskopi sinar-x penyebaran tenaga (EDX) dan spektroskopi inframerah Fourier transformasi (FTIR). Morfologi permukaan, struktur kristal, unsur kimia permukaan dan sudut sentuhan air static salutan $Cu(OH)_2$ telah dikaji secara terperinci.

MODIFICATION OF COPPER MESH TO ACHIEVE SUPERHYDROPHOBIC SURFACE

ABSTRACT

Modification of copper mesh to achieve a superhydrophobic surface has been presented in this thesis. A superhydrophobic copper mesh has been fabricated by immersing copper mesh in an aqueous solution consisting of ammonium persulfate ($(NH_4)_2S_2O_8$) and sodium hydroxide (NaOH) followed by treatment with stearic acid, a non-toxic, inexpensive and readily available low surface energy material. The combined effects of rough copper(II) hydroxide ($Cu(OH)_2$) micro-nano structures and coating with low surface energy stearic acid molecules were ascribed to the resulting superhydrophobic copper mesh surface. The modification was carried out under different ammonium persulfate concentration, stearic acid concentration and mesh number. It was found that the modified mesh with 500 and 2000 mesh number exhibited superhydrophobicity, with a water contact angle of 162.7° and 159°, respectively for 0.5 M $(NH_4)_2S_2O_8$. Besides, the surface of the $Cu(OH)_2$ nanoneedles modified with 0.006 M stearic acid showed a water contact angle of 152.7° which indicated superhydrophobicity. Higher stearic acid concentration caused the stearate crystals deposited onto the mesh surface. The prepared samples were characterized by using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and Fourier transform infrared spectroscopy (FTIR) techniques. The surface morphologies, crystal structures, surface chemical elements and static water contact angles of the $Cu(OH)_2$ coatings were studied in detail.

CHAPTER 1

INTRODUCTION

Recently, the continuous exploration of oil and gas and other manufacturing processes cause unwanted oil contamination and oil spillage that contribute to the large amount of oily wastewater. All of them cause the severe environmental hazard that affect the quality of water and marine ecosystems as well as human health. In addition, the contamination of local water bodies can create a catastrophic event under extreme conditions (Parisi and Narayan, 2021). Surface structures and microscopic surface roughness are widely known to greatly promote the superwetting state. Only excessive wetting states can be able to separate oil from water or water from oil mixture (Khan et al., 2020). Amongst the vast different technologies, membrane separation is known to be an effective technology that can be utilized to separate oil-water mixture. However, it is not without the drawback that require concerted effort for improvement.

1.1 Research Background

The conventional methods for oil-water separation includes physical adsorption, gravity separation, electrochemical separation, centrifugal separation, biological treatment, precipitation tanks, ultrasonic separation, centrifugation, and oil skimmers (Baig, 2020; Zhu et al., 2021). However, research on these technologies has been confined to inefficient processing, low separation capacity, time-consuming, and not environmentally friendly (Zhu et al., 2021). Moreover, these traditional methodologies also have drawbacks such as causing secondary contamination, higher energy consumption, and are not appropriate in separating oil-water emulsion, particularly for surfactant-stabilized emulsions (Yin et al., 2020). In the lights of these drawbacks, different approach was introduced to treat the stable oil-water emulsion by fabricating the superhydrophobic filter/membrane that is more advantageous compared to the conventional methods. Superhydrophobic effect can be best explained using the illustration of “lotus effect”. The “lotus effect” refers to an extremely high static water contact angle in conjunction with a very low sliding angle. It describes how little droplets with very poor adhesion may readily roll off solid surfaces and take away debris on the surface, resulting in self-cleaning (Kong et al., 2015).

Copper mesh which has defined pore size is an excellent supporting material to be used as filter or membrane. However, in order to achieve the superhydrophobic properties, surface modification is required. Some of the surface modification methods are spray coating, surface etching, immersion, dip coating, chemical vapor deposition, hydrothermal methods, solvothermal methods, layer-by-layer assembly, and electrochemical treatment (Baig, 2020).

It is challenging to fabricate filter or membrane that is able to perform oil-water separation as the filter/membrane must be durable, low-cost, highly efficient and safe to the environment. Such a filter can be developed modifying the copper mesh using numerous methods as mentioned before. Surface roughness and low surface energy materials is essential to produce a superhydrophobic meshes. The modification of the copper mesh is normally followed by acid treatment to make the surface superhydrophobic. The surface is said to be superhydrophobic if the water contact angle is above 150° and water slide angle less than 10° (Liu, Luo and Jia, 2020; Guo et al., 2018; Zhan et al., 2021). Abundance research articles has been successfully presented on the production of copper mesh with good water contact angle as well as showing higher efficiency of oil-water separation. The modified copper mesh is being studied for its separation efficiency, water contact angles, recycle time, and oil flux of the fabricated copper mesh. Reaction time, immersion time, temperature, pH and concentration of the solution are amongst the studied parameter to modify the copper mesh.

1.2 Problem Statement

Oil and water can be separated using a superhydrophobic copper mesh via surface modification. Chemical oxidation is one of the simplest methods to fabricate the copper mesh to make it hydrophobic. Nanoneedles arrays will form after oxidation process which make the surface rougher. Upon treatment with longer non-polar alkyl chain namely stearic acid, $Cu(OH)_2$ can exhibit its superhydrophobicity with water contact angle of more than 150°. Stearic acid, which includes 16-CH_2, 1-CH_3, and 1-COOH groups, is a non-toxic substance that is frequently utilized as a low surface energy material (Xu et al., 2019). This approach is eco-friendlier compared to other conventional method. Other than that, this method is simple and require less preparation time. However, the control of oxidation process to produce the cuprous oxide is difficult.

The common parameters that always be highlighted by researchers are exposing the mesh to different pH solution, temperature, abrasion test, and reaction time. Concentration of ammonium persulfate, stearic acid, and mesh number are rarely being discussed in the literature. Thus, the objectives of this study are to modify the copper mesh to achieve superhydrophobic surface via oxidation method together with polymer coating using stearic acid. Their performance in terms of wettability, surface morphologies and structures as well as surface chemistry will be compared.

1.3 Objectives

a. To modify the copper surface via oxidation and polymer coating method to achieve superhydrophobic effect.

b. To study the effect of mesh size, ammonium persulfate and stearic acid concentration on the modified copper mesh surface.

c. To characterize the surface properties of the copper mesh after surface modification.

CHAPTER 2

LITERATURE REVIEW

A myriad way to modify the copper mesh surface has been reported in this field. However, producing it with eco-friendly, high durability and concurrently having high separation efficiency is still demanding. Separation efficiency and water contact angle are critical aspects to be measured after the modification of the copper mesh. This has been discussed by a great number of authors in the literature as followed.

2.1 Physical Method of Mesh Modification

Table 2.1 shows the effect of spray coating on the surface energy of copper mesh. Spray coating is one of the most broadly utilized methods for coating meshes with low surface energy materials (Baig, 2020). The spray coating method was believed to be a cost-effective and simple method to modify the mesh with low surface energy materials. One of the significant advantages of spray coating is its scalable fabrication method (Ye et al., 2017; Guo et al., 2018). Yin et al. in 2020 prepared a superhydrophobic copper hydroxide coated mesh by using facile spraying the mixture of copper (II) chloride dehydrate, polyurethane (PU), and sodium hydroxide by using spray gun. In their work, stainless steel mesh with 1000 mesh size was employed because it has good mechanical strength with reasonable price. After the mixture were sprayed onto the stainless steel mesh, the hydrophilic copper hydroxide coated mesh was obtained. The chemical reaction can be shown by equation (2.1) (Yin et al., 2020). Then, the as-prepared mesh was immersed for 8 minutes with n-dodecanethiol and ethanol solution to gain its superhydrophobicity before being washed in ethanol to remove the excess n-dodecanethiol. Finally, before characterization, the superhydrophobic copper hydroxide coated meshes (SCM) were dried at ambient temperature for 1 hour.

$$CuCl_2 + 2NaOH \rightarrow Cu(OH)_2 + 2NaCl \tag{2.1}$$

Table 2.1 Summary of modification using spray coating

Matrix	**Deposited Material**	**Method**	**Performance**	**Reference**
Stainless steel mesh	$Cu(OH)_2$-n-dodecanethiol	Spray coating	> 99.00% after 10 cycles WCA: 154.4 ± 2°	Yin et al. (2020)
Stainless steel mesh	AP-Cu-ODT	Spray coating	> 99.98% WCA: 157°	Zhang et al. (2021)
Brass mesh	Cu_2O	Spray coating	WCA: 159.6° WSA: 1°	Niu and Kang (2018)
Stainless steel mesh	P(MMA-SMA-MAPOSS)	Spray coating	99.00% after 25 cycles WCA: 153° WSA: 4.5°	Guo et al. (2018)

Their study focusing on separating surfactant-stabilized water-in-oil emulsions at atmospheric pressure. The sizes of emulsified water droplets in surfactant-stabilized emulsions were typically less than 10 µm, making separation process more challenging. Before separation, water droplets less than 1000 nm could be seen whereas no water droplets were in the filtrate after separation process. The result showed that many tightly packed water droplets of various stabilized water-in-oil emulsions were separated effectively. The as-fabricated SCM was capable of separating the stabilised emulsions via a sieving effect driven by gravity. As a result, the separation flux was considerably lower. Because the surfactant was present in the emulsions, the water droplets barely accumulated together. A filter cake developed on the surface of the separation mesh improved the separation efficiency on some level. Nonetheless, the cake clogged the surface pores and reduced the effective filtration area of the membranes, resulting in a rapid drop in permeation flux. The obtained SCM showed great separation efficiency (> 99.00%) after 10 cycles of filtration with water contact angle still remained more than 150° (Yin et al., 2020).

Apart from that, another study (Zhang et al., 2021) reported a similar method to separate water-in-oil emulsions. Zhang et al. (2021) in their studies modified the stainless-steel mesh by spraying the inorganic Aluminium Phosphate (AP) and copper nanoparticles onto the mesh surface. AP can make a strong bond with stainless steel mesh while having less toxicity, strong adhesion, resist to oxidation and low cost. It can also increase the mechanical properties when paired with the copper as its coating. Copper was chosen because its oxidation process during the high temperature curing of AP did not affect the coordination process with octadecanethiol (ODT) (Zhang et al., 2021). The ODT in this case was used to make the surface superhydrophobic. In the end, AP-Cu-ODT coated SSMs was prepared to separate the oil-water emulsions. The efficiency was more than 99.98% for all emulsions. In addition, the durability of the fabricated mesh also being tested. AP-Cu-ODT could maintain higher separation efficiency (> 99.95%) after 10 cycles and water contact angle of 157°. Different pH value from 1 to 14 were also being tested to study their effect. It can be shown that even under alkaline condition (pH>13) and acidic condition (pH<2), the contact angle remained greater than 150°, which is related to the strong corrosion inhibition of octadecanethiol (ODT) and the amount of copper nanoparticles in the coating (Zhang et al., 2021).

Other than that, Niu and Kang (2018) in their studies fabricate a superhydrophobic brass mesh via spray deposition method. Because of its outstanding thermal and electrical conductivities as well as mechanical-work ability, brass has sparked a lot of interest in the electronic and marine industries. No surface energy material used in the process. To prepared its coating, copper sulfate pentahydrate ($CuSO_4.5H_2O$), seignette salt and sodium hydroxide (NaOH) were mixed together with certain concentration became a solution, then another chemical compound namely sodium borohydride ($NaBH_4$) as reductant. Both solution and reductant were sprayed onto the cleaned brass mesh. Upon drying using vacuum oven, the cuprous oxide (Cu_2O) coatings were formed on the brass mesh from the oxidation of copper and micro and nanostructures. A water contact angle of 159.6° and sliding angle of 1° were observed after the fabricated brass mesh was dried using vacuum oven (Niu and Kang, 2018).

In another study by Guo et al., 2018, the superhydrophobic-superoleophilic stainless steel mesh was made by spraying the copolymer solution (polyhedral oligomeric silsesquioxane, POSS hybrid acrylic polymer). The treated stainless steel mesh showed superhydrophobicity characteristic with water contact angle and water sliding angle of 153° and 4.5° respectively. After 25 cycles of separation for an n-hexane/water mixture for example, the separation efficiency remained over 99.00% and with 20 sandpaper abrasion cycles on the coated mesh, the water contact angle is still 145°. The separation efficiency for n-hexane/water mixture remains about 99.00% (Guo et al., 2018). Figure 2.1 shows the surface morphologies observed by scanning electron microscopy (SEM). Figure 2.1(a) and 2.1(b) shows the pristine mesh that have a very smooth and clean surface while Figure 2.1(c) and 2.1(c) shows the micro-spheres and submicron-spheres were created in different size. The binary hierarchical rough structures were formed on the mesh wires. The average pore size was decrease after mesh modification but the pores were still clear indicating the POSS hybrid acrylic polymer does not block the pores (Guo et al., 2018).

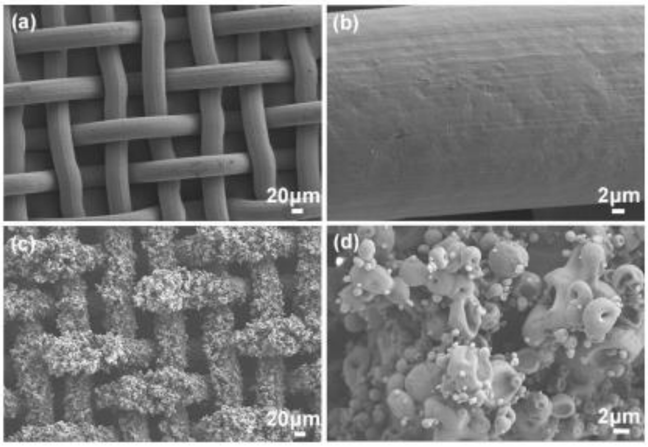


Figure 2.1 SEM images for (a) and (b) original mesh while (c) and (d) after coating with POSS hybrid acrylic polymer on mesh (Guo et al., 2018).

In their study, they also demonstrated the effect of pore size of the mesh with water contact angle and water sliding angle. From Figure 2.2, it shown that as the pore size increase more than 54 μm, the water contact angle decreased significantly while water sliding angle make a small increment only. The reason for this is that the pore size is too wide to contain adequate air within the structure, resulting in a low hydrophobic force that cannot hold the water droplet. In conclusion, the smaller the pore size of the mesh, the higher the flow resistance of oil during oil–water separation (Guo et al., 2018).

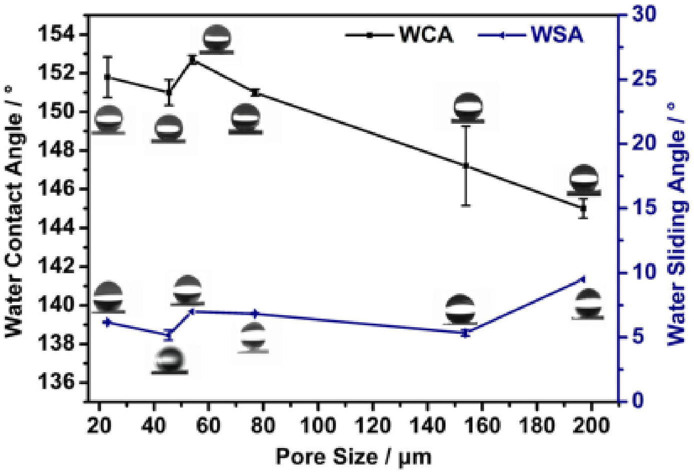


Figure 2.2 Effect of pore size of the mesh to water contact angle and water sliding angle (Guo et al., 2018).

2.2 Chemical Method of Mesh Modification

Table 2.2 presents the various chemical modification method on the copper mesh. In previous study, superhydrophobic Cu-MOF based copper mesh was prepared through chemical oxidation method to obtain $Cu(OH)_2$ nanoarrays on copper substrate followed by an in-situ growth of metal-organic framework (MOF) crystals to become Cu-MOF. Then, Cu-MOF was treated with methylpolysiloxane (PDMS) to obtain the superhydrophobic effect (Zhu et al., 2020). After 20 cycles, the water contact angle still above 150°, thus showing its superhydrophobic properties. The fabricated copper mesh was immersed in 1.03 mmol of 1,3,5-benzenetricarboxylic acid (H_3BTC) solution during its preparation process. The immersion time was varied from 10 to 120 minutes and the effect on water contact angle and water sliding angle were observed. The highest water contact angle was obtained at 60 minutes immersion time (155°) while water sliding angle was gradually decrease. This is due to the fact that the formation of Cu-MOF crystals requires a certain immersion period in order to produce a rich hierarchical structure, and the surface roughness of the material is strongly connected to its wettability.

Table 2.2 Summary of modification using chemical method.

Matrix	**Deposited Material**	**Method**	**Performance**	**Reference**
Copper mesh	Cu-MOF-PDMS	Chemical oxidation	WCA > 150° after 20 cycles	Zhu et al. (2020)
Copper mesh	$Cu(OH)_2$-TCMS	Chemical oxidation	> 99.85% WCA: 159° > 99.6% after 80 cycles WCA: 151° after 80 cycles	Zhao et al. (2021)
Stainless steel mesh	CrO_3 / H_2SO_4 / H_3PO_4 / $ZnSO_4$ / $NaNO_3$-FAS	Chemical oxidation	> 97.20% 95.00% after 70 cycles WCA > 156°	Fang et al. (2021)
Copper mesh	$AgNO_3$-stearic acid	Replacement method	> 98% WCA: 158° WSA < 5°	Xu et al. (2019)
Copper mesh	CuO-DDT	Thermal oxidation	> 95.00% WCA: 162° WSA: 6°	Yanlong et al. (2016)

Copper mesh and stainless steel mesh	$Cu(OH)_2$	In-situ displacement along with chemical oxidation	> 99.80%	Yuan et al. (2020)
Copper mesh	Cu_xS-stearic acid	Hydrothermal reaction	~100.00% after 100 cycles WCA: 160°, 158° after 100 cycles	Khosravi, Azizian, and Boukherroub (2019)
Copper mesh	$Cu_2S@Cu_2O$-PDMS	Chemical deposition	> 94.00%	Pi et al. (2017)
Copper mesh	CuCl-1-dodecanethiol	Chemical deposition	> 95.00%	Chen et al. (2018)
Copper tabs	CuO-cinnamic acid CuO-myristic acid	Chemical deposition	Cinnamic acid WCA: 154.2 ± 2° Myristic acid WCA: 164 ± 2°	Razavi et al. (2017)
Copper mesh	Cu-PDA-1-dodecanethiol	Electrodeposition	> 90.00% WCA: 152.4°	Cao et al. (2017)
Copper mesh	$Cu(OH)_2$-stearic acid	Chemical etching	> 97.00% for low concentration of polymer	Kang et al. (2020)

Copper mesh	Cu_2O	Chemical reaction	> 95.00%	Lei et al. (2019)

In addition, similar method also being studied by Zhao et al. in 2021. They manage to prepare a superhydrophobic copper mesh with robust superhyrophobicity via chemical oxidation method. Trichloromethylsilane (TCMS) was used as low surface energy material for further modification. The method introduced by this study has the advantages of higher performance in separating heavy and light oils and it can be observed with good repeatability (Zhao et al., 2021). The obtained separation efficiency after 80 separation cycles was more than 99.65% with 151° water contact angle. It was proven that the modified mesh could not function at the extended amount of time in a strong acidic or alkaline environment. Water contact angle and separation efficiency were the highest at neutral pH solution as depicted in Figure 2.3.

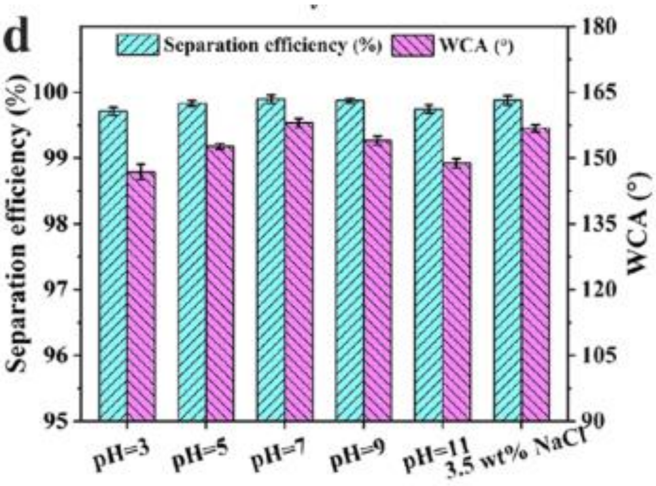


Figure 2.3 The effect of pH of the solution to separation efficiency and water contact angle (Zhao et al., 2021).

Apart from that, Fang et al. (2021) reported that a superhydrophobic mesh made with stainless-steel mesh was also prepared via chemical oxidation followed by fluoroalkylsilane (FAS) treatment. The meshes were prepared by subsequently immersed in aqueous mixture of chromium trioxide (CrO_3), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), zinc sulfate heptahydrate ($ZnSO_4.7H_2O$) and sodium nitrate ($NaNO_3$). After that, the as-prepared meshes were immediately heated in an oven set to 90°C for several reaction time before undergone FAS treatment. After 6 minutes oxidation reaction followed by 40 minutes FAS treatment, the mesh exhibited highest water contact angle with 162° and sliding angle of 6.2° representing superhydrophobicity. This modified mesh showed its stability under harsh conditions when exposed to higher temperature. The separation of oil and water mixture was driven by gravity and this mesh have shown a good resistance to high temperature of water and corrosive solutions. The water contact angle was still above 156° upon treated to these solutions. Other than that, the mesh showed an excellent separation efficiency with more than 95.00% after 70 separation cycles that confirmed its durable properties (Fang et al., 2021). However, the treatment with fluorine-containing polymer is usually complicated and the cost will be higher (Yuan et al., 2020).

Next, Xu et al. (2019) reported a method to produce superhydrophobic properties using replacement reaction. The copper mesh was immersed in the silver nitrate ($AgNO_3$) aqueous solution followed by stearic acid treatment (Xu et al., 2019). They varied the immersion time up to 6 minutes. Ideally, the optimum reaction time was 2 minutes whereby the highest water contact angle was obtained. As the reaction time increased to 6 minutes, the creation of micro-nano structures will increase, which impacted the pore size of the copper mesh and impeded superhydrophobicity. This efficient method obtained the separation efficiency of above 98.00% and water contact angle above 150° for different concentration of $AgNO_3$. The water contact angle observed was 158° with water sliding angle less than 5° showing its superhydrophobicity (Xu et al., 2019).

Besides, another study proposed a thermal oxidation method to prepare a superhydrophobic copper mesh. The surface was endowed with dodecanethiol (DDT) to make it superhydrophobic (Yanlong et al., 2016). They dried the copper mesh and treated it at high temperature (400°C) for 30 minutes in the oven and cooled at room temperature before modified with DDT solution. The method is relatively simple, low cost and time-saving. Thermal oxidation was employed to manufacture copper(II) oxide (CuO) protrusions on a copper mesh due to its technical simplicity and large-scale growth capacity. Lastly, it can be observed that the separation efficiency obtained was above 95.00% with water contact angle and water slide angle of 162° and 6°, respectively.

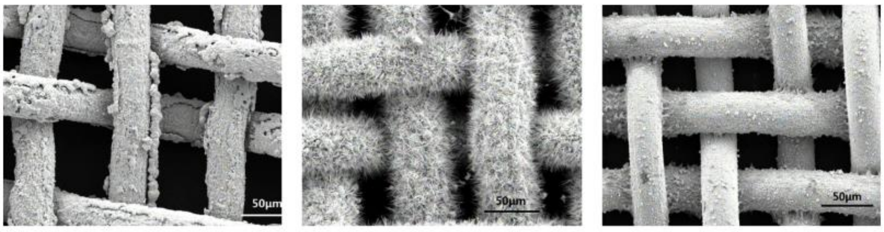
Moreover, another study reported an in-situ displacement along with chemical oxidation method on copper mesh and stainless-steel mesh to study its superhydrophobicity (Yuan et al., 2020). Three different meshes were prepared namely $Cu(OH)_2$ on copper substrate ($Cu(OH)_2$-CS) mesh, $Cu(OH)_2$ on stainless steel substrate ($Cu(OH)_2$-SSS) mesh, and copper on stainless steel substrate (Cu-SSS) mesh to study their permeation pressure, liquid flux and separation efficiency. Cu-SSS was prepared by immersing in a mixed solution containing copper(II) chloride ($CuCl_2$) and HCl while $Cu(OH)_2$-SSS was fabricated by reacting Cu-SSS with potassium persulfate ($K_2S_2O_8$) and sodium hydroxide (NaOH). $Cu(OH)_2$-CS was prepared by immersing the pristine copper mesh in a mixed solution of $K_2S_2O_8$ and NaOH. Equation (2.2) indicates a reaction between stainless steel mesh and $CuCl_2$ under acidic condition while equation

(2.3) represents the formation of $Cu(OH)_2$ on stainless steel substrate and copper substrate.

$$Fe + CuCl_2 \rightarrow FeCl_2 + Cu \tag{2.2}$$

$$Cu + K_2S_2O_8 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4 + K_2SO_4 \tag{2.3}$$

Uniquely, the method of in-situ displacement followed by chemical oxidation did not require any fluorination treatment thus make it a cost-effective method. In addition, from this method, they able to separate a multicomponent mixture of oil and water that usually happened in real case. The separation efficiency obtained was over 99.80% for three meshes. Nevertheless, $Cu(OH)_2$-CS separation efficiency was slightly higher than $Cu(OH)_2$-SSS. However, both meshes had significant separation efficiency compared when only copper on stainless steel substrate (Cu-SSS). The separation efficiency decreased as the number of reused increased. After 10 cycles, the separation efficiency was still above 99.00%. For $Cu(OH)_2$-SSS, the separation efficiency continuously dropped after 10 cycles due to the phenomenon of looseness and partial peeling while having micro-nano structures. In contrast, $Cu(OH)_2$-CS having only nanostructures was more robust and firm compared with other two meshes. The rough structure on the substrate will decrease when reused many times. Figure 2.4 shows the SEM images for the three different kinds of meshed prepared.



(a) Cu-SSS mesh (b) $Cu(OH)_2$-SSS (c) $Cu(OH)_2$-CS

Figure 2.4 The SEM images of a) Cu-SSS b) $Cu(OH)_2$, and c) $Cu(OH)_2$-CS mesh after 10 times reused (Yuan et al., 2020).

Study from Khosravi, Azizian, and Boukherroub (2019) showed an excellent separation efficiency of modifies copper mesh. They fabricate the Cu_xS/Cu (where x=1 and x=2) mesh via hydrothermal reaction, then dipped them into 0.1 M of stearic acid to get the superhydrophobic surface. They were capable of getting almost 100.00% oil-water separation efficiency from this method even after 100 separation cycles. The water contact angle at initial phase was 160° and after 100 cycles, it only decreased to 158°. Data implies that the superhydrophobicity of manufactured Cu_xS/Cu mesh is stable, and although the sample may be used numerous times for separation of oil from water mixtures, the performance was not affected. Nevertheless, by utilizing the hydrothermal method, special equipment such as an autoclave is needed. The equipment run at high temperature and pressure for a long time could add on another cost of operation apart from the cost of equipment itself.

In addition, similar study also being made by preparing a superhydrophobic $Cu_2S@Cu_2O$ followed by treatment with an inexpensive polydimethylsiloxane (PDMS) (Pi et al., 2017). The method that being utilized is chemical deposition method which was relatively simple and cost-effective. Furthermore, this superhydrophobic copper mesh also posed an outstanding stability with up to 6 months storage. However, the water contact angle decreases from time to time. The separation efficiency was more than 94% which was lower than the previous study by Khosravi, Azizian, and Boukherroub (2019).

Besides, another chemical deposition method was presented by Chen et al. (2018). They immersed a clean copper mesh in an acidic solution of copper(II) chloride ($CuCl_2$) to get the copper chloride (CuCl) crystal on the copper mesh surface namely CuCl-copper mesh. Then, the as-prepared mesh was treated with 1-dodecanethiol, a low surface energy material. The separation efficiency of oil and water mixture was found to be above 95.00%. It was found that at higher concentration of $CuCl_2$, the size of the CuCl crystal will be larger. The water contact angle will be increase then decrease. To sum up, larger crystal size deposited on the copper mesh is beneficial to obtain better hydrophobicity. However, too much deposit will reduce the water contact angle.

Apart from that, another similar study reported by Razavi et al. (2017) to obtain superhydrophobic effect via chemical deposition method. Because of its simplicity, cost-effectiveness, speed of deposition, and most crucially, the ability to coat any shaped substrates, liquid phase deposition was chosen as an optimal approach to coat the samples (Razavi et al., 2017). In thier study, they prepared different types of rough surface on two oxygen-free copper tabs from naturally derived hydrophobic materials. Cinnamic and myristic acid were chemical substances that were used to lower down the surface energy were obtained from two plant species. After CuO oxide structures were formed, the samples were immersed in the ethanol solution of cinnamic acid or myristic acid at different concentration to study their effects. It was found that the liquid deposition with myristic acid showed higher water contact angle (164 ± 2°) compared to cinnamic acid (154.2 ± 2°) at their optimum concentration. The optimum concentration was analysed when the resulting water contact angle was higher. Cinnamic acid was more sensitive to solution pH, displaying fast deterioration due to the elimination of the functional coating as well as the CuO nanostructures (Razavi et al., 2017).

Other than that, Cao et al. (2017) studied the electrodeposition method to obtain rough structure on bare copper mesh. The system used in this method was two-electrode system where platinum sheet served as anode. Copper chloride and anhydrous sodium sulphate were used as electrolyte. After obtaining the rough surface, the as-prepared copper mesh was immersed in dopamine polymerized (PDA), then followed by treatment with 1-dodecanethiol. After these two modifications, the superhydrophobic copper mesh was obtained with water contact angle of 152.4°. The separation efficiency is roughly more than 90.00% for all samples presented (Cao et al., 2017).

Chemical etching is chemical method available to fabricate superhydrophobic surface by corroding the surface of materials with a strong acid or alkali solution, resulting in a micro-nano rough texture on the surface (Zhu et al., 2021). The study conducted by Kang et al. (2020) utilized chemical etching to prepared $Cu(OH)_2$ film that have superhydrophobic properties upon treated with stearic acid (Kang et al., 2020). The etchant solution was produced by mixing different proportions of ammonium persulfate ($(NH_4)_2S_2O_8$) and sodium hydroxide (NaOH) in deionized water (DI). Then, subsequent steps which were drying and immersing in the etchant solution were done to obtain rough surface of $Cu(OH)_2$ film. After rewashed with deionized water, the sample was treated with stearic acid. The fabrication steps were demonstrated in Figure 2.5 below. The separation efficiency was observed based on crude oil and water separation under varying partially hydrolyzed polyacrylamide (HPAM) polymer concentration. When a polymer is introduced to crude oil and aqueous solution mixtures, the resulting emulsions are difficult to separate due to the increased solution viscosity. For 0 to 150 ppm concentration, the separation efficiency was above 97.00%. Increasing concentration to 300 and 1000 ppm, the separation efficiency was reduced to 90% (Kang et al., 2020).

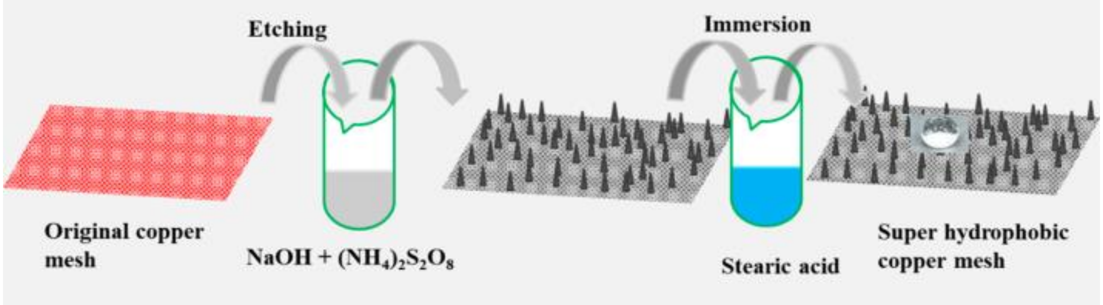


Figure 2.5 Fabrication of modified copper mesh by adopting chemical etching method followed by treatment with stearic acid (Kang et al., 2020).

Next, Lei et al. (2019) presented a superhydrophobic Cu_2O mesh fabrication method without the use of solvent by implementing the straightforward chemical reaction. In this work, a copper mesh reacted with hydrogen peroxide without any further treatment with low surface energy material. This situation happened due to Cu_2O substance already can served as low surface energy and rough structure after immersing in hydrogen peroxide solution (Lei et al., 2019). They observed the surface morphology and the effect of reaction time on water contact angle. The SEM images for original mesh and superhydrophobic Cu_2O mesh can be seen in Figure 2.6. The original mesh depicted a flat and very smooth surface while modified mesh contained a flower-tufted nanosheets structures that were dense and uniform in size. The modified mesh with 30 minutes reaction in hydrogen peroxide obtained highest water contact angle with 165.4° and sliding angle of 5.6°. Finally, they were also able to get more than 95% of separation efficiency for several oil-water mixture (Lei et al., 2019).

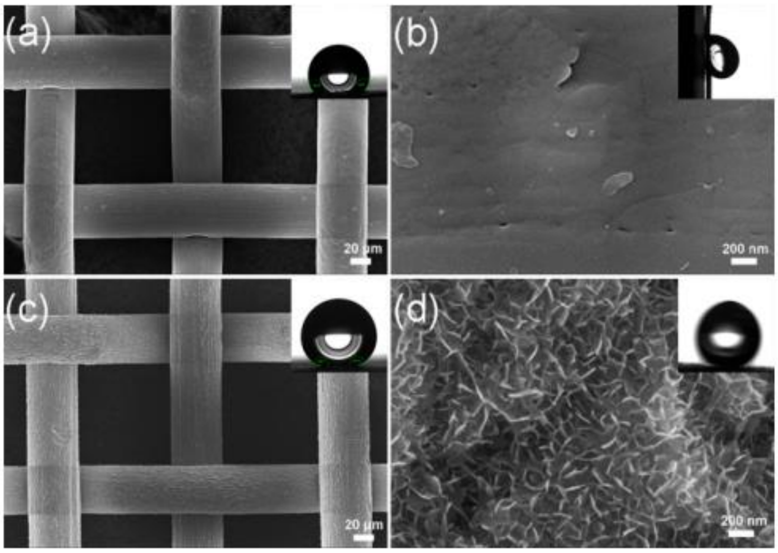


Figure 2.6 SEM images for (a) and (b) before coating and (c) and (d) after coating with superhydrophobic Cu_2O. The insets show its respective water contact angle and sliding angle images (Lei et al., 2019).

2.3 Polymer Coating

Table 2.3 shows the superhydrophobic mesh prepared via polymer coating. The superhydrophobic polymer material (SPM) was fabricated by spraying a reactive mixture onto a pre-activated substrate followed by "photopolymerization + hydrolytic polycondensation" of acrylate-terminated polyurethane (A-PU), vinyltriethoxysilane (VTES) as a bridge, and precipitated silica particle (PSP). The SPM had substantial mechanical strength and good superhydrophobicity due to the ideal combination of polymer skeleton and rough structure. It exhibited water contact angle more than 152° and sliding angle below 5°. The SPM's hierarchical rough structure demonstrated regeneration capability following abrasive treatments with more than 250 cycles, allowing the SPM to endure a wide range of mechanical damages. The damage SPM was proven appealing restorable behaviour by a simple sanding procedure of more than

40 cycles without the need of healing chemicals due to the roughness-regenerative qualities of hierarchical structure (Liu, Luo and Jia, 2020).

Table 2.3 Summary of modification using polymeric membrane.

Matrix	**Polymer Coated**	**Method**	**Performance**	**Reference**
Polymer membrane	A-PU, VTES and PSP	Spray coating	WCA: 152° WSA < 5°	Liu, Luo and Jia (2020)
Stainless steel mesh	DDVAC-N and DDVAC-O polymer	In-situ thermal polymerization	WCA: 158°	Jiang et al. (2017)
Copper mesh	$3,5\text{-DCF}_3\text{Ph}$ polymer	In-situ polymerization	98.20%	Li et al. (2021)
Steel mesh and cotton	Fluorate polymer	Spray coating	WCA: 164° WSA: 2°	Li et al. (2017)
Multi-walled carbon nanotube film	Polyvinylbenzene decoration and POTS layer	Chemical vapour deposition	> 99.70% after 20 cycles	Ye et al. (2019)
Stainless steel mesh	Ethylene vinyl acetate and polyethylene	Hot embossing method	WCA: 154° for 500 mesh number	Sun et al. (2019)
Stainless steel mesh	Waterborne silicone-acrylic copolymer (SAC)	Spray coating	>99.00% and WCA: >150° after 50 cycles WCA: 157.7° WSA: 3°	Ye et al. (2017)

Next, the superhydrophobic coated polymer was also prepared by utilizing the novel approach of in-situ thermal polymerization (ISTP) (Jiang et al., 2017). The polymer was coated on stainless steel mesh which was N,N-dimethyl-dodecyl-(4-vinylbenzyl) ammonium chloride (DDVAC). The resulting mesh displayed superhydrophobicity with a water contact of 158° and superoleophilicity with an oil contact angle of 0°. Furthermore, the mesh demonstrated a self-cleaning function with a low sliding angle. It also shown outstanding properties of stability, durability and long-term storage. A recent study by Li et al. (2021) concluded that the separation efficiency to separate oil and water mixture was 98.20% by utilizing in-situ growth polymerization of hierarchical layered micro- and nanoparticles on mesh surface via diazonium chemistry at room temperature. Figure 2.7 shows the self-cleaning mechanism for as-prepared copper mesh. The interface force between contamination and water is stronger than the adhesion force of contamination to the superhydrophobic surface. Thus, contaminations may be swiftly absorbed and moved away from the superhydrophobic surface. The surface will become clear from any contaminants (Li et al., 2021).

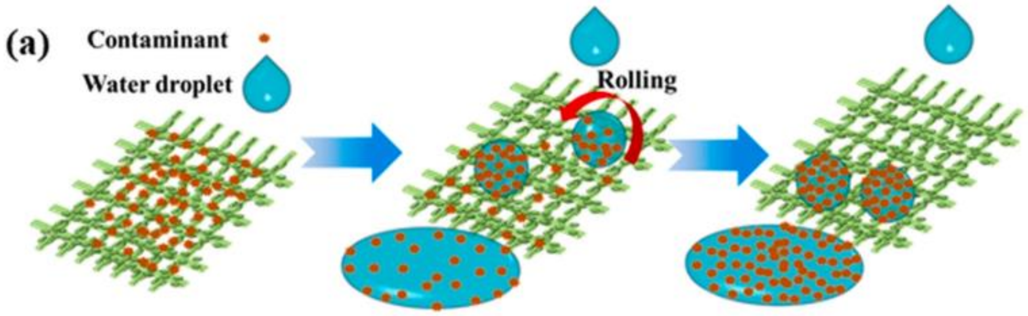


Figure 2.7 Self-cleaning mechanism of modified superhydrophobic copper mesh (Li et al., 2021).

Other than that, the superhydrophobic surface was also fabricated by spray coating the mesh with polymeric materials (Li et al., 2017). They prepared two types of treated surfaces which are treated steel mesh and treated cotton to separate immiscible oil-water mixtures and absorb oil from oil-water mixtures, respectively. The homogenous suspension containing the low surface energy fluorate polymer (1*H*,1*H*,2*H*,2*H*-Perfluorooctyltriethoxysilane) and aluminium oxide (Al_2O_3) nanoparticles was sprayed onto the substrates. Fluoric group that contained in fluorate polymer can served as low surface energy material. It was found that the modified steel mesh exhibited higher water contact angle (164°) and lower sliding angle (2°) from the treated surface. Using treated mesh and treated cotton, they effectively removed hexadecane from a hexadecane-water mixture. Because of its high porosity and compressibility, the stabilized water-in-oil emulsions can also be separated using treated cotton (Li et al., 2017).

In a study conducted by Ye et al. (2019), a solvothermal technique and chemical vapour deposition were used to create a polydivinylbenzene decoration and a POTS (1H,1H,2H,2H-perfluorooctyltriethoxysilane) layer. The film demonstrated exceptional superhydrophobicity and capability of demulsification with efficient water-in-oil emulsions separation. It also showed appealing reusability properties in separating chloroform in water-in-chloroform mixture with separation efficiency above 99.70% after 20 cycles of separation.

The hot embossing method offers the advantages of ease of handling, high efficiency, high fidelity, and relatively low cost. Polymeric superhydrophobic surfaces with biomimetic hierarchical roughness were created using a simple isothermal hot embossing approach that required no chemical treatments (Sun et al., 2019). The copolymer composite substrate (polyethylene/ethylene vinyl acetate, PE/EVA) was coated on different mesh numbers of stainless steel mesh. Specifically, in this technique, PE/EVA substrate (on the bottom) and stainless steel mesh (on top) were put together