Master of Science

A FACILE SUPERHYDROPHOBIC FABRICATION OF MELAMINE SPONGE FOR OIL ABSORPTION AND OIL/WATER SEPARATION

The Graduate School of the University of Ulsan

Department of Civil and Environmental Engineering

NGUYEN DINH MINH THAO

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Supervisor: Professor Byeong-Kyu Lee

A Master thesis

Submitted to
The Graduate School of the University of Ulsan
In partial Fulfillment of the Requirements
For the Degree of

Master of Environmental Engineering

By

Nguyen Dinh Minh Thao

Department of Civil and Environmental Engineering
University of Ulsan, Republic of Korea
February, 2020

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This certifies that the Master thesis of
NGUYEN DINH MINH THAO is approved

Committee Chairman: Prof. Hung-Suck Park

Committee Member: Prof. Jongho Kim

Committee Member: Prof. Byeong-Kyu Lee

Department of Civil and Environmental Engineering

University of Ulsan, Ulsan

Republic of Korea

December 2019

ABSTRACT

Superhydrophobic oil sorbent materials with highly oil absorption capacity, good durability and superior recyclability have attracted much interest in both academia and industry due to their potential for practical applications, such as self-cleaning, anti-wetting, anti-icing, anti-corrosion, etc. Superhydrophobic surfaces could help to minimizing the energy and water required for cleaning, reducing the utilization of pollution and waste caused by cleaning process and even can be applied for oil/water separation - one of the biggest issues in environmental field at this moment. One of the major challenges is the stability of materials when working on corrosive solutions. This dissertation investigates the fabrication, characterization of superhydrophobic open-cell sponge and its environmental applications.

There are numerous natural superhydrophobic materials, such as lotus leaf, rose petal, butterfly wings and water spider legs, in both animal and plant species. Inspired by nature, a novel superhydrophobic melamine sponge (MS) with copper oxide (CuO) coating was developed in a fast reaction via a facile and green method. The CuO layer used to roughen the surface of the substrate (MS) was prepared in a microwave to seed copper nucleuses in alkaline medium. Subsequently, the CuO-coated MS sponge was modified with stearic acid (SA) to increase the surface superhydrophobicity. The resulting modified sponge materials showed superior superhydrophobic properties: a static water contact angle (WCA) of 165.1° and dynamic WCAs (both sliding and shedding) much lower than 10°. In addition, the developed superhydrophobic non-fluorinated materials quickly absorbed various oils in water with high efficiency and selective separation capacity of oil droplets under environmental conditions of harsh resistance such as acidic, salty and alkaline. Moreover, the as-prepared sponges showed great stability and prominent recyclability with excellent sorption capacity retention even after 40 sorption-squeezing cycles under mechanical load tests without losing their superhydrophobicity. The high superhydrophobicity, facile,environmentally friendly fabrication process and low preparation cost of this novel oil sorbent sponge system supports its promising potential as a candidate material for oil spill clean-up, oily wastewater treatment and water remediation.

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LIST OF ABBREVIATIONS

WCA(s)	Water contact angle (s)
SEM	Scanning electron microscope
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
FT-IR	Fourier-transform infrared spectroscopy
AFM	Atomic force microscopy
TGA	Thermogramvimetric analysis
R_a	The average roughness
R_q	The root-mean-square roughness
R_{max}	The maximum height of the surface roughness
SA	Stearic acid
MS	Melamine sponge
MB	Methylene blue

CHAPTER 1 - INTRODUCTION

1.1. Research objectives and scope

With the increasing incidence oil spill accidents over water bodies, including oceans and rivers, and serious water pollution from industrial oil species, the resulting serious and worldwide environmental concerns have focused extensive research on successfully treating wastewater containing oily species [1]. The sinking of oil tankers or the oil leakage can cause serious environmental and ecological problem and threaten to human and fish life. For example, the Deepwater Horizon oil spill in 2010 in the Gulf of Mexico was known as the largest accidental oil spillage that affected greatly to the coastline areas and marine organisms [2]. Another example is the Prestige oil spill, which caused oil leaking from oil tanker MV Prestige sunk down Spain's north-western coast in 2002 [3]. The many present methods and technologies for cleaning up various oils and organic solvents, including the use of dispersant and solidifiers (chemical methods), skimmers and sorbents (mechanical recovery), and controlled burning or bioremediation method [4],[5],[6],[7],[8],[9], lead to other ecological and environmental problems, such as the formation of secondary pollutants, the need for further disposal in some cases, and various other limitations related to absorption capacity, fabrication method, etc. [10]. Numerous traditional separation methods such as flotation, centrifugation, ultrasonic separation, coagulation, gravity separation, and electrochemical and biological treatments are all widely applied for separating oil-water mixtures [11]. These methods may require complicated separation instruments and high disposal costs, and can also suffer from low separation efficiency, leading to several disadvantages in using most oil and water separation systems [12]. Therefore, it is essential to develop low-cost, facile and high-performance absorbent materials [13]. The commonly commercialized melamine sponge (MS) is a promising material due to its high elasticity, good thermal stability, ultra-low density, and low preparation cost [14]. In this work, we report a simple and eco-friendly fabrication method for the mass-

production of copper oxide (CuO)-coated MSs with superhydrophobicity. The synthesis process does not require long reaction time, high temperature or toxic reagents [15],[16]. Also, the abundant nanostructures of CuO, such as nanoflower-like [17], nanobelts [18], nanoplatelets [19], nanoneedles [20], nanowires [18], nanorods [21], nanotubes [22], and nanofluids [23], can be used to roughen the MS surface and thereby enhance the superhydrophobicity. After coating a CuO layer on the MS surface in a microwave oven, its superhydrophobicity is increased by modification with stearic acid (SA), due to its long-chain fatty acids. The superior chemical stability and robustness of the resulting sponge support its application for the separation of oil–water mixtures in complex environments, including acidic, basic, and saturated salt aqueous solutions. This study analyzed the superhydrophobicity of the developed and modified MSs (MS@CuO@SA) by measuring the static water contact angle (WCA) and advanced WCA (both shedding and sliding) under harsh environments such as acidic, neutral and basic conditions. The superhydrophobic properties of the modified MSs were measured at different pHs (acidic, neutral and basic environments) and the mechanical stability and durability were examined under mechanical loads and repeated use. Finally, the oil separation and absorption capacity of the MS sponges in various oil-water mixtures were investigated to check their feasibility as a prospective candidate for cleaning oil spills, chemical leaks and oil–water separation in practice.

1.2. Research Outline

This study focuses on :

- Using an effective and economic modification method for synthesizing superhydrophobic melamine sponge. A facile and green microwave method with lower energy consumption and shoterned reaction time was used as a treatment technique to fabricate copper nucleus on melamine sponge's skeleton.
- Synthesizing copper oxide nanostructure and stearic acid coating layer on MS's skeleton.
- Characterizing the superhydrophobic melamine sponge.
- Investigating the oil absoirption ability and oil/water separation under harsh environments.
- Checking the mechanical stability and reusability of the superhydrophobic MS.

CHAPTER 2 – BACKGROUND ON SUPERHYDROPHOBIC SURFACE

2.1. Wettability of a solid surface

The contact angle (θ) is defined as the quantitative measure of the wetting of a liquid-solid interface. Contact angle meter is used to determine of wetting characteristics of solid materials. Traditionally the static contact angle has been use to quantify the wettability, adhesiveness, and solid surface free energy. Sliding angle, or roll-off angle, is defined as the minimum tilting angle before the droplet starts to slide off, this dynamic angle can also be used to characterize the wettability of a solid surface.

For a hydrophilic solid surface, water droplets will spread out and wet the surface resulting in a CA less than 90°; however, for hydrophobic surfaces a contact angle greater than 90° will be created which is characteristic of anti-wetting surfaces. In general, there are four different types of wetting on solid surfaces which are shown schematically in fig.2.1 with their contact angles indicated by θ. CA can range from 180° to 0° depending on the magnitude of the solid/vapor and solid/liquid interfaces. The solid surfaces are mainly classified as hydrophobic (150° > CA ≥ 90°) or hydrophilic (CA < 90°). . If the water contact angle is above 150°, the surface is considered superhydrophobic. If the liquid drops are easily spread out over the entire surface forming a thin liquid layer on top of the solid and the contact angle of 0° is characteristic of this type of wetting condition – superhydrophilic.

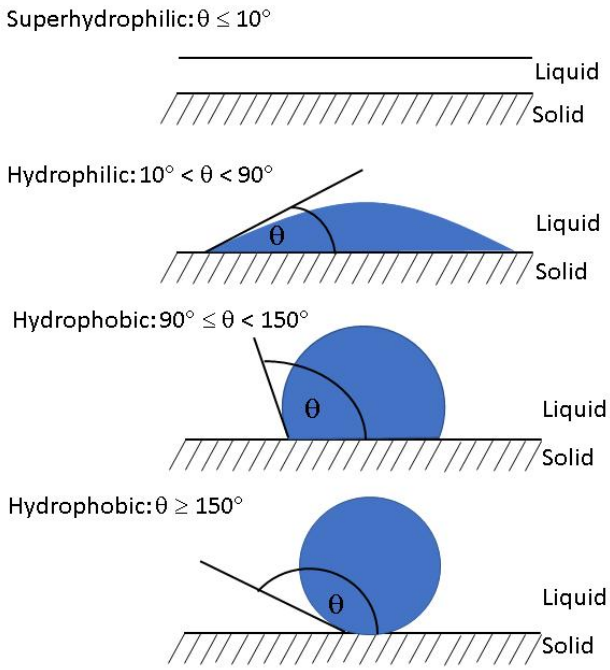

Figure 2.1. Different types of wetting on solid surface

Wetting on flat surfaces: The theoretical liquid contact angle on the flat surface (θ) can be correlated to three interfacial free energies: the solid–gas interfacial energy (γ_{SG}), the solid–liquid interfacial energy (γ_{SL}) and the liquid–gas interfacial energy (γ_{LG}) (Fig.2.2). The equilibrium θ is determined by Young's equation (1.1) which is developed by Thomas Young in 1805:

$$\gamma_{LG} \cos\theta = \gamma_{SG} - \gamma_{SL} \qquad (1.1)$$

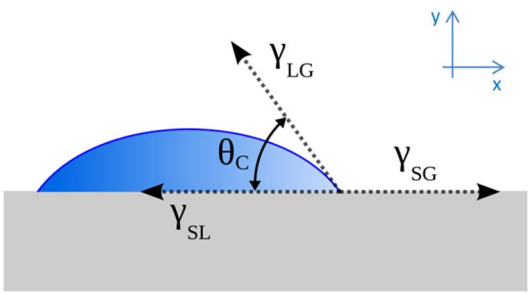

Fig.2.2. Schematic of a liquid drop showing the quantities in the Young equation

When the surface become rough, the Young's equation does not work well. When θ_{flat} is smaller than 90°, the solid surface is considered as hydrophilic; when θ_{flat} is greater than 90°, the solid surface is considered as hydrophobic.

Wetting on flat surfaces: The effect of surface roughness on wettability was first discussed by Wenzel in 1936, and then by Cassie and Baxter in 1944[24].

Wenzel suggested that surface roughness plays an important role in increasing the contact angles by increasing the surface area, which is in turn affects both the surface wettability and the anti-wettability depending on the nature of the surface. He corrected the contact angle equation of Young by adding a roughness factor. Wenzel wettability theory is expressed by equation (1.2):

$$\cos \theta^* = r \cos \theta \qquad (1.2)$$

where θ^* is the apparent contact angle, r is surface roughness factor that is denoted by the ratio of total surface area to the projected area, and θ is the equilibrium contact angle on smooth surface measured by Young's equation (1.1). According to Wenzel's assumption, the liquid entirely fills the protrusions of the rough surface when they become in contact (Fig.2.3 (a)).

According to Cassie-Baxter theory, it assumes that air pockets could be trapped by a water droplet which enables the droplet to roll off at relatively small angles due to reduction in solid-area fraction and correspondingly wetting area (Fig.2.3 (b)). The apparent contact angle proposed by Cassie-Baxter is given by equation (1.3):

$$\cos \theta_{CB} = f \cos\theta + (f - 1) \qquad (1.3)$$

where θ_{CB} is the Cassie-Baxter contact angle, f is the solid-area fraction, and θ is the contact angle on a smooth surface of the same material.

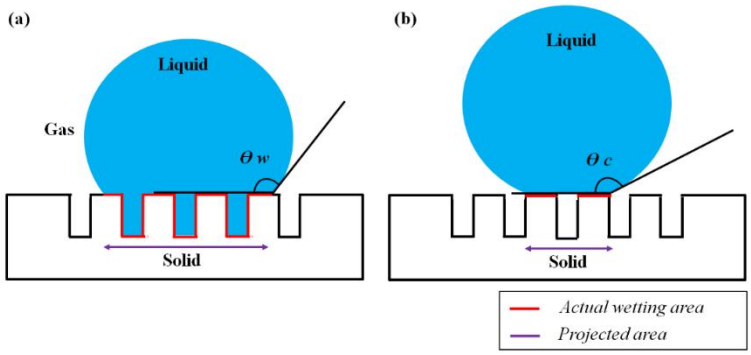

Fig.2.3. Wetting behavior of a droplet on solid substrates: (a) Wenzel state, (b) Cassie-Baxter state [25]

The difference between two models was the appearance of air gap between the liquid and the solid. Depending on the height and width of micro structure, the distance between the micro structures, the surface energy, and the shape of micro structure, the surface is followed Wenzel model or Cassie-Baxter model. Generally, superhydrophobicity is defined as following: a water droplet has a static contact angle above 150° with the surface and a roll-off angle less than 10°.

2.2. Superhydrophobic surface in nature

The most famous and well-known super water repellent surface in nature is the lotus leaf. When dropping water droplets onto the leaf surface, these droplets are immediately rolled off from the leaf then carried away all dirt and dust particles and let the surface clean. Also learning from nature such as: butterfly wings, rose petals, and the others (Figure 2.4-[26]) ; many newly discovered superhydrophobic surfaces/materials with smart surfaces and functional properties are gradually developed.

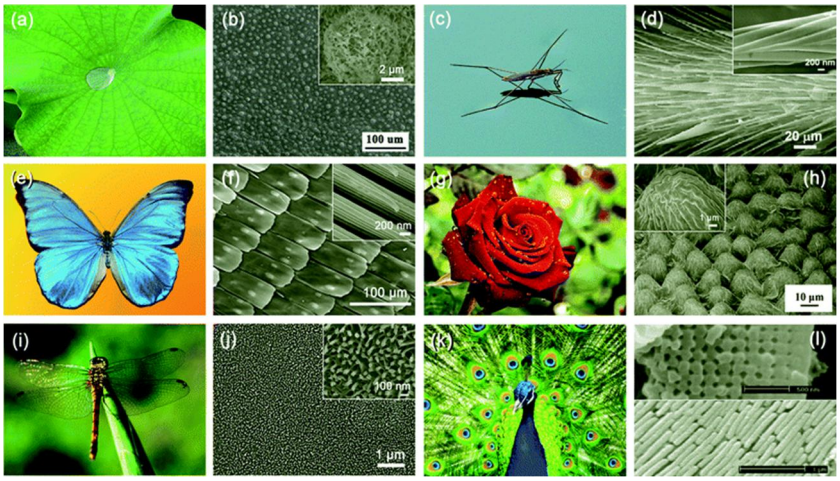

Figure 2.4. Some examples of superhydrophobic surface on nature

2.3. Applications of superhydrophobic surfaces

There are numerous of applications or superhydrophobic materials in science and engineering especially in daily life, argriculture and industry such as: anti-wetting, self-cleaning, oil/water separation, anti-icing, water resistance and so on. As shown in Figure 2.5:

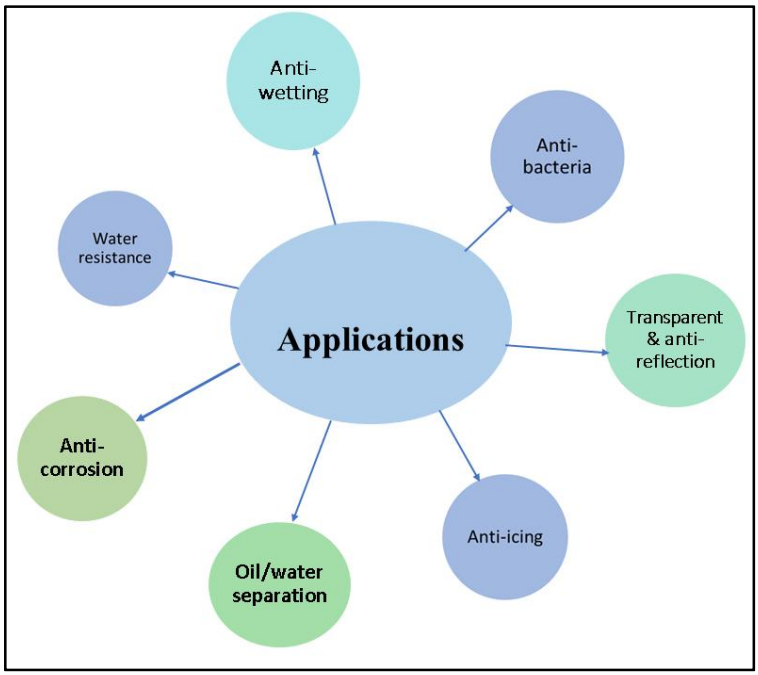

Figure 2.5. Applications of superhydrophobic material

Actually, there are not much commercially available products that applied this wetting property, most of products almost focused on anti-wetting, self-cleaning, or stain-free. A company named NeverWet has developed a family of superhydrophobic coatings which use both consumer and industry. This product completely repels water abd rolls off without touching the underlying surface by spayring it over clothes or any textiles/surfaces.

Or the Japanese largest toy manufacturer-Bandai^{TM} have created a maze-type game (named Aqua Drop – Fig 2.6) which used waterdrop instead of metal ball bearings. They use polyethylene as the base material in this game.

Figure 2.6. Four different versions of Aqua Drop maze game: coursety of Bandai [27]

2.4. Synthesis of superhydrophobic surfaces

A wide variety of physical and chemical methods have been explored to fabricate superhydrophobic surfaces through one of the following two approaches: (i) creating a rough surface on a hydrophobic material or (ii) modifying a rough surface with a hydrophobic coating. To fabricate superhydrophobic surfaces using a template-based approach there are two main requirements: 1) the surface must be sufficiently rough to allow for the formation of trapped air pockets underneath water droplets and 2) the surface should be a low surface energy material that is inherently hydrophobic.

2.4.1. Roughening a hydrophobic material

There are many ways to make rough surfaces, including laser/mechanical treatment [28], chemical etching [29, 30], lithography, sol–gel and hydrothermal processing [31, 32], layer-by-layer and colloidal assembling [33], electrical/chemical deposition [34], electrospinning [35, 36] etc. For example, Jin et al. reported a laser etching method to make superhydrophobic polydimethylsiloxane (PDMS) surface, which contains micro-, submicro- and nano-composite structures [37]. Yan *et al.* fabricated superhydrophobic poly(alkylpyrrole) films by a electrochemical synthesis method. The film surface consists of thousands of ―needle-like microstructures in a perpendicular alignment [38].

As described by Cassie and Baxter, multi-level roughness enables trapping of air under the water droplet, enhancing the surface hydrophobicity. Microstructured pillar arrays fabricated by photolithography and soft lithography are often used to provide a predefined roughness. The major issues facing wide application of these techniques include high fabrication cost, limited applications to large scale coating, and reduced flexibility in modulation of surface morphologies.

2.4.2. Modifying a rough surface with a hydrophobic coating

Generally, the wettability behavior of rough surfaces is governed by the interface chemistry. There are also several methods commonly used to modify surface chemistry. Although it is a relatively facile and one-step process to make superhydrophobic surfaces by using intrinsically hydrophobic materials, unfortunately, many materials do not possess a low enough surface free energy to be intrinsically hydrophobic. In order to make superhydrophobic surfaces on these intrinsically hydrophilic materials, a two-step fabrication process is usually required, i.e., making a rough surface first and then modifying it with chemicals, such as alkanethiols, organic silanes, and fatty acids, which can offer a low surface free energy after linked to the surface.

CHAPTER 3 – MATERIALS AND METHODS

3.1. Materials

Commercial MSs, a product of Germany (Product No. 1003064), were purchased from a local store in Ulsan, Korea. Copper (II) nitrate trihydrate ($Cu(NO_3)_2$) was obtained from OCL Company Ltd, Korea. Ammonium hydroxide solution (NH_4OH), copper (II) chloride ($CuCl_2$), SA, hexamethylenetetramine (HMTA, $C_6H_{12}N_4$), and ethyl alcohol 94.5 % were all supplied by Dae-Jung Chemicals and Metals Co., Ltd, Korea. The characteristic information of the oils and organic solvents used for testing the oil separation is summarized in table 1. All chemicals used for this experiment were of standard commercial grades and used as received without any further purification. Distilled water was used for all experiments.

Table 1. The organic solvents and oils used in the separation tests

Name	**Manufacturer**	**Specification**	**Density (kg/L, 15°C)**	**Viscosity (mm^2/s, 40°C)**
Gasoline	SK Energy, South Korea	Commercial product	0.77	0.673
Diesel engine oil	GS Oil, South Korea	KIXX HD1 C1-4/SL 15W-40	0.87	103.9
Hexane	Samchun Chemical , South Korea	Pure 99.99%	0.66	13.1
Vacuum pumping oil	Moresco, Japan	NEOVAC MR-200	0.89	71

Toluene	Daejung Chemicals and Metals Co Ltd, South Korea	Above 99.5%	0.8667	0.59
Soybean oil	Ottogi Ltd, South Korea	Soybean oil extract	0.73	56.3

3.2. Fabrication of superhydrophobic melamine sponge

Pristine MS pretreatment: The untreated MS was cut into 4 x 4 x 4 cm^3 cubes and cleaned several times with distilled water and ethylene alcohol 94.5% to remove impurities on the MS surface. After cleaning, the cubic sponges were dried in an air oven at 45 ℃ for 12 h, which did not modify the properties or structure of the MS.

Fabrication of a CuO layer on the MS surface: The Cu layers were fabricated on the MS surface via an immersion-microwave method. A seeding solution of Cu^{2+} was made by dropping slowly NH_4OH 25 % into 100mL $Cu(NO_3)_2$ 0.2M with slight stirring until the solution color became dark-blue and the pH reached 11. Then, the MS blocks were immersed into the prepared solution of $Cu(NO_3)_2$ and NH_4OH for 2 h, taken out and dried in the air oven for 12 h at 45℃. The samples were soaked in a mixture of 0.025M $CuCl_2$ and 0.025M HMTA at 1:1 molar ratio that had been stirred constantly for 2 h, and the pH was adjusted to 11 by dropping slowly NH_4OH. The beaker containing the mixed solution and MS blocks was placed in a Korean commercial microwave (Daewoo KR-G20EW, 2450 MHz ,1120W) and heated for 8 cycles (each consisting of 40 s of heating-on followed by 40 s of heating-off). After the heated beaker was removed and allowed to cool at room temperature for 20 min, the CuO-coated MS blocks (MS@CuO) were taken out and cleaned with ethanol/distilled water and dried in the oven at 45 ℃ for 12 h.

Superhydrophobization of MS@CuO: the MS@CuO sponges were immersed for 3 h in 100mL of SA 10mM dissolved in ethanol, removed from the solution and dried in the oven at 45 ℃ for 12 h. After the MS surface was coated with SA, a rough COu layer was grafted onto the outer surface as the final coating layer to attain the chemical bonding for promoting the

superhydrophobicity. Figure 3.1 shows the overall fabrication process for MS@CuO@SA.

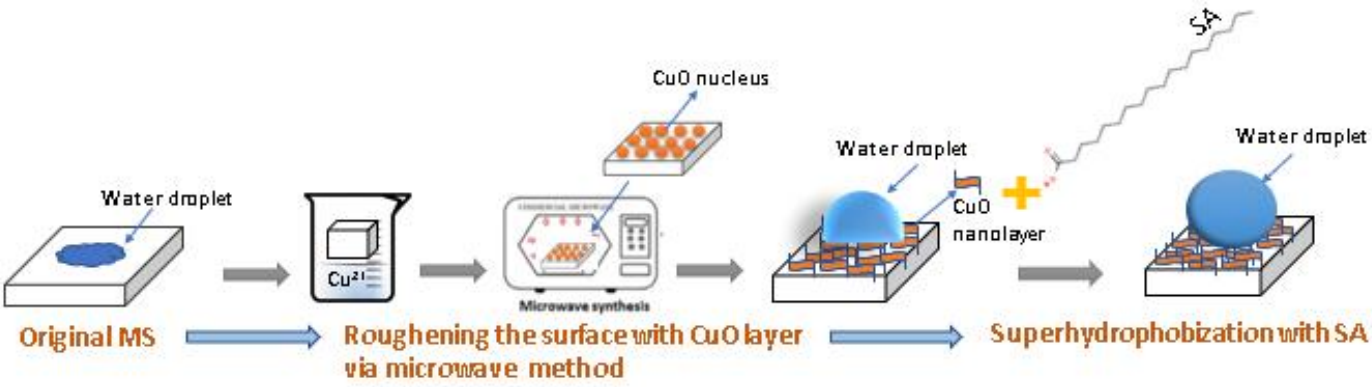

Figure 3.1. The synthesis process of MS@CuO@SA

3.3. Characterization methods

The morphology and structure of the fabricated sponges were examined by scanning electron microscopy (SEM) at a voltage of 15 kV with FE-SEM JEOL 6500 instrument. The elemental distribution was analyzed by energy dispersive spectroscopy (EDS). The composition and structural investigations were performed by using a Bruker AXS X-ray diffractometer. The X-ray diffraction (XRD) data were collected with monochromatic Cu-Kα (λ=0.154060 nm) radiation in the 2θ angular range = 30° - 80°. The element chemical states of the sponge samples were investigated by using an X-ray photoelectron spectrometer (XPS) on K-α Thermal Fisher Scientific spectrometer (model ESCALAB 250 XI) and Varian 670/620 Fourier-transform infrared spectroscopy (FT-IR). The surface roughness was evaluated by atomic force microscopy (AFM, multi-mode, Korea). The WCA was examined by using a contact angle meter SmartDrop instrument (Femtofab Co, Ltd, Korea). The static WCA and sliding WCA measurements were conducted at least 5 times in several areas with a droplet volume of 10μL with the average value being reported.

3.4. Oil absorption and oil/water separation test

To prove the oil absorption performance of the as-prepared sponges, six different types of oil and organic solvent dyed with oil red O dye (including

Toluene, Hexane, Soybean oil, Gasoline, Diesel and Vacuum oil) were used as sorbates. Three experiments were conducted with MS@CuO@SA sponges: i) the absorption of organic solvents/oils, ii) the separation capacity of different oils in water, and iii) under harsh environments.

The main purpose of the first experiment was to determine the maximum oil absorption capacity. The stainless-steel mesh was used for holding the sponge, which was fixed on a small tube [39]. One cube of MS@CuO@SA was placed on the mesh. To measure the maximum oil absorption capacity, oil droplets were dropped onto the sponge slowly until it became saturated due to oil absorption. The oil-saturated sorption state of the fabricated sponge was determined when this sponge was completely covered with oil and no more oil droplets dropped to the Petri disk underneath. The maximum oil absorption capacity (k) was calculated by the weight gain ratio according to equation (1)

$$k=\frac{M_a-M_b}{M_b} \qquad (1.4)$$

where M_a: the weight of the oil-saturated sponge (g)

M_b: the initial weight of the modified sponge (g).

The second experiment was about the determination of the oil-water separation efficiency and the third experiment was the oil absorption ability under harsh environments. Like the first experiment set-up, the sponge was placed in a tube which had stainless-steel mesh to keep the sponge sample, then the oil-water mixture (ratio 1:1, v/v) was poured into the tube containing the sponge. As the sponge quickly absorbed the oil, the oil penetrated through the sponge and dropped to a Petri dish underneath. The volume of water before and after the separation was measured as V_b and V_a, and the separation efficiency (k) was calculated by the following equation (1.5)

$$k=\frac{V_a}{V_b}\times 100\% \qquad (1.5)$$

In the oil absorption ability test under harsh environments, 80 mL of distilled water was placed in a beaker, and several hexane droplets were dropped by using a pipette. Figure 3.2 shows the oil drops floating on the surface of the water. A cube of the treated sponge (2x2x2 cm^3) was placed in the beaker and tweezers

were used to keep the sponges at the location of the oil droplets. After the oil absorbed sponge was removed, the purity of the remaining solution was checked by UV-Vis spectroscopy. The experiment was repeated using different types of oils/organic solvents with the same experimental procedure.

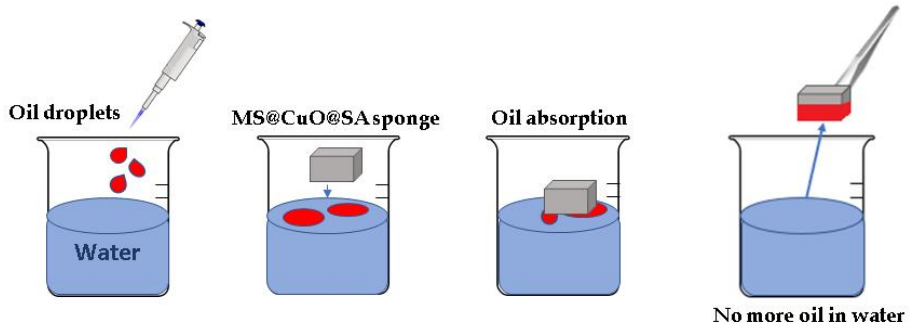

Figure 3.2. Experiment set up for oil/water separation ability test.

3.5. Stability and reusability tests of superhydrophobic melamine sponge

The durability and the reusability of the materials play an important factor in practical applications. Hence, mechanical stability tests were conducted with the treated MSs using a compression machine (Daekyung DTU-900MH300kN). Owing to the porosity and sponginess of the MS, the compression test was carried out to check and compare the stability between the original MS and the coated MS.

The recyclability of the MS@CuO@SA sponge was checked by a simple sorption-squeezing method. After absorbing the oil at a saturated point, the contaminated sponges were squeezed and then used in the next cycles. The mass of the MS before and after adsorption at the saturated point was recorded and calculated using equation (1.4).

CHAPTER 4 – RESULTS AND DISCUSSION

4.1. Characterizations of superhydrophobic melamine sponge

4.1.1. Surface morphology

The surface structure and morphology of the pristine and modified MS samples were characterized using FE-SEM images, as shown in Figure 4.1. Before the modification, the pristine MS had a porous and 3D texture, with a smooth surface and an open-cell foam structure, which is widely used as a cleaning function (Figure 4.1 a-c).

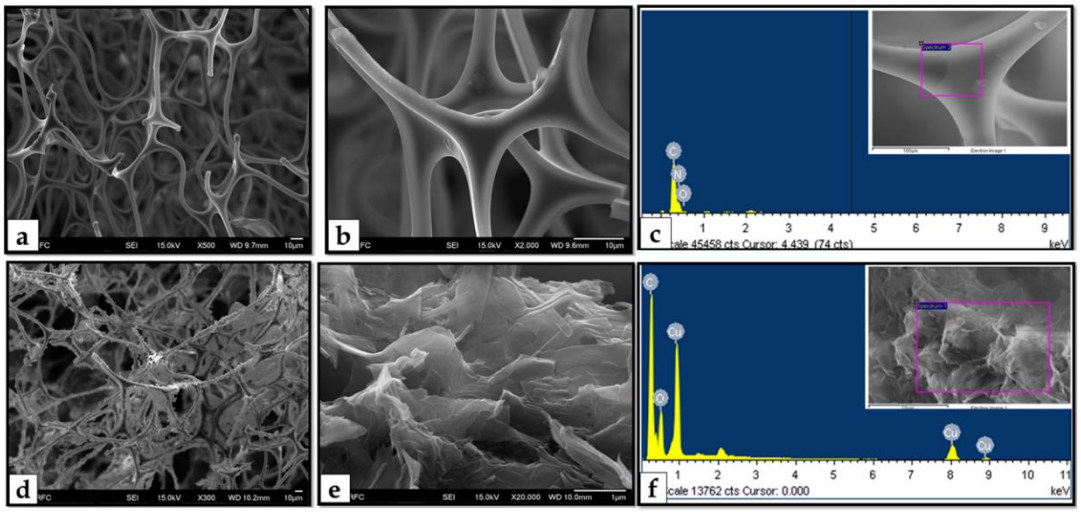

Figure 4.1. FE-SEM and EDS images of (a)(b)(c) original MS, and (d)(e)(f) modified MS –MS@CuO@SA sponge

The SEM images of the as-prepared MS are presented in Figure 4.1 d-f. Overall, the skeleton structure of the modified sponges was unchanged from that of the original MS. The two MS sponges before and after the modification revealed the same porous and 3-D intercrossed network structure. However, the modified MS showed a very rough surface due to the roughness developed on the MS fibers. MS@CuO@SA describes the nanostructure of a CuO layer on the MS surface. This kind of CuO nanostructure was grown on the pristine MS surface to form MS@CuO sponge by using a facile fabrication method in a commercial microwave oven. For simple and environmentally friendly

fabrication, the microwave was successfully used to form a CuO nanostructure on the MS surface as the CuO nanostructure could be grown very quickly and the required energy consumption was minimized, without needing specialized instruments. The association of the nanostructures increased the air trapped in the MS surface, which is a principal factor for enhancing the superhydrophobicity superhydrophobic properties according to the Cassie-Baxter model. The SEM-EDS images clearly show that the presence of copper elements attached on the sponge fibers and the modification process increases the surface roughness of MS.

The alkaline solution plays an important role in the CuO formation in the solution. The CuO nanostructure was formed by the hydrolysis of copper nitrate and HMTA. HMTA was used as an additive surfactant to develop the uniform micro-nanosphere morphology. HMTA as non-ionic cyclic tertiary amine can be easily degraded on heating [40]. However, the use of HMTA as an additive surfactant also brings undoubted advantages, against other alkaline reagents, because the fabrication process can be carried out at a lower temperature with HMTA [41]. Furthermore, HMTA not only provides the OH^- source but also acts as a pH buffer to release hydroxyl ions when heat is provided [41]. Hence, the more stabilizing the initial pH, the more controlling the uniformity of the CuO structure.

4.1.2. Atomic force microscopy

The topography and surface roughness of MS were investigated by AFM analysis. Figure 4.2 illustrates the 3D and 2D AFM images of the MS before and after the modification process. The roughness (R_a), root-mean-square roughness (R_q) and maximum height of the surface roughness (R_{max}) without modification were measured as 0.327 nm, 0.417 nm and 4.76 nm, respectively. The CuO and SA coating layers changed the MS surface roughness and increased R_a, R_q and R_{max} to 0.523 nm, 0.659 nm and 13 nm, respectively. According to the Cassie-Baxter model, the adhesion force between water and the MS surface was extremely low because of the trapped air in the micro-nano structure spaces, which allowed the water to easily roll off the interface between the water droplet and MS surface and thus induced the superhydrophobicity. Combined with the

SEM result, these observations agree with change in the MS surface roughness.

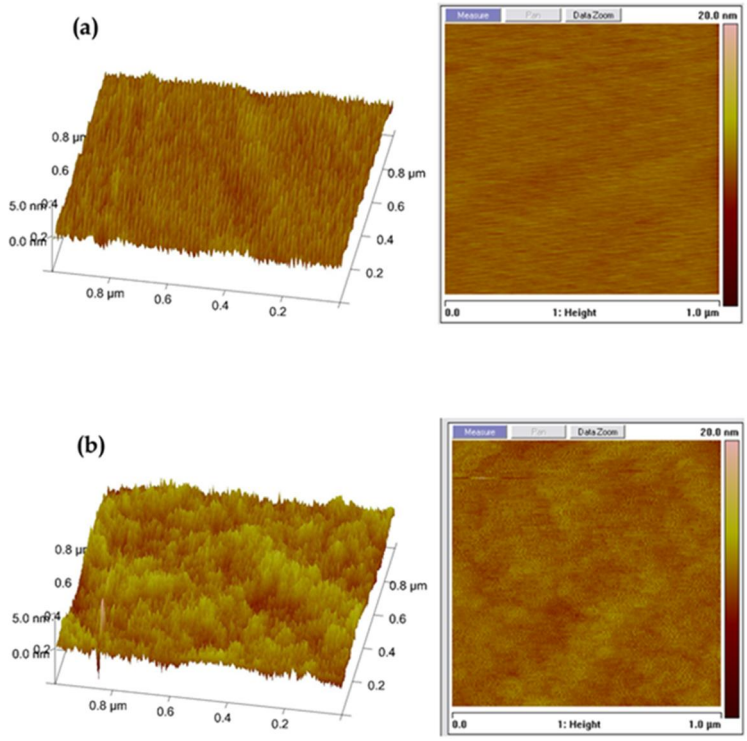

Figure 4.2. AFM images of the MS surface (a) before and (b) after the modification step.

4.1.3. Crystalline structure

Figure 4.3 represents the XRD patterns of the original MS and MS@CuO@SA sponges. The presence of CuO nanostructures on the coated MS surface was confirmed by the peaks detected at 2θ = 32.531°, 35.466°, 38.75°, 48.751°, 53.496°, 58.355°, 61.566°, 65.837°, 66.229°, 68.136°, 68.919°, 72.466°, and 75.273°, correspond to the lattice planes (110), (002), (111), (202), (020), (202), (113), (311), (220), (311) and (004), respectively. The diffraction peaks of the monoclinic structured CuO were indexed according to JCDPS standard. Furthermore, no impurities were found in the XRD patterns, which further confirmed the high purity of the CuO crystalline synthesized on the MS surface. Combined with the SEM and AFM results, these XRD patterns confirmed the successful loading of the CuO nanostructures on the original MS.

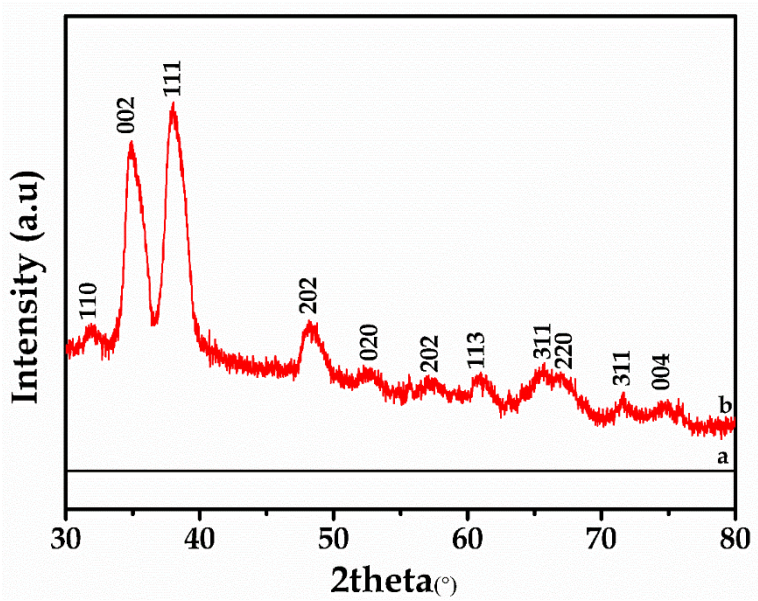

Figure 4.3. XRD patterns of (a) pristine melamine sponge (MS) and (b) MS@CuO@SA sponge

4.1.4. Element composition

XPS was used to examine the elemental composition of the original and modified sponges (Fig 4.4.1). Both sponges possessed the same N, C and O peaks due to the elements originating from MS. The major peaks revealed the binding energies of C1s, N1s and O1s at 286.6 eV, 405.5 eV and 533.9 eV, respectively. After the modification, the additional peak of Cu2p appeared at 934.3 eV from the formation of the CuO layer on the sponge skeleton structure. After the superhydrophobization step with SA in the modified MS, the peak intensity of C1s was increased strongly as compared to that of pristine MS.

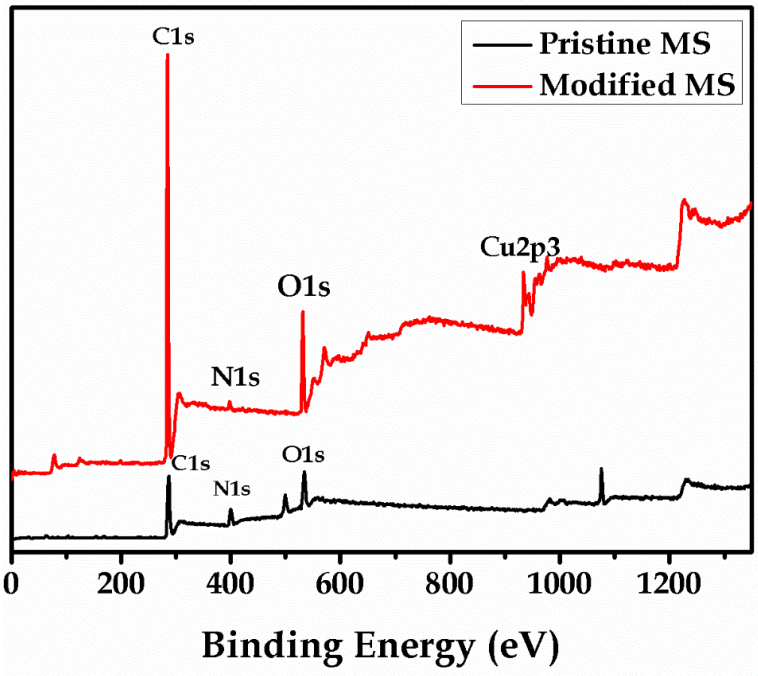

Figure 4.4.1 XPS spectra of MS before and after fabrication process

To confirm the interaction of the functional groups and the MS surface, the FT-IR spectra of the pristine MS and modified MS are compared in Figure 4.4.2. The spectrum of MS revealed prominent peaks at ~809, ~1154, ~1546, ~1584 and ~3396 cm^{-1}, which were ascribed to the bending vibrations of triazine ring, C-O, C=N and N-H stretching, respectively [42],[43],[44],[45]. Strong bending absorption peaks of C-H bonds at ~1341 and ~1471 cm^{-1} were also observed in the spectra for both untreated MS and modified MS. After the superhydrophobization with SA, the three new characteristic peaks appeared at ~1701, ~2850 and ~2925 cm^{-1}, where were associated with the O-C=O groups, and the asymmetric and symmetric C-H stretching vibration of $-CH_2$ groups, respectively, originating from SA [45],[46],[47],[48]. Compared to the pristine MS, the presence of these bands indicated the existence of a SA coating on the surface of MS@CuO's skeleton

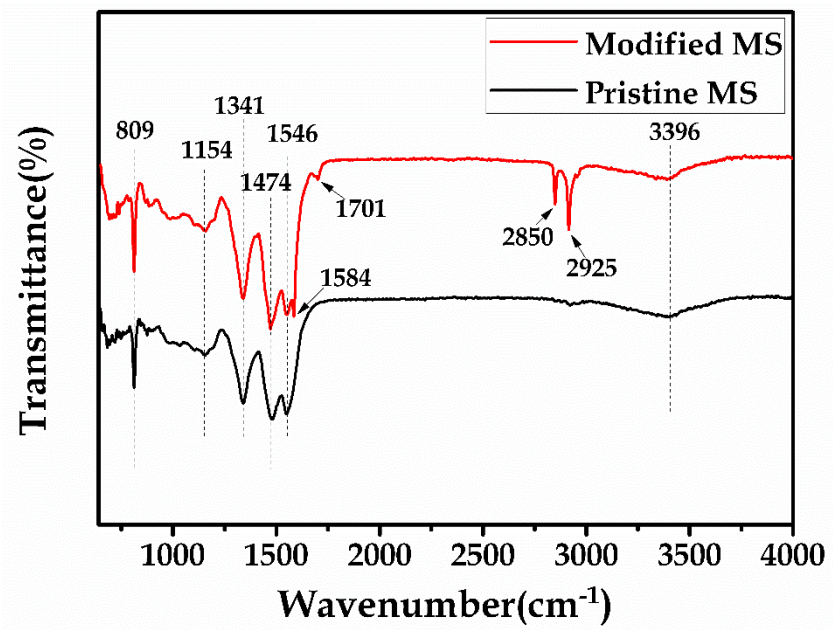

Figure 4.4.2 FT-IR spectra of the pristine sponge and the modified sponge

4.1.5. Thermogravimetric analysis

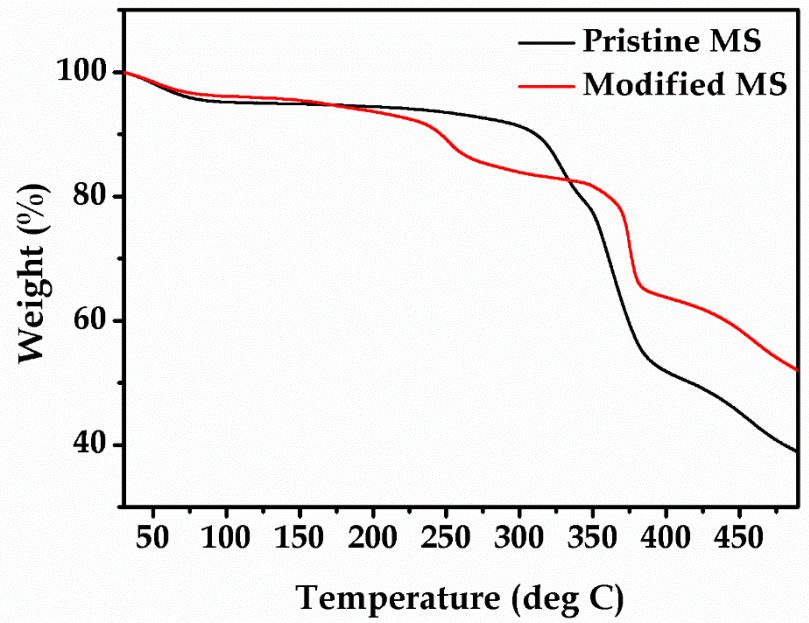

Figure 4.5. TGA spectra of the pristine MS and modified MS

The mass loss behavior and thermal stability of the original MS and the as-prepared MS were examined by thermogravimetric analysis (TGA) under a nitrogen gas atmosphere in a temperature range from 30 to 500 ℃. As shown in Figure 4.5, the TGA curves of MS exhibited four continuous temperature ranges

of ~30-130, ~130-330, ~330-410 and ~410-500℃,due to the evaporation of the absorbed water in the sponge, the formaldehyde elimination to form methylene bridges (HN-CH_2-NH), the breakdown of methylene bridges (main mass loss) and the thermal decomposition of the triazine ring, respectively [43],[45]. The first mass loss in the range ~30-130 ℃ of the pristine MS (~ 5 wt%) was slightly higher than that of the modified MS (~ 4 wt %). However, in the two temperature ranges from ~ 130- 410 ℃, the main mass loss, associated with the methylene bridges, occurred in the raw MS (~ 44.62 wt %) and in the treated MS (~ 32.28 wt %). The mass loss of the triazine ring in the region of ~ 410 – 500 ℃ of the modified MS was lower than that of the primary MS, which demonstrated that the thermal stability was improved after the modification process.

4.1.6. Wettability measurement

The surface wetting ability of the MS was confirmed by the static and dynamic (including shedding angle and sliding angle) WCA measurements. WCA was measured at five different locations with a 10 μL deionized water droplet. The pristine MS and the as-prepared MS exhibited obviously different WCAs (Figure 4.6). Theoretically, a surface with hydrophilic coatings attracts water, having a static WCA lower than 90°, while surfaces that repel water having static WCAs greater than 90° and 150° are termed hydrophobic and superhydrophobic surfaces, respectively. The original MS shows the super hydrophilic feature when the water droplet was dropped on the surface and was rapidly absorbed after a few seconds with a static WCA of almost 0°. Neither static WCA nor dynamic WCA of the raw MS sample could be recorded due to the good water absorption ability. After the CuO coating step and the superhydrophobization process with SA, the MS@CuO@SA sponge exhibited superhydrophobicity, which shows an almost perfect spherical shape of the water droplets deposited on the surface of the modified MS with static WCA of 165.1±1° and dynamic WCAs of 8±1°.

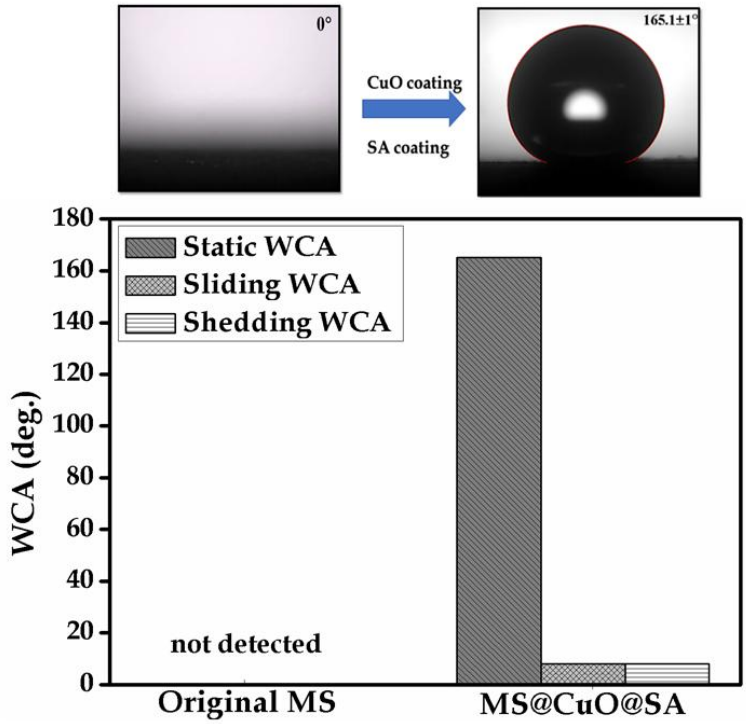

Figure 4.6. Water contact angle (WCA) of the original MS and modified MS

4.1.7. The effect of initial pH for the MS modification

This study investigated the stability in superhydrophobicity of the modified MSs prepared in different pH media. The WCAs of the modified MSs were measured at three different pHs, 4 (acidic), 7 (neutral) and 11 (basic), while maintaining the initial pHs by using NH_4OH or HCl. The measured static WCAs of the modified MSs prepared at initial pHs 4, 7 and 11 were 157.9±1°, 160.0±1°, and 165.1±1°, respectively, (Table 2), which satisfy the superhydrophobic property above 150°. Good superhydrophobic materials should also meet the dynamic WCA requirement, which is less than 10° in both sliding WCA and shedding WCA. The sliding and shedding WCAs of the modified MS, MS@CuO@SA sponge, prepared in acidic and neutral media, were higher than 10°. In the advanced WCA analysis, however, the modified MSs prepared at pH 11 completely satisfied the dynamic WCA conditions, which were 8±1° in both sliding WCA and shedding WCA. Based on this finding, the MS should be modified in the basic condition, such as pH11. Further modified MSs were

prepared at pH 11 and their superhydrophobicity properties were tested at different environmental conditions such as different pH values .

Table 2. The water contact angles (WCA) of MS in various initial pH media

SAMPLE	STATIC WCA(°)	ADVANCED WCA(°)	
		Sliding WCA	Shedding WCA
Original MS	not detected	not detected	not detected
MS@CuO@SA with pH 4	157.9 ± 1°	18 ± 1°	15 ± 1°
MS@CuO@SA with pH 7	160.0 ± 1°	14 ± 1°	13 ± 1°
MS@CuO@SA with pH 11	165.1 ± 1°	8 ± 1°	8 ± 1°

4.2. Applications

4.2.1. Anti-wetting

The distilled water was dyed with methylene blue (MB) and dropped onto the surfaces of pristine MS and the modified MS by using a syringe. The original MS absorbed all the water droplets quickly, whereas the MS modified with the CuO coating layer repelled the water drops. The surface changes due to the coating layer modifications with CuO and SA affected the wettability of the sponges. The MB water droplets were not absorbed onto the modified MS surface and the spherical surface shape was retained. According to the Cassie-Baxter theory, the stable air pockets could be trapped between the micro-nanostructure, which enabled the water droplets to roll off at small angles (Figure 4.7).

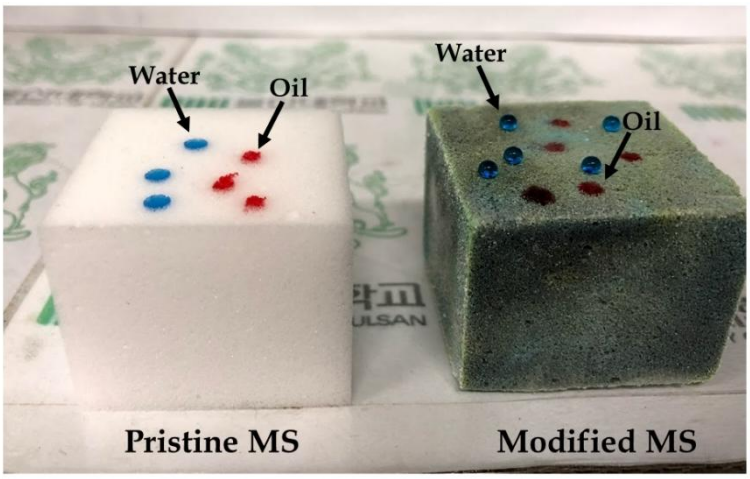

Figure 4.7. The water wettability of the original MS and modified MS

Additionally, the soaking experiment also demonstrated the wettability of the pristine MS and the modified MS. These two MSs were soaked in an aqueous solution to differentiate the wetting behavior between the two sponges in the soaking test. The pristine MS rapidly sank into the aqueous solution while the modified MS (superhydrophobic MS@CuO@SA sponge) floated on top of the solution (Figure 4.8).

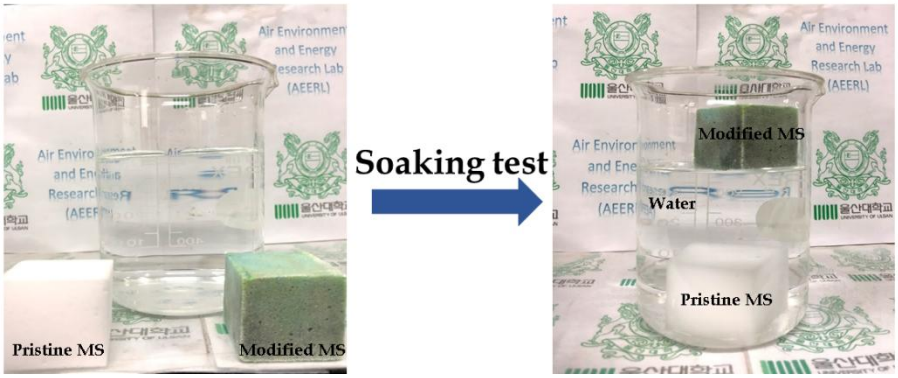

Figure 4.8. Soaking test for wetting property of the original MS and modified MS

Figure 4.9 shows several dark blue water droplets (dyed with MB) that were dropped on the cross-section of the modified MS. Both the exterior and the cut inner surface of the modified MS demonstrated superhydrophobic behavior and exhibited spherical water droplets without surface absorption.

Figure 4.9. The cross-section of the superhydrophobic sponge with the dark blue spherical water droplet (dyed with MB)

Furthermore, we also tested the chemical resistance of the superhydrophobic MS (MS@CuO@SA) toward corrosive solutions, e.g., acidic (HCl solution with pH = 3), basic (NaOH solution with pH = 11) and neutral (NaCl salt solution with pH = 7) liquid droplets. As demonstrated in figure 4.10, dropping three types of liquid droplets onto the surface of the MS sponge (MS@CuO@SA) did not significantly change its superhydrophobicity while retaining an almost spherical shape

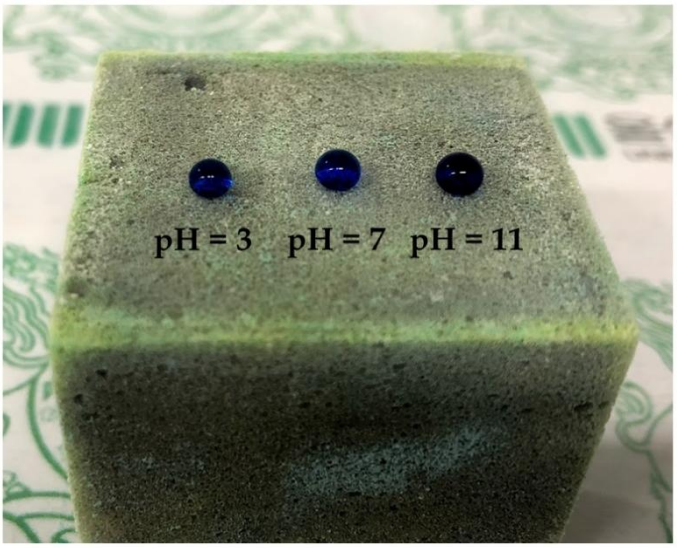

Figure 4.10. The aqueous droplets of HCl (pH =3), NaCl (pH =7) and NaOH (pH =11) solutions (dyed with MB)

Then we tried to immerse the modified MS into three types of corrosive solutions with ultra-sonification for more than 24 h. The bottom of the modified MS was effectively contacted with the corrosive solutions for more than 24 h. Then the modified MS was taken out of the solutions and cut into small specimens to measure the WCAs. The identified WCAs of all specimens remained much higher than 150°, which confirmed the good chemical resistance against the corrosive solutions (Table 3).

Table 3. The water contact angles (WCA) of the superhydrophobic MS immersed in different corrosive solutions for 24 hours

Treatments	Water contact angles
Before immersion	165.1±1°
In acidic solution (HCl solution , pH = 3)	160.2±1°
In salt solution (NaCl solution , pH = 7)	157.9±1°
In basic solution (NaOH solution , pH = 11)	156.7±1°

4.2.2. Oil absorption and oil/water separation test

Based on the successful fabrication of the superhydrophobic MS, the modified sponge (MS@CuO@SA) can be a good candidate for oil-water separation applications. To evaluate the absorption capacity of the fabricated sponge, various types of oil and organic solvent were used. Depending upon the different density and viscosity of the oils and organic liquids, the absorption capacity (g/g) of the sponge was up to 32-52 times its own weight. Figure 4.11 illustrates the absorption capacities of the tested oils and organic solvents.

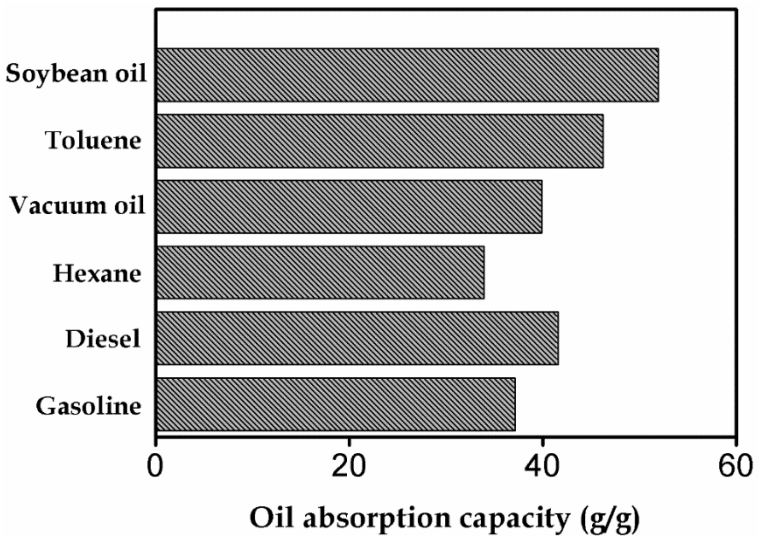

Figure 4.11. Oil absorption capacity of six types of oils/ organic solvents

In order to investigate the oil-water separation ability of the superhydrophobic MS sponge, the experiment was conducted to determine the separation capacity of six types of oil/organic solvent: hexane, toluene, vacuum oil, soybean oil, diesel, and gasoline. The mixture of oils and water (ratio 1:1, v/v) was poured onto the surface of the modified sponge and the surfaces of the MS sponge was blocked from the water to allow the oils to penetrate into the sponge. The separation capacity is shown in figure 4.12: the efficiencies of the fabricated sponges were 99.9, 99.8, 99.6, 99.3, 99.2 and 99.0% for hexane, toluene, gasoline, soybean oil, diesel and vacuum oil, respectively. These excellent results all exceeding 99% demonstrated the good separation efficiencies in each tested solvent or oil.

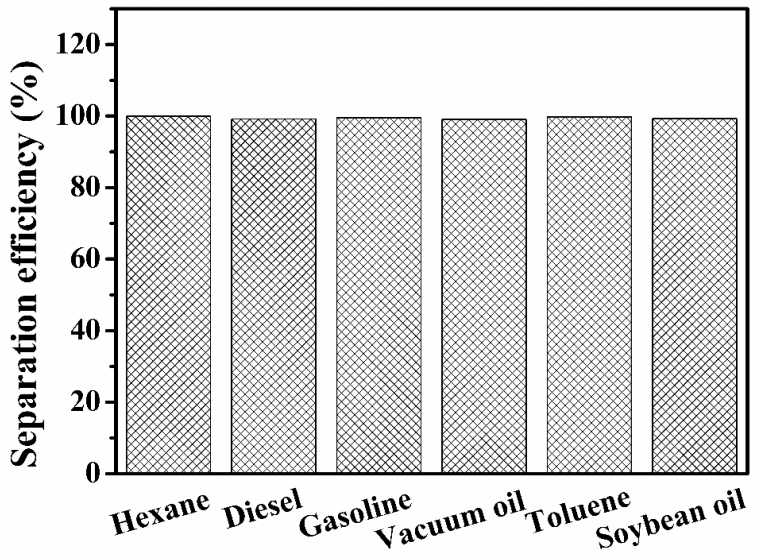

Figure 4.12. Separation efficiency of the modified MS@CuO@SA sponge with different types of oils/organic solvents

The experiment for floating oil absorption tests was also conducted in three different aqueous solution environments with different pHs: 3, 7 and 11. Figure 4.13 shows the images of the oil absorption (removal) process in three solutions, containing acidic HCl (pH =3), NaCl salt (pH =7), and basic NaOH (pH = 11), using n-hexane droplets dyed with red color dropped into each beaker. The superhydrophobic MSs were placed into the beakers using tweezers to move the modified sponges toward to the oil area. The floating oil was rapidly absorbed in the sponges and the remaining water was purified and cleared well without any signs of dyed oil on the water surface (Figure 4.13). This confirmed that the as-prepared sponge can absorb oil well in harsh environments.

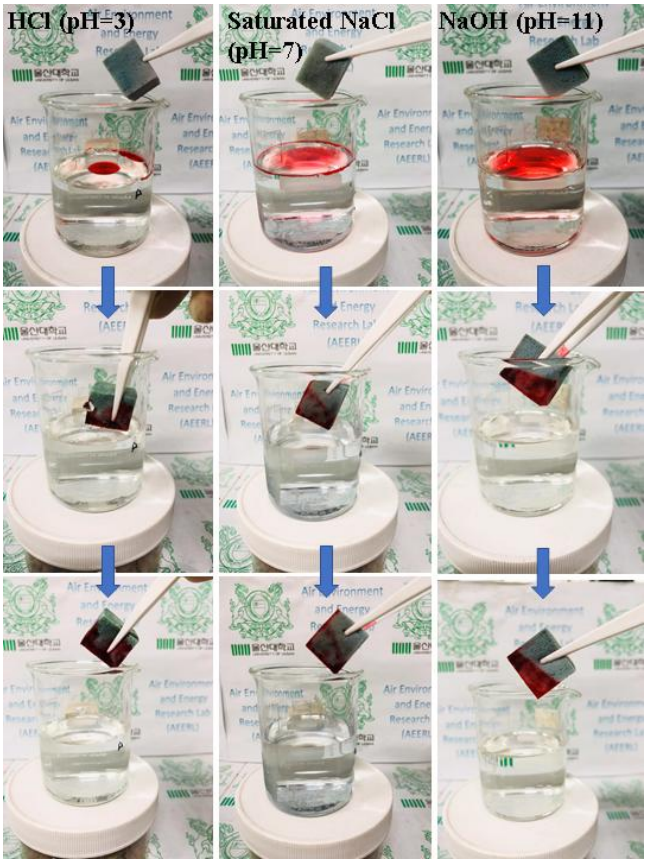

Figure 4.13. Floating oil removal tests by using MS@CuO@SA (a) in acidic, (b) salt (neutral), and (c) basic aqueous solutions.

4.3. Mechanical stability and reusability of superhydrophobic melamine sponge

For practical applications, we evaluated the stability and reusability of the prepared superhydrophobic sponges, as these are important factors for collecting and cleaning oil/organic solvents spills when considering the cost-effectiveness and ecological circumstances for sustainable use of the superhydrophobic sponge uses. The robustness of the superhydrophobic sponge was tested to evaluate its stability by an ultrasonic cleaning test (A1), wringing out the absorbed chemicals by hand (A2) and a compression test (A3), as shown in Figure 4.14. The porosity and good elastic structure of the superhydrophobic MS allowed it to retain its initial form after the compression test with 50% strain. The WCAs were not significantly affected by the 30-min ultrasonic cleaning test

or by wringing out the chemicals by hand. These results confirmed that the durability test did not affect the wetting ability of the prepared superhydrophobic MS.

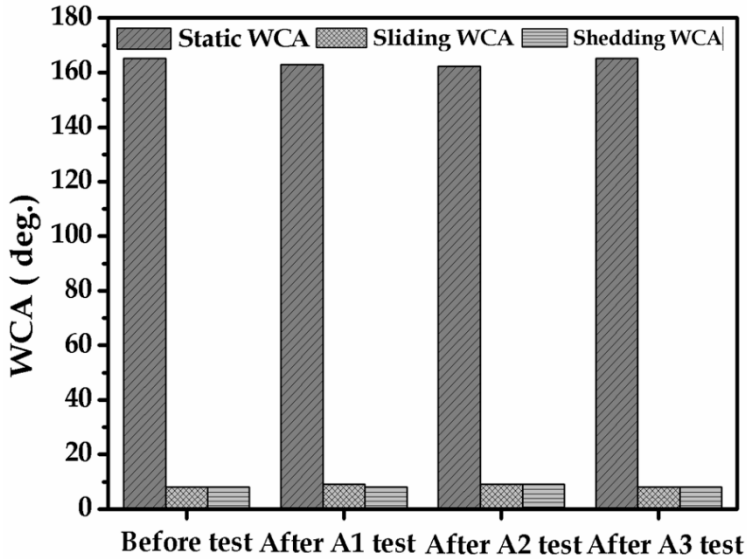

Figure 4.14. Stability test for MS@CuO@SA sponge

The reusability of the superhydrophobic sponges was tested by 40 absorption-squeezing cycles with various oils and organic solvents (Figure 4.15). Most of the absorbed oil could be recovered by merely manually squeezing the sponges, and then the sponge slightly contaminated with a small amount of oil remaining after squeezing could be applied for the next cycle of oil absorption. The sorption capacities of sponges with gasoline, diesel, hexane and toluene were almost stable after even 40 cycles, except the MS's sorption capacities for the vacuum oil and soybean oil, which exhibited a greater decrease in oil absorption capacity due to the residual oils remaining in the pore structure of the MSs.

Overall, the MS@CuO@SA sponge demonstrated excellent stability, including environmental stability and chemical resistance. The reusability test also confirmed that this superhydrophobic sponge can be a low-cost, robust and prospective absorbent for oil absorption and oil/water separation applications, even with oils or organic solvents in various density conditions.

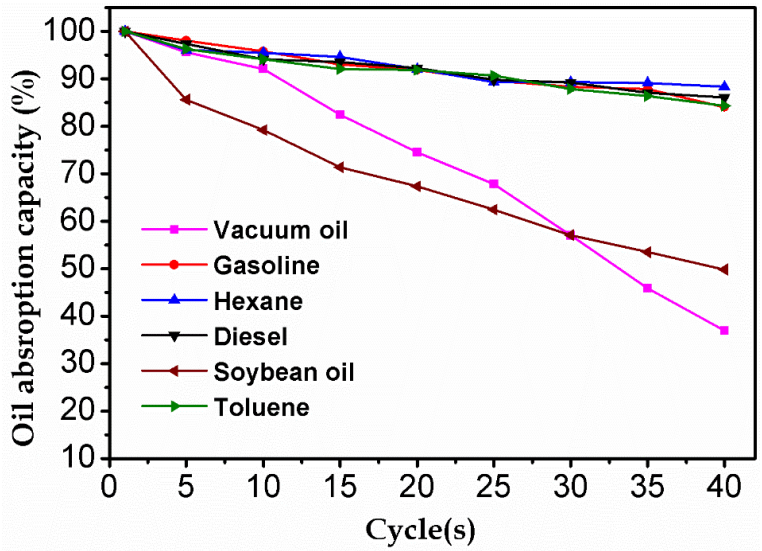

Figure 4.15. Oil absorption capacity of superhydrophobic MS after 40 cycles

CHAPTER 5- CONCLUSIONS AND FUTUTER WORK

5.1 Conclusions

A superior and novel superhydrophobic MS (MS@CuO@SA sponge) was successfully fabricated via a novel, simple and environmentally friendly method, in which a commercial MS was modified by combining CuO and SA layers to roughen the MS surface while reducing the surface energy. The modified sponge exhibited a high static WCA (165°C) and low dynamic WCAs (shedding WCA = 8°±1 and sliding WCA = 8°±1). The MS@CuO@SA sponge showed high absorption capacity for a wide range of oils and organic solvents with different densities and viscosities. In particular, the novel superhydrophobic sponges exhibited excellent sorption capacities of up to 52 times their own weight and outstanding reusability with good sorption capacity retention even after 40 cycles and high separation capacities that exceeded 99%. The MS@CuO@SA sponge was also effective for removing, absorbing and separating various oils and organic solvents under harsh environments, such as corrosive solutions containing acidic (pH = 3), saline (pH = 7) or basic (pH = 11) solutions, while retaining good superhydrophobicity with WCAs much higher than 150°. Therefore, the superhydrophobic MS@CuO@SA sponge, which showed excellent absorption performance in various harsh environmental conditions, robust stability, high chemical resistance and extraordinary reusability, is a prospective sorbent material for cleaning up oil spills, recovering organic chemicals and remediating water pollution even under complicated and harsh environments

5.2 Future works

In this study, using the cheap, flexible, porous and good elascity sponge to develop superhydrophobic material with potential applications, this obtained superhydrophobic melamine sponge could be used for practical applications, especially oil/water separation .

Moreover, the newly creating different superhydrophobic surfaces could be applied in many applications. For example, superhydrophobic metal or ceramic substrates could be applied for anti-fogging, anti-cing or anti-corosion etc. And recycling waste to superhydrophobic materials such as coffee waste or eggshell which can be saved energy and protect the environment.

With this facile and environmentally friendly fabrication, It is hoped that this technique and this superhydrophobic material could contribute to the advancemence of materials and further to the research of practical applications.

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