Emerging Wettabilities and their applications of water, oil and liquid metals

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Emerging Wettabilities and their applications of water, oil and liquid metals

Zhenwei Yu

This thesis is presented as part of the requirements for the conferral of the degree:

Doctor of Philosophy

Supervisor:
Prof. Xiaolin Wang

The University of Wollongong
Institute of Superconducting and Electronic Materials

March 2018
Declaration

I, Zhenwei Yu, declare that this thesis is submitted in partial fulfilment of the requirements for the conferral of the Doctor of Philosophy, from the University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Zhenwei Yu

March 28, 2018
Abstract

Over the past ten years, interfacial materials system, superwettability with water and oil, have been widely studied and utilized in practical applications such as self-cleaning, oil/water separation, water collection, anti-fogging, and anti-icing. Although the materials with superwettability show excellent performance of applications compared with the traditional methodology, they still suffer from various disadvantages including poor durability, high cost and complex preparation method. So, design and simple fabrication of advanced superwettability materials with low cost, good chemical and mechanical stability are of significance in environmental safety, water resource shortage, and other domains. Furthermore, new interfacial materials system, liquid metal/liquid/solid type wettability, has been attracted increasing attentions in recent years due to the unique and superior chemical properties of room temperature liquid metals. New applications and phenomena have been explored in the field of electronics, optics, fluid dynamics, and robots.

There is a critical need to develop durable and reusable materials for oil-water separation, especially in harsh environments. Traditional anti-fouling mesh-based separation technologies are not reusable and limited by poor temperature resistance. Here we report a novel superhydrophilic and underwater superoleophobic NiO/Ni mesh which shows superior oil/water separation in harsh environments. With reusable and durable properties, that can separate different oil-water mixtures with and without sand and soil contaminants, with a $>99\%$ separation efficiency and up to $5.4 \times 10^4$ L m$^{-2}$ h$^{-1}$ permeate flux. The material is able to retain its superior performance for over the 20 cycles we measured and for mixtures of sticky oils its performance is easily recoverable after a quick
heat treatment. Our separation methodology is solely gravity-driven and consequently is expected to be highly energy-efficient. We anticipate that our separation methodology will have numerous applications, including the clean-up of oil spills, wastewater treatment and other harsh condition oil-water separations.

With the impacts of climate change and impending crisis of clean drinking water, designing functional materials for water harvesting from the fog with large water capacity has received much attention in recent years. Nature has evolved different strategies for surviving dry, arid, xeric conditions. Nature is a school for human beings. Inspired by the Stenocara beetle, superhydrophilic/superhydrophobic patterned surfaces were fabricated on the silica polydimethylsiloxane (PDMS)-coated superhydrophobic surfaces using a pulsed laser deposition approach with masks. The resultant samples with patterned wettability demonstrated water harvesting efficiency in comparison with the silica PDMS-coated superhydrophobic surface and the Pt nanoparticles-coated superhydrophilic surface. The maximum water harvesting efficiency can reach about 5.3 g cm\(^{-2}\) h\(^{-1}\). Both the size and the percentage of the Pt-coated superhydrophilic square regions on the patterned surface affected the condensation and coalescence of the water droplet, as well as the final water harvesting efficiency. The present water harvesting strategy should provide an avenue to alleviate the water crisis facing mankind in certain arid regions of the world.

We discovered a heart beating phenomenon of liquid metals dominated by deformation and Column charge repulsion. A small DC voltage can induce beating effect of liquid metal inside graphite ring anode in alkaline solutions. The beating performance has studied with the applied voltage and liquid metal droplet size. This approach provides
a convenient way to achieve liquid metal oscillations, which has fundamental and practical significance.

Voltage induced electrochemical lithography for liquid metals was demonstrated at room temperature, which is non-contact, maskless, and material-reusable. The ability to form a hole in liquid metal in an electrolyte through an applied voltage enables us to create any patterns of choice in liquid metals. We have investigated the effects of the voltage, the electrode tip distance to the liquid metal surface, and the electrolyte concentration on the hole formation process. The evolution of the hole formation was investigated with short pulses or the application of a continuous DC voltage. Various patterns in liquid metal can be simply fabricated using electrochemical hole/dot matrix printing, continuous “writing” and movable type printing method. Our findings offer novel liquid metal patterning techniques for further development of liquid metal applications in electronics, optics, and microfluidics.

We have discovered that liquid metals are capable of penetrating any solids with macro- or micropores and climbing the walls of a solid container under an applied voltage. We demonstrate the two effects in various porous materials such as wiper papers, thick sponges, fabric, and metallic meshes. The two effects mimic two of the three well-known superfluid properties for liquid helium that only occur at near-zero Kelvin temperature. The underlying mechanism is that the high surface tension of liquid metal can be significantly reduced to near-zero by voltage. It is the extremely low surface tension that causes the liquid metal to be superwet and drive its own motion on a solid surface. Our new findings offer new opportunities for novel microfluidic applications and could
promote further exploration for more exotic fluidic states of liquid metals that mimic superfluids.
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## List of Abbreviations

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<th>Full name</th>
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<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>CA</td>
<td>Contact angle</td>
</tr>
<tr>
<td>WCA</td>
<td>Water contact angle</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>FAS</td>
<td>Fluoroalkyltriethoxysilane</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>PU</td>
<td>Polyurethane</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-assembled monolayers</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>NPs</td>
<td>Nano particles</td>
</tr>
<tr>
<td>OCA</td>
<td>Oil contact angle</td>
</tr>
<tr>
<td>UFA</td>
<td>Ultraflyweight aerogel</td>
</tr>
<tr>
<td>TCF</td>
<td>Twisted carbon fiber</td>
</tr>
<tr>
<td>CMB</td>
<td>Carbon microbelt</td>
</tr>
<tr>
<td>CMP</td>
<td>Conjugated microporous polymer</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>BN</td>
<td>Boron nitride</td>
</tr>
<tr>
<td>POSS</td>
<td>Polyhedral oligomeric silsesquioxane</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>PEGDA</td>
<td>Poly(ethylene glycol) diacrylate</td>
</tr>
<tr>
<td>PAM</td>
<td>Polyacrylamide</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>LbL</td>
<td>Layer-by-layer</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>NC</td>
<td>Nitrocellulose</td>
</tr>
<tr>
<td>PAA</td>
<td>Poly-(acrylic acid)</td>
</tr>
<tr>
<td>NFM</td>
<td>Nanofiber-based mesh</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>UWOCA</td>
<td>Underwater oil contact angle</td>
</tr>
<tr>
<td>PNIPAM</td>
<td>Poly(N-isopropylacrylamide)</td>
</tr>
<tr>
<td>TPU</td>
<td>Elastic polyurethane</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>OTS</td>
<td>Octadecyltrichlorosilane</td>
</tr>
<tr>
<td>eGaIn</td>
<td>Eutectic Gallium-Indium</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethylmethacrylate</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>Nd: YAG</td>
<td>Neodymium-doped yttrium aluminum garnet</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled display</td>
</tr>
<tr>
<td>SHL</td>
<td>Superhydrophilic</td>
</tr>
<tr>
<td>SHB</td>
<td>Superhydrophobic</td>
</tr>
<tr>
<td>fps</td>
<td>Frame-per-second</td>
</tr>
<tr>
<td>Symbol</td>
<td>Name</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>$\theta_{CA}$</td>
<td>Contact angle</td>
</tr>
<tr>
<td>$\theta_Y$</td>
<td>Contact angle in Young’s model</td>
</tr>
<tr>
<td>$\gamma_{SL}$</td>
<td>The interfacial energy between solid and liquid</td>
</tr>
<tr>
<td>$\gamma_{SV}$</td>
<td>The interfacial energy between solid and vapour</td>
</tr>
<tr>
<td>$\gamma_{LV}$</td>
<td>The interfacial energy between liquid and vapour</td>
</tr>
<tr>
<td>$\theta_W$</td>
<td>Contact angle in Wenzel model</td>
</tr>
<tr>
<td>$r$</td>
<td>The ratio of the actual surface area of the rough surface to the apparent area</td>
</tr>
<tr>
<td>$f_S$</td>
<td>The fraction of the surface that is in contact with the liquid</td>
</tr>
<tr>
<td>$\theta_{CB}$</td>
<td>Contact angle in Cassie model</td>
</tr>
<tr>
<td>$\theta_A$</td>
<td>Advancing angle</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>$\theta_R$</td>
<td>Reducing angle</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Surface tension</td>
</tr>
<tr>
<td>$r_0$</td>
<td>The local radius of the liquid droplet</td>
</tr>
<tr>
<td>$R_0$</td>
<td>The radius of the liquid droplet</td>
</tr>
<tr>
<td>$F$</td>
<td>The permeate flux</td>
</tr>
<tr>
<td>$V$</td>
<td>The volume of water</td>
</tr>
<tr>
<td>$S$</td>
<td>The area of the mesh</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$R$</td>
<td>The separation efficiency</td>
</tr>
<tr>
<td>$M_1$</td>
<td>The weight of the collected water</td>
</tr>
<tr>
<td>$M_2$</td>
<td>The weight of the residual oil</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$g$</td>
<td>The acceleration due to gravity</td>
</tr>
<tr>
<td>$h_{\text{max}}$</td>
<td>The maximum height of liquid</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>Time in one liquid metal beating cycle</td>
</tr>
<tr>
<td>$r_f$</td>
<td>The speed of the hole formation</td>
</tr>
<tr>
<td>$R_{\text{hole}}$</td>
<td>The maximum size of the hole</td>
</tr>
<tr>
<td>$d$</td>
<td>The tip distance</td>
</tr>
<tr>
<td>$v$</td>
<td>Voltage</td>
</tr>
<tr>
<td>$h$</td>
<td>The distance from the top edge of the cup to the</td>
</tr>
<tr>
<td></td>
<td>galinstan</td>
</tr>
</tbody>
</table>
Chapter 1. Introduction

1.1. General background

Interfacial materials system has attracted a lot of attention during a long period in both academia and industry. Wettability of solid surfaces by gas, water and oil in gas, water and oil environments have been widely studied. Figure 1.1 summarized all the possibility of wetting state by gas, water and oil. Inner white circle showed four states of water and oil on flat substrates in the air, which including hydrophilicity, oleophilicity, hydrophobicity and oleophobicity. After introducing roughness and low or high surface energy coating, superwetting states have been obtained in air, such as superhydrophobicity, superhydrophilicity, superoleophobicity and superoleophilicity. Besides superwetting states in the air, under liquid superwetting states have also been explored. Outer blue circle showed superwetting states underwater, which including underwater superoleophobicity, superoleophilicity, superaerophobicity, and superaerophilicity. Outer orange circle showed superwetting states under-oil, which including under-oil superhydrophobicity, superhydrophilicity, superaerophobicity and superaerophilicity. Many achievements have been made based on these superwetting states from the fundamental research to practical applications. For example, superhydrophobicity enable self-cleaning surfaces because water roll off the superhydrophobic surface in a small sliding angle without residue and remove the dust on its path. The tiny water droplets can be spread on the superhydrophilic surface to form a thin water film, which achieves anti-fogging behaviour. For underwater superaerophobicity, an air barrier between the surface and solution was formed and could prevent the migration of corrosive ions, which achieve anti-
corrosion behaviour.\textsuperscript{9-12} By a combination of superhydrophobicity and superoleophilicity or superhydrophilicity and superoleophobicity, the materials have the ability to remove the oil or water from oil/water mixture.\textsuperscript{13-19}

![Diagram of superwettability system](image)

Figure 1.1. The system of “superwettability” based on gas, water and oil.\textsuperscript{1}

In addition, instead of the traditional medium (gas, water and oil), room temperature liquid metals interface with surfaces have been studied recently, which extend the wetting model by new compelling materials.\textsuperscript{20, 21} The ability to pattern or manipulate liquid metals on the surface under different conditions is important for many applications, such as reconfigurable electronics,\textsuperscript{22-24} antennas,\textsuperscript{25-28} optics,\textsuperscript{29, 30} microfluidic devices.\textsuperscript{31-33} It is vital
that understanding liquid metals interact with the surface under different conditions would enable researchers to discover new effects and develop new applications.

1.2. Thesis structure

In this thesis, the scope of the research is briefly outlined below as follows:

Chapter 1 introduces the general background, major issues, research interests for interfacial materials system by water, oil and liquid metals.

Chapter 2 presents a literature review on theoretical basis of wettability and major applications, including oil/water separation, water harvesting, manipulation of liquid metal surface tension.

Chapter 3 presents a novel reusable superhydrophilic NiO/Ni mesh for oil/water separation.

Chapter 4 presents desert beetle-inspired superwettable patterned surfaces for water harvesting.

Chapter 5 presents the galinstan heart beating effect at room temperature.

Chapter 6 demonstrates a novel liquid metal patterning technique: voltage induced non-contact electrochemical lithography at room temperature.

Chapter 7 presents the discovery of room temperature penetration and wall climbing effects for liquid metals of voltage-stimulated heartbeat of liquid metal.
Chapter 2. Literature Review

2.1. Theoretical basis of wettability

Figure 2.1. Four different states in which water droplet contact with a surface.

Under the normal circumstances, a sessile droplet will form a sphere shape which will be classified by the surface when it is located on a substrate. A contact angle $\theta_{CA}$ can be measured between the droplet and the substrate surface at the cross-sectional view. Commonly, the surface is identified as hydrophilic when $\theta_{CA} < 90^\circ$; in contrast, the surface is said to be hydrophobic if $\theta_{CA} > 90^\circ$. Especially, with $\theta_{CA} > 150^\circ$, the surface is usually regarded as a superhydrophobic surface. And for $\theta_{CA} < 10^\circ$, the surface is usually regarded as a superhydrophilic surface which is completely wet with water. (Figure 2.1)

2.1.1 The Young’s model

In 1805, Thomas Young depicted the equilibrium forces on the interface between a liquid droplet and a flat substrate. The contact angle $\theta_Y$ of the droplet is connected with the liquid surface tension ($\gamma_{LV}$), the solid surface energy ($\gamma_{SV}$) and interfacial energy between the solid-liquid ($\gamma_{SL}$) as following:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_Y$$

(2.1)
Figure 2.2 illustrates the typical wetting behaviour of a droplet under Young's model, Wenzel's model and Cassie's model.

![Diagram of droplet behavior](image)

**Figure 2.2.** The typical wetting behaviour of a droplet on the solid substrates. (a) Young’s model. (b) Wenzel’s model. (c) Cassie’s model.\(^{35}\)

The Young’s model here describes an ideal model because it is only suitable for extremely flat and chemically homogeneous surfaces. It was assumed that the surface doesn’t change its characteristics by the interactions of the testing droplet with the surface. In fact, most solid surfaces are rough, which plays an important role in addressing the wettability of solid surfaces. Therefore, the Wenzel model\(^{36}\) (Figure 2.2b) and the Cassie-Baxter model\(^{37}\) (Figure 2.2c) were established to describe a rough surface’s wettability properties.

### 2.1.2 The Wenzel model

The Wenzel model (Figure 2.2b) is described as follows:

\[
\cos \theta_W = r \cos \theta_Y
\]  

(2.2)

where \(r\) is the ratio of the actual rough surface area to the apparent area, \(\theta_Y\) is the contact angle (CA) of a flat surface and \(\theta_W\) is the contact angle of a real surface. In this model, the surface roughness can enhance either wetting state (\(\theta_W < 90^\circ\)) or non-wetting state (\(\theta_W > 90^\circ\)), highly related to the chemical properties of the substrate surface. If the contact angle
of the flat surface is larger than 90°, it would be risen by the surface morphology. On the contrary, the contact angle reduces while the contact angle of the flat surface is less than 90°.

2.1.3 The Cassie model

The Cassie-Baxter model depicted a liquid behaviour on a rough surface which cannot be penetrated by the liquid, and the air can be trapped in the grooves:

$$\cos \theta_{CB} = f_S (\cos \theta_Y + 1) - 1$$ (2.3)

where $f_S$ is the fraction of the liquid-contacted surface area. Because the air is trapped in the grooves, the corresponding $\theta_{CB}$ is greater than the contact angle of the smooth surface with the same material. So, surface morphology plays a significant role in the wetting behaviour.

2.1.4 Surface energy gradient

![Figure 2.3. Schematic diagram of spindle-knots and joint on the spider silk.](image)

Surface energy gradient, which is normally obtained by a difference in surface topography and morphology, is used to be analysed in the applications of liquid transportation and water collection based on wettability. For example, the water contact angle (WCA) of the joint is larger than that of the spindle-knot because the surface of the
spindle-knot is rougher than that of the joint (Figure 2.3). The surface energy of the spindle-knot is higher than that of the joint. So the surface energy gradient is obtained between the spindle-knot and the joint. The equation is shown as follow:

\[ F = \int_{L_j}^{L_k} \gamma (\cos \theta_A - \cos \theta_R) \, dl \]  

where \( \gamma \) represents the surface tension of water, \( \theta_A \) and \( \theta_R \) are the respective advancing and receding angles of water drops, and \( dl \) is the integrating variable along the length from the joint \( (L_j) \) to the spindle-knot \( (L_k) \).

### 2.1.5 Laplace pressure equation

Furthermore, Laplace pressure difference was generated by cone-shaped topography for liquid drop transportation, which can be described as follow:

\[ \Delta P = \int_{r_1}^{r_2} \frac{2\gamma}{(r_0 + R_0)^2} \sin \beta \, dz \]

where \( r_0 \) is the local radius and \( R_0 \) is the radius of the liquid droplet. The direction of the liquid droplet transportation is from the high curvature position to the low curvature position due to Laplace pressure difference.

### 2.2 Superwettability for oil/water separation

Oil/water separation is considered as a global issue due to the increasing oil leakage during marine transportation and massive volumes of oily wastewater in industry. Aquatic environments and ecology have been under a severe threat. For example, hundreds and thousands living species were damaged or destroyed in the Exxon Valdez oil spill. Therefore, a great amount of attention has been attracted on oil/water separation in both research and industry. To solve these problems, traditional methods for oil spill accidents,
such as in-situ burning, oil absorption by porous materials and vacuum suction, have been used to clean the oil from seawater. Additional, in preparation for the oily wastewater from industries, a variety of techniques, such as skimming\textsuperscript{50}, flotation\textsuperscript{51, 52}, are used for oil/water separation. However, the disadvantages of all these methods are very evident, such as inefficiency, high energy consumption, high operational cost and secondary pollution. Thus, the development of advanced technologies/materials for highly efficient low-cost oil/water separation are desired.

Figure 2.4. Typical materials used for oil/water separation.\textsuperscript{17}

In the past few years, oil/water separation based on materials superwettability have attracted much attention. A number of functional superwettetable materials for oil/water separation have been studied (Figure 2.4).\textsuperscript{17} To date, three different type of wettability materials, including superhydrophobic/superoleophilic, superhydrophilic/underwater
superoleophobic and superoleophobic and superhydrophilic, have been designed and fabricated for oil/water separation.

2.2.1 Superhydrophobic and superoleophilic materials

The superhydrophobic and superoleophilic materials can repel water completely while absorbing oil (for porous materials) and be wetted and penetrated by oil (for filter materials). This kind of materials can achieve high efficiency and good selectivity for oil/water separation, which are applicable to separate the disperse oil/water mixtures. Table 2.1 shows some typical examples of the superhydrophobic and superoleophilic filtration materials.\textsuperscript{53-66}

Table 2.1. Typical superhydrophobic and superoleophilic separation filters fabricated by different approaches.\textsuperscript{13}

<table>
<thead>
<tr>
<th></th>
<th>Materials</th>
<th>Method</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PTFE/mesh</td>
<td>Spray coating</td>
<td>Crater-like</td>
</tr>
<tr>
<td>2</td>
<td>Fatty acids/mesh</td>
<td>Electrochemical</td>
<td>Clusters</td>
</tr>
<tr>
<td></td>
<td></td>
<td>deposition/SAM</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Alkylphosphonic acid/Ni</td>
<td>Wet chemistry/SAM</td>
<td>Flowers</td>
</tr>
<tr>
<td>4</td>
<td>FAS/mesh</td>
<td>SAM</td>
<td>Hierarchical</td>
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<tr>
<td>5</td>
<td>Hexadecanethiol/mesh</td>
<td>Acid etching/SAM</td>
<td>Porous</td>
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<td>6</td>
<td>Dodecanethiol/mesh</td>
<td>Alkali etching/SAM</td>
<td>Needle-like</td>
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<td>CNT/mesh</td>
<td>CVD</td>
<td>Vertical array</td>
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<td>FAS/mesh</td>
<td>Electrochemical</td>
<td>Needle-like</td>
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<td>etching/SAM</td>
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<td>9</td>
<td>ZnO/mesh</td>
<td>Solution approach</td>
<td>Nanorod array</td>
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<tr>
<td></td>
<td>Material</td>
<td>Preparation Method</td>
<td>Shape/Structure</td>
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<td>ZnO/PTFE/mesh</td>
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<td>Rod- or flower-like</td>
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<td>PU/PS</td>
<td>Polymerization/spin-coating</td>
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<td>PS</td>
<td>Spray</td>
<td>Beads/fibers</td>
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<td>PU/SiO2</td>
<td>Electrospinning</td>
<td>Bead-on-string</td>
</tr>
<tr>
<td>14</td>
<td>Ceramic/SiO2/PU-PDMS</td>
<td>Sol-gel</td>
<td>Porous/spheres</td>
</tr>
</tbody>
</table>


Figure 2.5. Scanning electron microscope (SEM) images of the pristine and Cu nano particles (NPs) coated copper mesh film. (a) Integral view of a pristine copper mesh film. (b) Integral view of a Cu NPs coated copper mesh film. (c) Enlarged view of copper mesh
wires of the Cu NPs coated copper mesh film. (d) The higher magnification image of the as-coated Cu NPs on one single copper wire.67

In 2004, Jiang’s group first proposed a Teflon-coated stainless-steel mesh with micro and nano structured rough mesh surface exhibits superhydrophobic and superoleophilic properties.53 The WCA of this mesh film is about 150 degrees, and diesel oil contact angle for it is nearly zero. The as-prepared mesh film could be used to separate the water and diesel oil mixture. As shown in Figure 2.5, Wang et al. reported a butterfly wing inspired Cu NPs coated copper mesh was prepared by electrochemical deposition and followed by a thiol coating.67 It was demonstrated that the as-prepared film is recyclable as WCA of the film remains larger than 150 degrees after numerous times of oil/water separation processes. Moreover, the as-prepared film exhibited excellent thermal stability and retained its superhydrophobic property after ultrasonic treatment in the nonpolar solution. Zhou et al. presented a superhydrophobic cotton fabric, which was prepared by vapor phase deposition with polyaniline and fluorinated alkyl silane.68 The as-prepared cotton fabric exhibits superhydrophobic and superoleophilic behaviours and shows oil/water separation with 97.8% efficiency. The obtained superhydrophobic fabric showed reusability, chemical stability, and mechanical durability.
Gao et al. fabricated a uniform layer of graphdiyne-based on copper foam with honeycomb-like microstructure and ordered nanostructure by the in situ Glaser-Hay coupling method. After the PDMS coating, the WCA of the as-prepared foam was close to 160 degrees. The foam also showed high resistance toward abrasion cycles. Tian et al. prepared an aligned ZnO nanorod array-coated stainless-steel mesh film
by a two-step solution approach. This excellent oil/water separation process could be well controlled by the size of microscale mesh pores and the nanostructure surface.

Figure 2.7. Snapshots of the removal process of motor oil (dyed with Solvent Red 24 for clear observation) (a) and chloroform (b) from water using the graphene-based sponges. Oil- and organic solvent-absorption capacities of the graphene-based sponges (c). Absorption recyclability of the graphene-based sponges for oils (d) and organic solvents (e).

Gen et al. reported marshmallow-like flexible gel was prepared by a facile one-pot reaction from organoalkoxysilanes. The as-prepared gel showed superhydrophobic property and can absorb oil from water. The flexible gel could maintain its functions from -210 to 320 °C. Jayaramulu et al. reported Sponge@HFGO@ZIF-8 was obtained by
bathing a sponge into the mixture of exfoliated highly fluorinated graphene oxide and a methanolic solution of the ZIF-8 growth components for one night. The as-prepared sponge shows superhydrophobic behaviour with a large WCA of 162° and superoleophilicity with zero oil contact angle (OCA), which reveals superior oil absorption capacity. Nguyen et al. reported a superhydrophobic and superoleophilic sponge was prepared by dip coating method using the hydrophobic graphene nanosheets. (Figure 2.7) The as-prepared graphene-based sponge shows great absorption capacities and good reusability. Zhu et al. fabricated a robust 3D porous polyurethane sponge with superhydrophobic polysiloxane layer coating through a one-step solution immersion method. The sponge shows superior oil-absorption capacity and mechanical/chemical durability. Table 2.2 summarised the fabrication method of 3D porous absorbents and the oil/water separation performance of the materials.

Table 2.2. Comparison of various 3D porous absorbents for selective oil/water separation.

<table>
<thead>
<tr>
<th></th>
<th>3D absorbent</th>
<th>Preparation method</th>
<th>WCA [°]</th>
<th>Density [mg cm⁻³]</th>
<th>Absorption capacity [g g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CNT sponge</td>
<td>CVD</td>
<td>156</td>
<td>5-10</td>
<td>up to 180</td>
</tr>
<tr>
<td>2</td>
<td>Magnetic CNT sponge</td>
<td>CVD</td>
<td>140</td>
<td>15</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>Spongy graphene</td>
<td>Hydrothermal reduction self-assembly and freeze-drying</td>
<td>114</td>
<td>12</td>
<td>20-86</td>
</tr>
<tr>
<td>4</td>
<td>UFA</td>
<td>“Sol-cryo” method and hydrazine vapor reduction</td>
<td>-</td>
<td>≥0.16</td>
<td>215-913</td>
</tr>
<tr>
<td></td>
<td>Description</td>
<td>Preparation Method</td>
<td>Page</td>
<td>Volume Range</td>
<td>Total Range</td>
</tr>
<tr>
<td>---</td>
<td>------------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------</td>
<td>------</td>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>5</td>
<td>Carbon NPs coated carbon sponge</td>
<td>Combustion-assisted in situ carbon deposition</td>
<td>149</td>
<td>9-13</td>
<td>58-143</td>
</tr>
<tr>
<td>6</td>
<td>TCF aerogel</td>
<td>Pyrolysis of cotton</td>
<td>-</td>
<td>12</td>
<td>50-192</td>
</tr>
<tr>
<td>7</td>
<td>CMB aerogel</td>
<td>Pyrolysis of waste paper</td>
<td>-</td>
<td>5.8</td>
<td>56-188</td>
</tr>
<tr>
<td>8</td>
<td>Carbon nanofiber aerogel</td>
<td>Template hydrothermal method, freeze-drying and pyrolysis</td>
<td>136</td>
<td>10</td>
<td>51-139</td>
</tr>
<tr>
<td>9</td>
<td>Carbon nanofiber aerogel</td>
<td>Pyrolysis of bacterial cellulose</td>
<td>129</td>
<td>4-6</td>
<td>106-312</td>
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<tr>
<td>10</td>
<td>Elastic carbon foam</td>
<td>Pyrolysis of melamine sponge</td>
<td>-</td>
<td>5</td>
<td>148-411</td>
</tr>
<tr>
<td>11</td>
<td>Magnetic carbon-based form</td>
<td>Pyrolysis of metal acrylate grafted PU sponge/methyltrichlorosilane coating</td>
<td>152</td>
<td>8.9</td>
<td>up to 102</td>
</tr>
<tr>
<td>12</td>
<td>Polyimide aerogel</td>
<td>Freeze-drying and imidation</td>
<td>128-142</td>
<td>16-200</td>
<td>30-195</td>
</tr>
<tr>
<td>13</td>
<td>Macroporous polystyrene material</td>
<td>Polymerization from Pickering HIPE</td>
<td>122</td>
<td>84</td>
<td>5-33</td>
</tr>
<tr>
<td>14</td>
<td>CMP aerogel</td>
<td>Polymerization and freeze-drying</td>
<td>-</td>
<td>30</td>
<td>20-53</td>
</tr>
<tr>
<td>15</td>
<td>Macroporous polysiloxane-based gel</td>
<td>Polymerization and ambient condition drying</td>
<td>153</td>
<td>120</td>
<td>up to 14</td>
</tr>
<tr>
<td>16</td>
<td>Mercapto-functionalized polydopamine coated melamine sponge</td>
<td>Two-step immersion coating</td>
<td>163</td>
<td>-</td>
<td>79-195</td>
</tr>
<tr>
<td>17</td>
<td>Methyltrichlorosilane coated PU sponge</td>
<td>One-step solution immersion method</td>
<td>157</td>
<td>-</td>
<td>15-25</td>
</tr>
<tr>
<td>18</td>
<td>PDMS-TiO$_2$ coated PU sponge</td>
<td>Sol-gel polymerization</td>
<td>154</td>
<td>-</td>
<td>43</td>
</tr>
<tr>
<td>19</td>
<td>Graphene coated melamine sponge</td>
<td>Dip coating</td>
<td>162</td>
<td>11</td>
<td>54-165</td>
</tr>
<tr>
<td>20</td>
<td>Graphene/PVDF aerogel</td>
<td>Solvothermal method</td>
<td>153</td>
<td>-</td>
<td>20-70</td>
</tr>
</tbody>
</table>


Let et al. reported highly porous boron nitride (BN) nanosheets with the significantly large surface area (1,427 m$^2$ g$^{-1}$) were synthesised by a thermal treatment process (Figure 2.8). These BN nanosheets show superhydrophobic behaviour and exhibit fascinating absorbing performance, which are reusable for oil/water separation through reclamation upon burning in air. Typical works on magnetically controllable oil-absorbing materials are summarised in Table 2.3. $^{93-104}$
Figure 2.8. Oils and organic solutions absorption properties. (a) Gravimetric absorption capacities of the porous nanosheets for five organic solvents and oils. (b) Comparison of the absorption capacities of the porous BN nanosheets with non-porous BN nanosheets, commercial bulk BN particles and activated carbon. (c) Photograph of the set-up for oil absorption tests with white porous BN nanosheets. (d) Photograph of porous BN
nanosheets saturated with oil after 2 min of absorption, inset showing the absorption process after 20 s. (e) Photograph of burning oil-saturated porous BN nanosheets in air for cleaning purpose, inset showing the color change after burning. (f) Photograph of the cleaned nanosheets for second oil absorption test, inset showing the absorption result after 2 min. 

Table 2.3. Magnetically controllable oil-absorbing materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Method</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 PE/steel pellets</td>
<td>Thermal-melt process</td>
<td>Milli/microbeads</td>
</tr>
<tr>
<td>2 Iron powder</td>
<td>-</td>
<td>Powder</td>
</tr>
<tr>
<td>3 Resin/Fe$_3$O$_4$ NPs/oleic acid</td>
<td>Radical polymerization</td>
<td>3D network</td>
</tr>
<tr>
<td>4 Activated carbon/iron oxide</td>
<td>Solution approach</td>
<td>Porous</td>
</tr>
<tr>
<td>5 Activated carbon/clay/iron oxide</td>
<td>Solution approach</td>
<td>Porous</td>
</tr>
<tr>
<td>6 Vermiculite/iron/PS</td>
<td>Reduction/dip-coating</td>
<td>Lamellar</td>
</tr>
<tr>
<td>7 Iron carbide/iron/graphite</td>
<td>Reduction</td>
<td>Micro/nanospheres</td>
</tr>
<tr>
<td>8 Organoclays/iron oxide NPs</td>
<td>In situ coprecipitation</td>
<td>Lamellar/NPs</td>
</tr>
<tr>
<td>9 C/Fe$_2$O$_3$/silane</td>
<td>Thermal decomposition /SAM</td>
<td>NPs</td>
</tr>
<tr>
<td>10 Activated carbon/iron oxide</td>
<td>Solution approach</td>
<td>Porous</td>
</tr>
<tr>
<td>11 PU foam/iron oxide/PTFE</td>
<td>Coating process</td>
<td>Porous</td>
</tr>
<tr>
<td>12 Fe/C</td>
<td>Sintering process</td>
<td>3D macroporous</td>
</tr>
<tr>
<td>13 Collagen/Fe$_3$O$_4$ NP</td>
<td>SAM</td>
<td>Fiber</td>
</tr>
</tbody>
</table>

**2.2.2 Superhydrophilic and underwater superoleophobic materials**

Innovative materials with superhydrophilicity and underwater superoleophobicity have been developed for the effective “water-removing” oil/water separation. A superhydrophilic surface, on which water could fully cover, must display superoleophobicity underwater. Because the water would be trapped into the rough surface
structure of the superhydrophilic surface. Many hydrophilic coatings have been prepared on variant rough substrates to achieve the superhydrophilicity.

Figure 2.9. “Water-removing” type of PAM hydrogel coated mesh for oil/water separation with superhydrophilic and underwater superoleophobic properties. (a-b) Diagrams
illustrate the effect of surface structure on the wetting behaviour of solid substrates in oil/water/solid three-phase systems. Liquid 1 on (a) smooth surface and (b) micro/nanostructured surface in liquid 2 phase. (c-d) SEM images of PAM hydrogel-coated mesh. (e) The surface shows extremely low-oil adhesion even under large preload. (f-g) The separation process of crude oil/water mixtures by utilising the hydrogel coated mesh.\(^{13}\)

Tuteja et al. reported a breakthrough that a hydro-responsive mesh film showed superhydrophilic behaviour in air and underwater superoleophobicity.\(^{105}\) The mesh was prepared through coating fluorodecyl POSS + x -PEGDA (polyhedral oligometric silsesquioxane + x -poly(ethylene glycol) diacrylate) on a stainless-steel mesh. The oil/water separation efficiencies of the membrane could be larger than 90\% even when the droplet size was as small as 1 \(\mu\)m. Xue et al. reported a polyacrylamide (PAM) hydrogel-coated mesh was fabricated by in situ radical polymerisation (Figure 2.9).\(^{106}\) The as-prepared mesh exhibited superhydrophilic and underwater superoleophobic behaviours with an OCA of 155.3\(^\circ\), and with very low adhesion force. The mesh could separate water quickly from the oil and water mixture with high separation efficiency.
Figure 2.10. Structure characterization of nanowire-haired membrane. a) Photograph of a large-scale nanowire-haired membrane. The insets are photographs of a water droplet on the membrane. b) SEM image of nanowire-haired membrane (scale bar: 50 μm). The inset is a low-magnification SEM image with scale bar of 200 μm. c) X-Ray Diffraction (XRD) spectrum of the nanowire-haired membrane. d) and e) The top-view and cross-section SEM images of the nanowire-haired membrane showing the nanowires growing out of the frame of the membrane (scale bar: 5 μm). f) Transmission Electron Microscope (TEM) image of nanowires. (scale bar: 1 μm).

Zhang et al. prepared a Cu(OH)$_2$ nanowire-haired copper mesh by chemical reaction (Figure 2.10).$^{107}$ The as-prepared Cu(OH)$_2$ nanowires are 10-15 μm in length and 200-500 nm in diameters. The separation efficiencies of the mesh membrane for dispersed oil/water mixture are excellent. Moreover, the obtained mesh membrane also shows anti-oil fouling property and alkaline resistance, which are valuable for oil/water separation. Zhang et al. reported a TiO$_2$ mesh was fabricated by the layer-by-layer (LbL) assembly.$^{108}$ The as-prepared mesh shows underwater superoleophobicity with the self-cleaning property that allows for separation oil and water mixture. After oil/water separation process, the
contaminated mesh could be recovered by UV illumination. Dong et al. prepared a hydrophilic graphene oxide (GO) nanosheets coated mesh by dip coating method.\textsuperscript{109} The oil contact angles of the GO coated mesh are all above 150 degrees for various oils. The mesh could separate oil from oil and water mixtures, with up to 98% efficiency and 84 L m\(^{-2}\) s\(^{-1}\) water flux.

Figure 2.11. SEM images of the perforated nitrocellulose (NC) membrane (p-NC-0.5). a) Large-area view of p-NC-0.5 membrane with micropore arrays. b) The higher magnification SEM image of the selected smooth surface of the p-NC-0.5 membrane. c) Enlarged top view of a single pore of the perforated NC membrane. d) Cross-sectional
SEM image of the p-NC-0.5 membrane, in which the tongue-shaped perforated pore can be clearly observed, as indicated by white dash lines. (The arrows indicate other three adjacent pores.)

Gao et al. reported a porous NC membrane was obtained by a perforating method (Figure 2.11). SEM images demonstrated ordered and uniform perforated micropore arrays and 450 nm average pore size of random nanopores distributed on the surface. The obtained membrane showed underwater superoleophobic and high efficiency of oil/water separation due to its hierarchical topography.

Figure 2.12. a) Formation of a superhydrophilic underwater superoleophobic PAA-g-PVDF membrane by a salt-induced phase-inversion process. b) Photograph of an as-
prepared PAA-g-PVDF membrane. c) Cross-section and d) top-view SEM images of the membrane. Photographs of an underwater oil droplet (e) and a water droplet on the membrane (f). The PAA-g-PVDF membrane was prepared by using PAA-g-PVDF with a graft ratio of 2.5 wt% in the case of a salt concentration of 35%.

Zhang et al. reported that a poly-(acrylic acid)-grafted Polyvinylidene fluoride (PVDF) membrane was prepared by a salt-induced phase-inversion method (Figure 2.12). PAA-g-PVDF micelles were assembled during the solvent exchange at the NaCl nucleates in the interface of two solutions. The as-prepared membrane exhibited superhydrophilic and underwater superoleophobic properties due to salt-induced micro/nanoscale hierarchical morphology on the membrane surface.
Ma et al. fabricated a nanofiber-based mesh by hydrothermal treatment for glass powder on stainless-steel mesh (Figure 2.13). The as-obtained mesh shows superhydrophilicity and underwater superoleophobicity to a wide range of oils, such as petroleum, canola oil, pump oil, hexane, and chloroform. The measured WCA and underwater OCA were $0^\circ$ and $153^\circ$, respectively, for water and chloroform. The NF mesh was successfully applied to separate both layered oil/water mixtures and oil-in-water emulsions with good separating ability. Yong et al. reported a simple mechanical drilling process to prepare a wood sheet with microhole array. The as-prepared wood sheet exhibited underwater superoleophobic with ultralow oil adhesion. The wood sheet also showed strong water absorbing ability, which makes it a promising candidate for large-scale oil/water separation.

2.2.3 Combination of superhydrophilicity and superoleophobicity
Logically, the surface tension of water is much larger than that of oils. The materials with both superhydrophilic and superoleophobic materials are hard to prepare due to the contradictory selection of the materials surface energy. Surprisingly, by assembled hydrophobic and hydrophilic molecules, a surface with oleophobicity and hydrophilicity was obtained.

![Liquids on flat and layer-by-layer composite coatings](image)

Figure 2.14. Hexadecane and water droplet deposited on flat and layer-by-layer composite coatings.\textsuperscript{114}

Brown et al. reported a superhydrophilic and superoleophobic coated stainless steel mesh was prepared by combining polyelectrolyte-fluorosurfactant complex with SiO\textsubscript{2} nanoparticles by the layer-by-layer spray (Figure 2.14).\textsuperscript{114} The fluorosurfactant coating
resulted in a low and high surface tension group, which enables the mesh to trap large oil molecules on the surface and allow water molecules to penetrate.

2.2.4 Stimuli-responsive materials for oil/water separation
Figure 2.1. a) An apparatus with a liquid column of water-in-hexadecane emulsion above the membrane before applying an electric field. b) The water in-hexadecane emulsion is demulsified into the water-rich and the hexadecane-rich phases upon applying an electric field. c) After the onset of demulsification, water-rich permeate passes through while hexadecane-rich retentate is retained above the membrane when a voltage $V \approx 2.0$ kV is applied. d) An apparatus used for continuous separation of water-in-hexadecane emulsions. Water-rich permeate passes through the membrane module at the bottom, while hexadecane-rich permeate passes through the hydrophobic and oleophilic membrane on the side-wall. In (a-d) water is dyed blue and hexadecane is dyed red. e) TGA data for the water-rich and hexadecane-rich permeates.\textsuperscript{115}

Moreover, a variety of responsive materials for oil/water separation have also been studied.\textsuperscript{115-118} Ou et al. reported a thermo-responsive polymer membrane was prepared by incorporation poly(N-isopropylacrylamide) (PNIPAM) to an elastic polyurethane (TPU) microfiber web.\textsuperscript{117} By changing the small range temperature of membrane from 25 to 45 °C; the TPU-PNIPAM membrane could be switched from superhydrophilicity to superhydrophobicity. A high efficient oil/water emulsion separation processes can be achieved by using the flexible TPU-PNIPAM membrane at both temperatures. Won et al. reported voltage-controlled membrane-based operation was established for oil/water separation with $\geq 99.9\%$ separation efficiency (Figure 2.15).\textsuperscript{115} The nylon membrane with re-entrant texture was dip-coated with fluorodecyl POSS + PDMS for half an hour. Wang et al. presented a pH-responsive copper mesh film was fabricated by a series of experiments, including electrochemical deposition, Au sputter-coating and a thiol mixture of HS(CH$_2$)$_9$CH$_3$ and HS(CH$_2$)$_{10}$COOH coating.\textsuperscript{118} The as-prepared mesh film exhibits superhydrophobicity for the neutral and acidic droplets and superoleophilicity in the air
while superhydrophilicity for the basic droplets and underwater superoleophobicity. It’s demonstrated that the controllable separation process of water and oil mixture was successfully conducted by tuning the pH value of the solution.

2.3 Superwettability for water harvesting
Figure 2.16. Summary of animal and plant species found to collect water from fog. A combination of chemistry and structuring results in interception of water from fog and transport to the mouth, roots or another area where it can be used.\textsuperscript{119}
Water/fog harvesting is a subject of high importance because it has practical application for resolving the problem of severe water shortages in drought region. Natural organisms have unique characteristics that help them survive in harsh environments. For example, the Namib Desert beetles, spider web, cactus, have adopted water harvesting features as shown in Figure 2.16. Inspired by these biological features, various materials have been synthesised with water harvesting abilities.

2.3.1 Namib Desert beetle inspired materials

Figure 2.17. The water-capturing surface of the fused overwings (elytra) of the desert beetle *Stenocara*. a) Adult female, dorsal view; peaks and troughs are evident on the surface of the elytra. b) A ‘bump’ on the elytra, stained with Red O for 15 min and then with 60% isopropanol for 10 min, a procedure that tests for waxes. Depressed areas of the otherwise black elytra are stained positively (waxy, colored), whereas the peaks of the bumps remain unstained (wax-free; black). c) Scanning electron micrograph of the textured surface of the depressed areas. Scale bars, a, 10 mm; b, 0.2 mm; c, 10 mm.

Parker and Lawrence discovered 0.5 mm diameter bunches on the elytra of Namib Desert beetle (*Stenocara*) with an interval of 0.5-1.5 mm (Figure 2.17). The bumpy back
surface contains hydrophilic (non-waxy) and hydrophobic (wax-coated) areas. The hydrophilic area trapped the water from fog and allow water droplet growing up. After the weight of the water droplet is larger than the adhesion force, the droplet would roll down the Stenocara’s back which could collect water from early morning fog

Inspired by this desert beetle, various surface materials with hydrophilic and hydrophobic pattern have been fabricated. Thickett et al. reported biomimetic, micropatterned surface coatings with structural and chemical features were fabricated by dewetting thin polymer films to obtain a hydrophobic surface with hydrophilic bumps. The water capturing ability was optimized through controlling the surface morphology and bump density.

Wang et al. prepared a composite surface with patterned wettability by the thermal-pressing method of the 1H,1H,2H,2H-perfluorodecanethiol modified gauze and the polystyrene plane sheet. The as-prepared surface mimicked the back of Stenocara beetles with hydrophilic-superhydrophobic patterned hybrid surfaces exhibit outstanding fog harvesting performance.
Figure 2.18. Schematic illustration of the fabrication process of bioinspired surfaces with star-shaped wettability patterns, superhydrophilic surface composed of TiO$_2$ nanoparticles (a), superhydrophobic surface modified with FAS (b), and bioinspired gradient surface with a star-shaped wettability pattern (c). SEM images of the surface structures on the TiO$_2$ film from the top view (d) and side view with a thickness of ~19.2 mm (e). Optical images show the superhydrophilic properties on an unmodified TiO$_2$ film with CA $\approx$ 51 (f) and the superhydrophobic properties on a FAS-modified TiO$_2$ film with CA $>$ 1501 (g). Fog-collecting efficiency of different wettable surfaces (h).$^{131}$
Bai et al. reported star-shaped wettability patterns were prepared on the superhydrophobic TiO$_2$ surface with selective UV light illumination with photomasks (Figure 2.18). By comparing various patterned surface such as circle patterned, uniformly superhydrophilic, and uniformly superhydrophobic, the as-prepared star-shaped pattern was found to exhibit better water collection efficiency which implicated in both surface energy gradient and Laplace pressure gradient.

2.3.2 Cactus inspired materials

Figure 2.19. Appearance and surface structures of the cactus. (a) Optical image of a plant of *O. microdasys* stem covered with well-distributed clusters of spines and trichomes. (b,c) Magnified optical images of a single cluster with spines growing from the trichomes in the
top (b) and side (c) view. (d) SEM image of a single spine divided into three regions, the tip (e) with an apex angle (2a) and oriented barbs, the middle (f,g) with gradient grooves, and the base with belt-structured trichomes. (f,g) Magnified images of regions near the base and the tip of the cactus spine, respectively. The microgrooves near the base are wider and sparser than those near the tip. (h) Magnified image of a single barb with an apex angle (2b) covering the tip of the spine (e). Scale bars, 5 cm (a), 500 mm (b,c), 100 mm (d), 20 mm (e-g) and 2 mm (h).133

Ju et al. discovered a water harvesting system in one of the cactus (Opuntia microdasys) (Figure 2.19).133 The bundles of spines and trichomes were distributed uniformly on the surface of the cactus. Each bundle is composed of barbs, grooves and trichomes, which have different functions in water harvesting process. By integrating multi-function structures, the gradient of the surface energy and Laplace pressure, the cactus’ water harvesting system can collect tiny water droplets on spine, transport big droplets along the grooves and absorb the water droplets to the trichomes, demonstrating excellent water harvesting efficiency. Following on, Ju and co-workers discovered cone-arrayed surface on the cactus stem and fabricated PDMS cone patterns.134 The hexagonal-patterned cone-arrayed surface was found to exhibit more efficient water harvesting performance than the tetragonal one.

Cao et al. prepared a cactus-inspired conical micro-tip patterned surface by a modified magnetic particle-assisted molding using PDMS and cobalt particles under the magnetic field.135 A continuous fog collector was assembled with the micro-pattern surface on a hydrophilic cotton surface. The water collection efficiencies of the collector are about 0.2, 0.3, and 0.5 mL/min under the fog velocities at ~25, ~48 and ~70 cm/s, respectively.
2.3.3 Spider silk-inspired materials

Figure 2.20. Artificial spider silk that mimics the structure and water collection capability of natural spider silk. a, Optical image of spindle-knot/joint structure with periodicity of $394.6 \pm 16.1 \mu m$. b-d, SEM images of a spindle-knot (b), a stretched porous structure on the joint (c) and a random porous structure on the spindle-knot (d). e-j, Directional water collection on artificial spider silk. When the artificial spider silk is placed in the mist at 0 s, tiny water drops randomly condense on the artificial spider silk at 7.708 s (e), and then directionally move from joint to spindle-knot with the volume increasing from 7.955 s to 8.717 s (f-j).
Zheng and co-workers discovered that the silk fibre of the cribellate spider *Uloborus walckenaerius* had surrounded by periodic puffs and joints, which could rebuild its fibre structure in a humid environment (Figure 2.20).\(^3\) The wet-rebuilt silk fibre had periodic spindle-knots with 85 \(\mu\)m apart. Then the artificial spider silk with about 400 \(\mu\)m apart periodic spindle-knots was fabricated. The diameters of the spindle-knots were about 21 and 43.7 \(\mu\)m and the diameters of the joints were about 6 and 13.5 \(\mu\)m for the cribellate spider silk and man-made spider silk, respectively. The structure integration led to the surface energy gradient and Laplace pressure differences between the spindle-knots and the joints, which plays a key role in directional water harvesting ability.

Yang et al. presented a sponge-like cotton fabric was fabricated by a surface-initiated atom transfer radical polymerisation method.\(^1\) It was demonstrated that the average diameter of the as-prepared PNIPAAm-cotton fabric is 800 nm. The fabric could be switched in between superhydrophobicity and superhydrophilicity using temperature control in a small range (16 to 32 °C), which showed an excellent water harvesting capability. Thakur et al. reported three different membranes were fabricated by electrospinning based on pristine (PNIPAM fibres, pristine PVDF) fibres, and PNIPAM-PVDF bead-on-string fibres.\(^1\) It was observed that the surface of PNIPAM and PVDF membranes were smooth, while the PNIPAM-PVDF membrane showed hierarchical structure. The maximum water collection rate on the PNIPAM-PVDF membrane was measured to be 1150 mg cm\(^{-2}\) h\(^{-1}\) at 25 °C and 909 mg cm\(^{-2}\) h\(^{-1}\) at 40 °C.

### 2.4 Room temperature gallium-based liquid metals wettability and their applications
Room temperature liquid metals have recently attracted much attention as the only materials that have both metallic and fluidic properties. Mercury is the one of liquid metal, but it is toxic. Gallium and its alloys are low toxic, which promise practical applications. Benefit on these liquid property, these metals offer potential opportunities for electronics that are soft, flexible, stretchable, and even reconfigurable. The ability to pattern materials into individual electronic components in various material surfaces is required for manufacturing electronic devices. Liquid metals as the key component of deformable systems are used. Figuring out how the interface between the liquid metals and different patterned and material surfaces under different conditions is critical.

### 2.4.1 Room temperature liquid metals wettability

Table 2.4. Contact angles of galinstan on different materials in oxygen content below 0.5 ppm.\(^{138}\)

<table>
<thead>
<tr>
<th>Type</th>
<th>Material</th>
<th>Contact Angles $\theta_{a}^{R}$</th>
<th>Contact Angles $\theta_{r}^{R}$</th>
<th>Contact Angles $\theta_{a}^{R} - \theta_{r}^{R}$</th>
<th>Surface Roughness $R_{a}$/nm</th>
<th>Surface Roughness $R_{r}$/nm</th>
<th>Surface Roughness $R_{max}$/nm</th>
<th>Surfaces Area Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductor</td>
<td>Tungsten</td>
<td>161.3</td>
<td>119.6</td>
<td>41.7</td>
<td>3.31</td>
<td>2.54</td>
<td>27.27</td>
<td>0.13%</td>
</tr>
<tr>
<td>Insulator</td>
<td>Silicon nitride</td>
<td>147.0</td>
<td>126.1</td>
<td>20.9</td>
<td>1.38</td>
<td>1.09</td>
<td>13.43</td>
<td>0.37%</td>
</tr>
<tr>
<td></td>
<td>Glass</td>
<td>146.8</td>
<td>121.5</td>
<td>25.3</td>
<td>2.05</td>
<td>1.38</td>
<td>30.2</td>
<td>0.30%</td>
</tr>
<tr>
<td>Polymer</td>
<td>Parylene</td>
<td>146.3</td>
<td>112.6</td>
<td>33.7</td>
<td>13.48</td>
<td>9.02</td>
<td>105.37</td>
<td>0.85%</td>
</tr>
<tr>
<td></td>
<td>Teflon(^{x})</td>
<td>161.2</td>
<td>144.4</td>
<td>16.8</td>
<td>2.04</td>
<td>1.62</td>
<td>21.03</td>
<td>0.59%</td>
</tr>
<tr>
<td>Mica</td>
<td>Phlogopite</td>
<td>148.0</td>
<td>124.5</td>
<td>23.5</td>
<td>1.97</td>
<td>1.59</td>
<td>13.57</td>
<td>0.23%</td>
</tr>
<tr>
<td></td>
<td>Muscovite</td>
<td>163.6</td>
<td>148.1</td>
<td>15.5</td>
<td>1.02</td>
<td>0.82</td>
<td>7.64</td>
<td>0.11%</td>
</tr>
</tbody>
</table>

Table 2.4 shows the CAs of galinstan on various type of solid surfaces such as Tungsten, Si$_3$N$_4$, glass, parylene, Teflon, phlogopite and muscovite.\(^{138}\) The roughness information of the surface was measured by AFM. The advancing and receding CAs of galinstan on Tungsten substrate were 161.3° and 119.6°, which showed the largest CA hysteresis of 41.7°. The advancing CAs of galinstan on Teflon and muscovite were
161.2° and 163.6°, respectively. The CA hysteresis of galinstan were 20.9°, 25.3°, 33.7°, 16.8°, 23.5° and 15.5° for Si₃N₄, glass, parylene, Teflon, phlogopite and muscovite, respectively. So, it was demonstrated all the tested surfaces could not be wetted by galinstan when the oxygen content was below 0.5 ppm.

Liu et al. also observed that the unexpected results of advancing and receding CAs of galinstan on the glass in ambient air are 165° and 7°, respectively, compared with the contact angles of 146.8° and 121.5° on the glass in oxygen content below 0.5 ppm, respectively (Figure 2.21). This is because an oxide skin is formed on the galinstan surface in the oxygen environment, and the skin is thin and sticky. All the material surfaces could

Figure 2.21. Three-phase contact regions of Galinstan on glass in ambient air (~20.9% oxygen). (a) Advancing angle. (b) Near receding angle. Pinning of the oxide skin causes the receding angle to be very low. Both (a) and (b) include an inset showing the larger field of view. The measurement of receding CA ended prematurely when the droplet was separated from the top needle.\textsuperscript{138}
be wetted by the oxide skin of the galinstan. The surface tension of galinstan (534.6 mN/m) was tested by the pendant-drop method in a nitrogen atmosphere at 28 °C.
Figure 2.22. (a) Schematic and (b) FIB secondary electron images of GaInSn dewetting during Ga⁺-induced fracturing of top oxide shell on OTS-coated nanograss surface at vacuum level of 0.13-1.3 mPa, (c) corresponding SEM images showing the residual oxide film attached to the nanograss; advancing and receding contact angles of GaInSn on OTS-coated (d) micropillar and (e) nanograss superhydrophobic surfaces using the volume variation method in air at 98 kPa.\textsuperscript{20}

Doudrick et al. studied interface behaviours of room temperature gallium based liquid metal and substrate; they proposed two modes to explain why galinstan could wet or non-wet the solid surfaces (Figure 2.22).\textsuperscript{20} In the first mode, the oxide skin of galinstan was not damaged when galinstan made contact with the substrate. The liquid metal could not wet most of the solid surfaces due to the nanoscale roughness of the oxide skin, which is independent of the surface energy or morphology of substrate. Secondly, if the oxide skin is fractured, a complicated interface was formed including old oxide skin, new oxide skin, bare liquid metal and the substrate surface. The liquid metal could wet the substrate surface due to the adhesion between the new oxide skin and the substrate surface.
Figure 2.23. (a) An eutectic Gallium-Indium (eGaIn) droplet on a surface of indium foil (100 μm thick) that has been sputter coated with indium for 2 min. The droplet does not wet the surface. (b) An eGaIn droplet on a surface of indium foil (100 μm thick). The droplet rapidly wets in seconds. (c) A galinstan droplet on a surface of tin foil (20 μm thick). The droplet wets the surface slowly over a period of days, demonstrating reactive wetting. Scale bar in each image is 1 mm in length.139

Kramer et al. presented wetting behaviours between room temperature gallium based liquid metals and thin films of In and Sn (Figure 2.23).139 For the various surfaces such as indium coated Si substrate, indium foil, indium coated tin foil and tin foil, the eGaIn only wetted the indium foil. The contact angle of eGaIn reduced rapidly from 140° to 10° in 8.2 seconds. On the other hand, galinstan only wetted the tin foil. The contact angle of galinstan reduced from 145° to 20° in 4 days. The wettability of gallium based liquid metals could be influenced by both surface component and morphology.
Figure 2.24. Contact angle of Galinstan droplets on (a, b) a bare glass slide, (c, d) Cytop-coated glass slide, and (e, f) Teflon-coated glass slide, before (panels a, c, and e) and after (panels b, d, and f) the hydrochloric acid (HCl) vapor treatment.\textsuperscript{140}

Kim and co-workers solved the adherent oxide skin problem on the surface of the gallium-based liquid metal in the air by using HCl vapor treatment (Figure 2.24).\textsuperscript{140} The contact angles of galinstan droplet were 127.6°, 129.8° and 140.3° on a glass substrate, Cytop-coated surface, and Teflon-coated surface, respectively. The presence of the oxide skin also led to the irregular shape of the droplets. After the HCl treatment, the contact angles of galinstan droplet increased to 139.5°, 148° and 152.5° on these substrates. The
shape of the galinstan droplets became spherical. The oxide skin mainly was gallium oxide. It was removed because it reacted with HCl vapor and transformed to gallium chloride which is not an adherent material. After the HCl treatment, the galinstan drop could bounce off on a Teflon-coated surface, which indicated the non-wetting property of the liquid metal in an ambient environment.

2.4.2 Emerging studies of liquid metals featuring surface tension manipulation

![Figure 2.25](image)

Figure 2.25. The electric-field-induced transformations of liquid metal objects in water. a) Schematic for electric-field-induced transformation from a pool of liquid metal into a sphere. b) Snapshots of liquid metal transformation from the original flattened state 1 to intermediate states 2 and 3 and finally to a sphere 4. c) Sequential transformation for a circular sheet of liquid metal film to change from its initial flattened state 1 to intermediate states 2 and 3 and finally to a sphere 4. d) Schematic for electric-field-induced merging of two separate spheres into a single one. e) Snapshots of the process in which two separate
droplets combine into a fused sphere from state 1 to state 4. f) The area versus time curve for the transition from the original liquid metal film to a sphere in (c).\textsuperscript{141}

Sheng et al. discovered a series of room temperature liquid metal phenomena by manipulating the surface tension of liquid metal under an electric field, including self-rotation, rapid merging, planar locomotion and transformation from a liquid metal film to a tiny drop.\textsuperscript{141} As shown in Figure 2.25, once the voltage was applied, the puddle of liquid metal was gathered together rapidly. In addition, a thin liquid metal film flowed from the anode to the cathode, and eventually gather at the cathode to form a liquid metal drop. The surface area of liquid metal decreased dramatically to roughly a thousand times smaller in size.
Figure 2.26. Spreading enabled by a surface oxide. (A) Oxidative spreading of a bead of liquid metal in 1 M NaOH solution. (Left) A needle serves as a top electrical contact to the droplet. (Right) A wire serves as a bottom electrical contact to the droplet. (A, i) The drop assumes a spherical shape initially due to its large surface tension; (A, ii) upon application of an oxidative potential, the metal assumes a new equilibrium shape; (A, iii) above a critical potential, the metal flattens and spreads without bound and ultimately forms fingering patterns that further increase its surface area and destabilising the metal. (B-D) The unshaded region denotes oxidative potentials. (B) The areal footprint of a drop of eGaIn as a function of time and potential identifies the critical potential above which spreading occurs without bound (solid circles) and below which the droplet adopts equilibrium shapes (hashed symbols). (C) An electrocapillary curve of eGaIn measured by sessile drop profile in 1 M NaOH. (D) A cyclic voltammogram of eGaIn. (E) The measured capacitance and calculated capacitive energy of eGaIn from impedance spectroscopy.  

Tsai et al. first showed that a liuqid gallium droplet was transformed from a spheroid shape to a thin film by an applied voltage. Khan and co-workers reported that the interfacial tension of a liquid metal could be manipulated rapidly and reversibly by using modest voltages. The surface tension of liquid metal could be tuned in the range of ~500 mJ/m² to near zero, lead to the manipulation of the liquid metal shape. As shown in Figure 2.26, the galinstan became flat and spread greatly in NaOH solution under an applied voltage. Moreover, a couple of phenomena and applications were demonstrated, which indicate that the ability to control the interfacial properties of the liquid metal raises extraordinary opportunities in microfluidics and electronics.
Figure 2.27. Oscillation behavior of copper wire in liquid metal machine. a) Top down view (scale bar, 5 mm). b) Side view (scale bar, 5 mm). c) Position of the copper wire during one period. d) Time evolution of the copper wire during 3 s.\textsuperscript{144}

Yuan et al. demonstrated the spontaneous oscillation phenomenon of a copper wire in aluminum granules inserted-liquid metal droplet under a extend magnetic field in NaOH solution, reminiscent of playing the violin.\textsuperscript{144} Figure 2.27a and b showed the top view and side view of the basic cycle of wire oscillation which the period is about 0.8 s. The driving
force came from hydrogen generation at the wire surface on which Aluminum was deposited.

Figure 2.28. Working mechanism of the liquid metal enabled pump. (A) Schematic of the experimental setup, the overall polymethylmethacrylate (PMMA) channel length is 65 mm and the gap between the electrodes is 40 mm. (B) Schematic of the Galinstan droplet surface charge distribution when placed in the droplet chamber filled with NaOH solution. (C) Schematic of the Galinstan droplet surface charge distribution when an electric field is applied between the graphite electrodes. (D) Sequential snapshots for the pumping effect of a Galinstan droplet with 2.7-mm diameter in the PMMA channel filled with NaOH solution (0.3 mol/L), while a square wave signal (200-Hz, 5 V_{pp}, 2.5-V DC offset and 50%
duty cycle) is applied between the two graphite electrodes. A droplet of dye is used to demonstrate the pumping effect.145

Tang and co-workers developed a gallium-based liquid metal pumping system in various kinds of PMMA channels under an electric field.145 NaOH solutions were filled in the channel, which could remove the oxide layer of the galinstan. One of the experimental setups was shown in Figure 2.28a. Without an electric field, the galinstan droplet had a uniform electric double layer. After applied the electric field, the unbalance electric double layer induced the liquid flow. A high flow rate of 1800 μL/min was obtained in 0.3 mol/L NaOH solution with 200-Hz, 5V_{p-p} square wave with 2.5 V DC offset, as shown in Figure 2.28d.
Chapter 3 Experiments

3.1 Experimental preparation

3.1.1 Fabrication of NiO/Ni mesh

NiO/Ni meshes with micro/nanoscale hierarchical structure were fabricated by a simple heat treatment process. We have used two different types of nickel meshes, one of which has a pore size of about 25 μm and the other type is with a very small pore size. Both nickel meshes are composed of parallel staggered mesh made from nickel fibres with a diameter of approximately 50 μm. In a typical procedure, the neat nickel meshes (25 mm × 25 mm) were sequentially cleaned with detergent, deionized water, ethanol, acetone, and deionized water before being dried at 80 °C for 1 h. A tube furnace was preheated to 1000 °C and kept at this temperature. The NiO/Ni meshes were prepared via heat treatment in the tube furnace at 1000 °C under atmosphere for 10 minutes. After that, the nickel/nickel oxide meshes were quenched in the air at room temperature. The original untreated nickel meshes have a metallic lustre, while the treated meshes are black in color.

3.1.2 Fabrication of the patterned superhydrophilic/superhydrophobic surface

First, a superhydrophobic coating was applied on the acrylic diffuser plastic as the starting material of the substrates for the experiments, using a commercially available superhydrophobic silica poly(dimethylsiloxane) (PDMS) aerogel particle spray (Rust-Oleum Neverwet) according to the manufacturer’s instructions. After 24 hours of drying,
the substrates were coated by Pt nanoparticles through pulsed laser deposition. The as-prepared samples were superhydrophobic with a low sliding angle. Secondly, a hydrophilic layer was coated on these substrates by pulsed laser deposition using a neodymium-doped yttrium aluminum garnet (Nd: YAG) laser with an output wavelength of 355 nm. A Pt target was used for coating. Before deposition, stainless steel meshes with various mesh numbers (#150, #200, and #300) were placed on the substrates as masks. The depositions were performed at room temperature under the following conditions: a vacuum level of \( \sim 8.9 \times 10^{-4} \) Pa, the laser power is 2 W, the distance between target and substrate is 7 cm, and the deposition time is 20 minutes.

3.1.3 Experimental setup of galinstan heart beating

A galinstan droplet was placed in a glass vessel (diameter of 9 cm) with 0.5 mol/L NaOH solutions at room temperature. A piece of blue reference paper was placed under the vessel. A copper wire anode was connected to a graphite ring, which had an inner diameter of 10 mm and an outer diameter of 30 mm. The galinstan droplet was placed in the graphite ring and touched its inner wall. A copper wire cathode was placed in the solution. The applied DC voltages were supplied from 0 to 5 V by a GW laboratory DC power supply, model GPS-1850.

3.1.4 Experimental setup of liquid metal patterning

Galinstan films were prepared on an insulated, transparent vessel. About 20-50 μL of galinstan was put into the vessel to form a liquid metal film. The 0.01 mol/L NaCl solutions was made using a 99% NaCl commercial solution and deionized water. The liquid metal hole formation processes were recorded using a video camera. In the
experiments, about 30 mL of 0.01 mol/L NaCl solution was added to the vessel. A copper wire anode (0.1 mm in diameter and 7 cm in length) and three conductive polymer electrodes in different geometric shapes were placed above the top center of the liquid metal film at a distance of h.

3.1.5 Experimental setup of liquid metal penetration and wall-climbing effects.

Penetration effect: A container of 1 mol/L NaOH solution was prepared as the electrolyte at room temperature. A sponge was fixed in a plastic holder, which was put into the container and submerged in the NaOH solution electrolyte. After a 150 μL droplet of galinstan was set on the sponge, two copper wires each with a diameter of 0.5 mm were used, one connected to the electrolyte and the other connected to the galinstan. The applied DC voltages across the two copper wires were supplied from 0 to 20 V by a GW laboratory DC power supply (model GPS-1850).

Wall-climbing: A container of 1 mol/L NaOH solution was prepared at room temperature. A small transparent container was placed in the container and submerged in the solution. A given amount of galinstan was initially placed in the small container. Two copper wires each with a diameter of 0.5 mm were used, one connected to the electrolyte and the other connected to the galinstan.
3.2 Experimental equipment

3.2.1 Vertical tube furnace

Figure 3.1. The vertical tube furnace VF-1800 from Crystal Systems Corporation.

The vertical tube furnace VF-1800 (Figure 3.1) is designed for sintering materials with a maximum operating temperature of 1800 °C. The size of the furnace is 760 mm in height and 400 mm in diameter. The alumina ceramic insulation structure on the chamber allows the temperature in the furnace to be more stable. The single heating zone is managed
by a PID temperature controller with a maximum heating rate of 5 °C/min and a maximum cooling rate of 10 °C/min.

3.2.2 Scanning Electronic Microscopy (SEM)

The Scanning Electron Microscope is a type of electron microscope that images the sample surface by scanning it with a high energy beam of electrons. It consists of an electron optical column, a vacuum system, and various electronics. The electron gun at the top of the column produces a high energy electron beam, which is focused down to a fine spot (< 4 nm in diameter) on the specimen. This beam is scanned in a rectangular raster pattern over the specimen. Secondary electrons are produced on the specimen surface and are detected by a suitable detector. The amplitude of the secondary electron signal varies with time, according to the topography of the specimen surface. Then, the signal is amplified and used to display the corresponding specimen surface information.

In SEM, the magnification is totally determined by the electronic circuitry that scans the beam over the specimen’s surface. Magnification can be as high as 300,000x, which is usually more than sufficient. In principle, the resolution of an SEM is determined by the beam diameter on the surface of the specimen. However, the practical resolution depends on the properties of the specimen, the specimen preparation technique, and also on many instrumental parameters, such as the beam intensity, accelerating voltage, scanning speed, a distance of the lens from the specimen’s surface, and the angle of the specimen concerning the detector, etc. Under optimum conditions, a resolution of 1 nm can be achieved.
In this thesis, SEM images were performed using a JEOL JSM-6700F (Japan) scanning electron microscope (acceleration voltage 15 kV).

3.2.3 Contact angle measurement

![Contact angle measurement](image)

Figure 3.2. An OCA-15EC contact angle machine from DataPhysics, Germany.

Contact angle measurement is the preferred and most accurate method of much vital laboratory measurement and research for determining the interactions at the solid/gas/liquid interface. Video-based optical contact angle measuring instrument (OCA-15EC) mainly consists of the linear stage, Charged Coupled Device (CCD) video camera, the electronic multiple dosing system, as shown in Figure 3.2. The cross-sectional image of the sessile droplet is taken by the CCD. The contact angle can be calculated by the built-in software automatically with an accuracy of ± 0.1°.
In this thesis, contact angles were measured on an OCA-15EC machine (Data-Physics, Germany). At least five different positions were measured then averaged to obtain a reliable value for the sample.

### 3.2.4 Adhesion force measurement

The underwater oil-adhesion force was dynamically measured; an oil droplet on a wire loop was vertically placed in contact with the surface and then moved away from the surface in an upwards direction. The adhesion force between the oil and the surface was recorded using a highly sensitive microelectromechanical balance system. An oil droplet came into contact with the mesh surface and was squeezed, before being moved away from the surface.

### 3.2.5 Pulsed Laser Deposition (PLD)

Pulsed Laser Deposition is a widely used thin film deposition technique that is employed to fabricate thin films in various forms, including ultra-thin films, multi-layer thin films, etc. With this technique, multi-component materials can be ablated from the target and deposited onto a substrate to form stoichiometric layers, which will have the same chemical components as the target material.
PLD relies on a high-power laser (Figure 3.3) to create an ejected plume of material from a target. The vapour (plume) is collected on a substrate placed at a short distance from the target. Although the physical processes of material removal are quite complex, as an approximation, the ejection of material occurs due to the rapid explosion of the target surface due to superheating. Unlike thermal evaporation, which produces a vapour composition dependent on the vapour pressures of the elements in the target materials, the laser-induced expulsion produces a plume of material with stoichiometry similar to that of the target material. It is generally easier to obtain the desired film stoichiometry for multi-element materials using PLD than with other deposition techniques.
3.2.6 3D printer

Figure 3.4. Me3D 3D printer.

3D Printing is the process of continuously adding layers of material with a computer controlled device to create a three-dimensional object. It’s more broadly known as the additive manufacturing because you add material to make a part, rather than cut it away from a piece of stock. Modern printers are becoming more versatile though, producing finished products, prostheses, biomaterials, even jet engine and rocket parts. The impact
and applications of 3D printing are rapidly growing as more people are exposed to the technology.

In this thesis, the conductive polymer electrodes and the plastic holders were fabricated by using a 3D printer (Me3D, Australia) (Figure 3.4).
Chapter 4. A novel reusable superhydrophilic NiO/Ni mesh produced by a facile fabrication method for oil/water separation

4.1. Introduction

Oil spills and wastewater discharges released during the sinking of oil tankers and ships or untreated household wastewater are catastrophic for marine and other aquatic ecosystems and for local residents’ health. The Gulf of Mexico oil spill in 2010 was one of the largest offshore oil spill accidents in the history of the oil industry and is an unprecedented environmental disaster.\textsuperscript{146-148} The growing environmental and economic concerns related to this issue have highlighted the need for materials that can effectively separate oil and water.\textsuperscript{105, 149, 150}

The present implemented techniques, including dissolved air flotation, distillation, centrifugation, electrophoresis, and pressure filtration, are widely used for oil/water separation. They consume a great deal of energy during the separation process, however, with low efficiency and high cost. Therefore, it would be very desirable to develop alternative approaches for highly efficient, low energy consuming, and cost-effective oil/water separation, specifically, those driven by gravitational force.

Oil/water separation based on materials’ special wettability is a highly promising method.\textsuperscript{151-155} Oil removal techniques using superhydrophobic and superoleophilic
materials are a successful example of introducing materials’ special wettability into the field of oil/water separation using oil filtration and absorbents. Meshes coated with superhydrophobic and superoleophilic materials were reported to be capable of successful oil/water separation.\textsuperscript{53, 63} The meshes are easily fouled or even blocked by oils, however, because their intrinsic oleophilic property affects the separation efficiency. Interestingly, water-removing materials with both superhydrophilic and superoleophobic properties show more advantages in oil/water separation. A superhydrophilic and underwa superoleophobic hydrogel-coated mesh can selectively and effectively separate oil/water mixtures, such as mixtures of water with vegetable oil, gasoline, diesel, and even crude oil.\textsuperscript{106} Other types of separators based on nanoparticles,\textsuperscript{92, 103} porous foams\textsuperscript{156, 157} and membranes\textsuperscript{105, 107, 110, 158-161} with coatings of superhydrophobic/superoleophilic or superhydrophilic-/superoleophobic materials have been reported for oil/water separation. The mesh type separators have advantages for large-scale oil/water separation compared to foams, membranes, and particles.

It should be noted that most of the coating materials are organic;\textsuperscript{71, 106, 162} they are unstable when exposed to harsh conditions and not reusable. Therefore, there is a great need to design stable materials or meshes for practical applications in oil/water separation. To fulfil the requirements of large-scale production, we propose the following criteria for ideal water-oil separation in harsh environments: 1) temperature resistant; 2) durability; 3) chemically stable; 4) flexible; 5) low-cost. To meet these criteria, the selection of the materials for both the coating and the mesh are critical. Hence, it is preferable to choose metal oxides for coatings, as they are very stable in air, water, and oil at high temperature. The use of stainless steel meshes coated with a ZnO layer for oil/water separation has
already been reported, although these meshes are not ideal for practical application due to the complex coating process and the poor mechanical strength of the coating layer.

In this work, we chose nickel mesh as the framework, because of its low cost, wide availability, chemical and mechanical robustness, and inherent fibrous microscale structure. NiO/Ni meshes with micro/nanoscale hierarchical structure can be easily fabricated using a simple heat treatment. The NiO/Ni mesh shows superhydrophilic and underwater superoleophobic properties and exhibits superior oil/water separation performance under harsh conditions with high efficiency and reusability.

4.2. Experimental section

4.2.1. Fabrication of NiO/Ni mesh

NiO/Ni meshes with micro/nanoscale hierarchical structure were fabricated by a simple heat treatment. We have used two different type of Ni meshes. One has a pore size of about 25 μm and the other has a very small pore size. Both nickel meshes are composed of parallel staggered mesh made from nickel fibres with a diameter of approximately 50 μm. In a typical procedure, the neat nickel meshes (25 mm × 25 mm) were sequentially cleaned with detergent, deionized water, ethanol, acetone, and deionized water before being dried at 80 °C for 1 h. A tube furnace was preheated to 1000 °C and kept in this temperature. The NiO/Ni meshes were prepared via heat treatment in the tube furnace at 1000 °C under an ambient atmosphere for 10 mins. After that, the nickel/nickel oxide meshes were quenched in air at room temperature. The neat nickel meshes have a metallic lustre, while the treated meshes are black in colour.
4.2.2. Instruction and characterization

SEM images were obtained using a JEOL JSM-6700F (Japan) scanning electron microscope (acceleration voltage 15 kV). Optical microscopy images were collected on a MTI microscope (US). Contact angles were measured on an OCA-15EC machine (Data-Physics, Germany) at ambient temperature. Dichloromethane (about 4 μL) droplets were dropped carefully onto the surface of the NiO/Ni meshes, which were immersed in water. At least five different positions were measured and averaged to obtain a reliable value for the same sample. The underwater oil-adhesion force was dynamically measured; an oil droplet on a wire loop was vertically placed in contact with the surface and then moved away from the surface in an upwards direction. The adhesion force between the oil and the surface was recorded using a highly sensitive microelectromechanical balance system. An oil droplet comes into contact with the mesh surface and is squeezed, before being moved away from the surface.

4.2.3. Oil/Water Separation Experiments

The as-prepared pre-wetted NiO/Ni mesh was fixed between a glass tube and a beaker. The diameter of the tube was 20 mm. A mixture of water and oil was poured slowly onto the NiO/Ni mesh. The separation was achieved by the weight of the liquids. Then, the separated oil and water were collected in the glass tube and the beaker, respectively. Several oil/water mixtures were prepared by mixing pure water/sea water and oil (namely, petrol, paraffin oil, vegetable oil, and hexane) with and without sand and soil.

4.3. Results and discussion
Figure 4.1. (a-b) SEM images of a neat Ni mesh surface at low and high magnification.

Figure 4.2. (a-d) SEM images of a NiO/Ni mesh surface at low and high magnification, with the inset photograph in (a) showing the bendable of the NiO/Ni mesh.

Generally, a rough surface, especially a hierarchically micro/nanostructured surface, is a prerequisite to achieving extreme wettability, because it amplifies the surface’s intrinsic wetting behaviour.\textsuperscript{39,164} The surface of a neat Ni mesh is clean and smooth (Figure
after heat treatment, the diameters of the Ni wires do not show obvious changes. However, a layer of nickel oxide is formed on the surface as a result of oxidation at high temperature as shown in Figure 4.2. There are no evident cracks or peeling on the mesh surface after heat-treatment. At higher magnification, the NiO layer appears to be composed of nanoplates that are homogeneous in size (~100 nm in diameter) and distribution (Figure 4.2c, d). These nanostructured NiO, along with the inherent micro-sized fibres of the mesh, constitute a hierarchically micro/nanostructured surface. It is notable that this facile approach of ours does not require any chemical surface modification and allows large-scale fabrication of these NiO/Ni meshes for oil/water separation, given that Ni meshes are commercially available. The formation of micro/nanoscale hierarchical structures on the mesh surface is fundamental to underwater superoleophobicity with extremely low oil-adhesion. The principle of oil wetting in water on a porous membrane of NiO on Ni with a micro/nano-hierarchical structure presented in this work is schematically shown in Figure 4.3.
Figure 4.3. Schematic diagrams of oil wetting on a porous membrane of NiO on Ni with a micro/nano-hierarchical structure in water.

![Schematic diagrams of oil wetting](image)

Figure 4.4. Photographs of a water droplet on neat Ni mesh (a) and of an underwater oil droplet (dichloromethane) on neat Ni mesh. (b) Photographs of a water droplet on the NiO/Ni mesh (c) and of an underwater oil droplet (dichloromethane) on the NiO/Ni mesh, showing a contact angle of 153° (d).

As is well known, the wetting of a solid surface greatly depends on its chemical composition and micro/nanostructure.\textsuperscript{13,35} To evaluate the water and oil wettability of the Ni and NiO/Ni meshes, we conducted a series of contact angle measurements in air and under water. In air, the neat Ni meshes show hydrophilic and superoleophilic behaviours, with water and oil contact angles of 40+ and zero degrees, respectively (Figure 4.4a, b). This is because the surface tension of oil is much lower than that of water; oleophilicity thus requires lower surface free energy than hydrophilicity. After sintering at 1000 °C for 10 min, when a water droplet (2 μL) is in contact with the mesh surface, it immediately
spreads out and permeates into the mesh. This result reveals that the NiO/Ni meshes are superhydrophilic with zero contact angle. Obviously, the surface roughness enhances the hydrophilicity on the hydrophilic solid surface in accordance with the Wenzel model. We have found that the NiO is intrinsically hydrophilic. According to our observations, an oil droplet also spreads out and goes into the mesh quickly, leading to superoleophilicity. Both the superhydrophilicity and the superoleophilicity are obviously caused by the multi-scale surface structure together with the high surface free energy. NiO/Ni meshes are superamphiphilic in air.

Figure 4.5. Oil-adhesion properties of the NiO/Ni mesh in an oil/water/solid system for a selection of oils with different contact times in terms of their oil-adhesion force. The inset photographs show the underwater oil-adhesion during measurements on the mesh surface using oils with different viscosity.
Remarkably, the NiO/Ni meshes become superoleophobic when they are immersed in water. When an oil (e.g. dichloromethane) droplet is placed on the mesh surface underwater, the oil droplet stays on the film with a high contact angle (>150°) (Figure 4.4d). The superoleophobicity achieved in the oil/water/solid three-phase system is mainly attributed to the microstructure of the sample surface having superamphiphilicity. In water, because of the superhydrophilicity, our NiO/Ni mesh is totally permeated by water (Figure 4.4c) and water also trapped inside the rough microstructure. These trapped water molecules will greatly reduce the contact area between the oil and the nickel oxide mesh surface, resulting in a large oil contact angle in water (superoleophobicity).

When the neat Ni mesh is immersed in water, however, the air/water/solid composite interface is transformed into an oil/water/solid composite interface, with the formerly trapped air escaping from the mesh in the form of air bubbles. This causes the dichloromethane droplet to strongly adhere to the mesh surface with a contact angle of 120° rather than 150°.

To assess the interaction between the mesh and the oil underwater, we have performed measurements of adhesion forces for different oils, including octane, dichloromethane, and vegetable oil. Figure 4.5 shows the oil-adhesion properties of NiO/Ni mesh for three different oils with different viscosities and contact times with the mesh. Our results show that the oil adhesion force increases with contact time. The forces increase dramatically for dichloromethane and vegetable oil for 300 s contact time. The adhesion forces remain almost the same for 10 s contact time. Octane was not found to stick to the mesh at all. The adhesion force of vegetable oil shows the largest adhesion at 9 μN when the oil is in contact with the mesh for a 300 s contact time, which is 4 times larger than the force for contact
times of less than 10 s. The octane, dichloromethane, and vegetable oil droplets maintain their spherical shape throughout the measurements, with no residual oil on the mesh surface. These results clearly demonstrate that the oils that we have tested do not stick to our NiO/Ni meshes, except for vegetable oil, and that the meshes are reusable without any surface treatments. According to Figure 4.5, we can see that although the adhesion force for the vegetable oil is largest compared to other oils, the contact angle for vegetable oil is still greater than 150°. That means our mesh is still superoleophobic for vegetable oil too. Because the vegetable oil’s viscosity is higher than other two oils, when it contacts with mesh surface, a thin layer of vegetable oil may stick on the NiO. This may be the reason for the large adhesion force.

The superhydrophilicity and underwater superoleophobicity of our NiO/Ni meshes can find great applications in oil/water separation with superior performance in harsh environments, as we predicted in the introduction. The NiO/Ni meshes are flexible and robust enough for use in separation devices on a large scale.

Figure 4.6. Photographs of the oil/water separation process using (a) the original Ni mesh and (b) the NiO/Ni mesh. Paraffin oil was used as typical oil and dyed with oil atrovirens dye for clear observation.
The experiments on oil/water separation were carried out by using the set-up illustrated in Figure 4.6. A mixture of paraffin oil and water (30%, v/v) with a density of ~0.94 g/ml was poured onto the NiO/Ni mesh, which had been pre-wetted with water and fixed between two Teflon flanges. Figure 4.6a shows the oil/water separation process of the original Ni mesh. We can see that both water and oil go through the untreated Ni mesh completely. This means the bare Ni mesh has no ability of oil/water separation. The only force driving the oil and water separation is the weight of the liquid itself. Due to the higher density of water, it is able to gravitate towards the bottom of the oil/water mixture in addition to the contribution from the mesh’s superhydrophilicity. Water is then able to permeate through the mesh quickly, and no visible oil remains in the collected water. Oil is retained above the mesh because of the mesh’s underwater superoleophobic property, as shown in Figure 4.6b.

To mimic harsh environments in the real world, we have performed oil/water separation using mixtures of seawater (collected in the local harbour) and paraffin oil (containing solvent blue at 0.1 wt.%) with and without sand and soil.

According to our observations, NiO/Ni meshes show superior oil/water separation performance for all three different mixtures. Water can pass through the mesh quickly and leaves the oil and sand/soil above the mesh. To test the reusability of our NiO/Ni meshes, the oil/water separation experiments were carried out for 20 cycles. Our results showed that the separation performance remains superior throughout the repeated experiments. This strongly indicates that the NiO/Ni mesh morphology and its superhydrophilicity and underwater superoleophilicity with low adhesion are not affected by sand and soil.
Figure 4.7. (a) Cycling tests of permeate flux of the NiO/Ni mesh using various mixtures: pure water - paraffin oil mixture, sea water - paraffin oil mixture, sea water - paraffin oil mixture with sand, and sea water - paraffin oil mixture with soil. (b) The separation efficiency for different cycles of the NiO/Ni mesh for the sea water - paraffin oil mixture, (c) Photograph of burning of oil-contaminated NiO/Ni mesh in air for cleaning purposes. (d) Optical image of NiO/Ni mesh surface after oil/water separation followed by burning under an ambient atmosphere.

To quantitatively demonstrate the superior water/oil separation performance of our NiO/Ni meshes, we have calculated the water permeation speed and separation efficiency. The results of tests of the water permeation speed and separation efficiency as a function of measurement time are shown in Figure 4.7a and b.
The permeate flux \( (F) \) was calculated by the following equation:

\[
F = \frac{V}{St}
\]  

(3.1)

where \( V \) is the volume of water that permeates through the mesh, \( S \) is the area of the mesh, and \( t \) is the permeation time. The \( F \) for water/petrol separation (Figure 4.7a) is \( 5.4 \times 10^4 \) L m\(^{-2}\) h\(^{-1}\) over the 20 cycles that we measured. The permeate flux of NiO/Ni mesh for oil and sea water separation is \( 5.4 \times 10^4 \) L m\(^{-2}\) h\(^{-1}\) in the first, fifth, tenth, and fifteenth cycles, and it slightly decreased to \( 5.2 \times 10^4 \) L m\(^{-2}\) h\(^{-1}\) in the twentieth cycle. For the separation of both the oil/sea water mixture with soil and the oil/sea water mixture with sand, the permeate fluxes are approximately \( 4 \times 10^4 \) and \( 5 \times 10^4 \) L m\(^{-2}\) h\(^{-1}\), respectively, and they remain constant over the 20 cycles, indicating that the NiO/Ni meshes are highly resistant to fouling by oil. Moreover, almost no visible oil can be found in the collected water. To quantify the water/oil separation efficiency, we measured the residual oil content in the collected water. After the separation process, the oil was collected and weighed. The separation efficiency, \( R \), was calculated according to \( R = \frac{(M1 - M2)}{M1} \times 100\% \), where \( M1 \) and \( M2 \) are the weight of the collected water and the weight of the residual oil in it after the separation process. Remarkably, the separation efficiency for the oil/sea water mixture, the oil/sea water mixture with soil, and the oil/sea water mixture with sand are above 99% for all the cycles, as shown in Figure 4.7b.

To further study the separation capability of the NiO/Ni meshes, the intrusion pressure at the mesh interface can be calculated using the equation below:

\[
P = \rho gh_{max}
\]  

(3.2)

where \( P \) is the pressure, \( \rho \) is the density of the oil, \( g \) is the acceleration due to gravity, and \( h_{max} \) is the maximum height of liquid that the nickel oxide mesh can repel. We found that
the interface between the mesh and the water can withstand pressure of more than 2352 N/m², which shows that water/oil separation by the NiO/Ni mesh is easily driven by gravity.

We have shown that a variety of oil/water mixtures with impurities have been successfully separated through the same process, including gasoline, hexane, and paraffin oils. It should be noted that the superior oil/water separation performance of the NiO/Ni mesh can be easily recovered for the above oil/water mixtures by simply rinsing the mesh surface with water. Nevertheless, any meshes used for oil/water separation would be contaminated eventually by oil, especially highly viscous oil. Vegetable oil and crude oil are particularly sticky and strongly adhesive. Water flushing by itself is then not enough to remove the sticky oil and recover the mesh’s performance. There are no good solutions for recovering the separation capability for other types of meshes. As the autoignition temperatures of most oils are below 600 °C and the autoignition temperature of carbon and hydrocarbon are below 700 °C, however, the NiO/Ni mesh can be reused many times by simply burning it in air to remove the oil contamination (Figure 4.7c) while maintaining the morphology and chemical composition of the mesh. Most of the organic coated meshes, however, would cease to function if heated over 200 °C. Our NiO/Ni mesh would be fully recovered by this simple treatment.

The separation of water/canola oil was performed using the NiO/Ni mesh. We can see that the water is separated from the canola oil. The water permeation speed was as high as $5.2 \times 10^4$ L m$^{-2}$ h$^{-1}$ in the first cycle. The separation efficiency was reduced greatly for the second cycle, however, as the canola oil adheres to the mesh surface and impedes the water permeation. We then burned the mesh. The oil was completely removed, and the surface
morphology was recovered and showed little difference compared to a freshly made NiO/Ni mesh. The separation of water/canola oil was conducted again under the same conditions. We found that the microstructure of the NiO layer was completely recovered (Figure 4.7d), and the same initial water permeation speed was retained for the same mesh. This process can be repeated many times without any significant change. This indicates that this water-removing mesh is the best candidate for the treatment of industrial-oil-polluted water and oil spill clean-up.

4.4. Conclusions

In summary, we have developed a novel superhydrophilic and underwater superoleophobic NiO/Ni mesh with multi-scale surface structure, which shows superior oil/water separation in harsh environments. It can separate different oil-water mixtures with and without sand or soil, with > 99% separation efficiency and up to $5.4 \times 10^4$ L m$^{-2}$ h$^{-1}$ permeate flux. The mesh is reusable and durable, and its superior performance can be easily recovered by a very short heat treatment that is only needed for sticky oils. Our separation methodology is solely gravity-driven and consequently is expected to be highly energy-efficient. Our findings pave the way for this new type of mesh to be useful in numerous applications, including the clean-up of oil spills, wastewater treatment, and oil-water separation under other harsh conditions.
Chapter 5. Desert beetle-inspired superwettable patterned surfaces for water harvesting

5.1. Introduction

Water is the most fundamental substance needed for the survival of all living organisms, and lack of it has disastrous consequences. Dry weather and severe drought have many devastating results, as seen in many countries across the world.\textsuperscript{165, 166} The shortage of freshwater is a serious problem that has to be faced and must be solved. The climate change models have predicted an increase in the extent of drought,\textsuperscript{167, 168} although existing technologies have been able to make some impact on the water shortage issue through desalination plants and filtration systems. This has been progressing slowly, however, due to cost-ineffective facilities.\textsuperscript{169}

In nature, some organisms have evolved different elegant strategies for harvesting water from the humid ambient air.\textsuperscript{38, 128, 131, 133, 170, 171} In particular, the Namib Desert beetle (Stenocara sp.) consisting of an array of hydrophilic bumps on a superhydrophobic background for water harvesting from fog-laden wind is one of most promising.\textsuperscript{128} Learning from nature has long been a source of bio-inspiration for scientists and engineers to design and construct novel materials and devices. Inspired by the Namib Desert beetle with the unique water harvesting ability, many different synthesis strategies have been developed to fabricate two-dimensional superwettable patterned surfaces for water
However, for practical applications, it is very desirable to develop new systems/materials with high water collecting efficiency and low fabrication cost.

In this chapter, inspired by the Stenocara beetle with the hydrophilic/superhydrophobic patterned surface for harvesting drinking water, superhydrophilic/superhydrophobic patterns have been fabricated on the superhydrophobic surfaces by using the pulsed laser deposition (PLD) approach with a patterned mask. In comparison with the single superhydrophobic or superhydrophilic surfaces, the resultant superwettable patterned surfaces exhibited superior water harvesting ability, which is suited to not only night-time desert environments with high humidity but also high-level steam, such as in thermal desalination plants and waste steam in steel plants and steam engine systems. This strategy reported here can be readily and widely adopted for the fabrication of large-scale complicated superhydrophilic patterns on superhydrophobic surfaces with superior water collecting efficiency, which represents a key step towards the superhydrophilic patterning of superhydrophobic surfaces for practical applications in the water harvesting field.

5.2. Experimental Section

5.2.1. Fabrication of superhydrophobic surface with high adhesion.

Firstly, a superhydrophobic coating was applied on acrylic diffuser plastic, using a commercially available superhydrophobic silica poly(dimethylsiloxane) (PDMS) aerogel particle spray (Rust-Oleum Neverwet) in accordance with the manufacturer’s instructions. After 24 hours of drying, the substrates were deposited by Pt nanoparticles through pulsed laser deposition. The as-prepared samples were superhydrophobic with a low sliding angle.
Secondly, a hydrophilic layer was coated on these substrates by pulsed laser deposition using a neodymium-doped yttrium aluminum garnet (Nd: YAG) laser with an output wavelength of 355 nm. A Pt target was used for coating. Before deposition, stainless steel meshes with various mesh numbers: #150, #200, and #300) were placed on the substrates as masks. The depositions were performed at room temperature under the following conditions: vacuum level of \( \approx 8.9 \times 10^{-4} \) Pa, the laser power of 2 W, the distance between target and substrate of 7 cm, and deposition time of 20 minutes.

5.2.2. Characterization of sample surfaces.

The microstructures were examined using an optical microscope. The measurements of the contact and sliding angles were performed on a goniometer system (Dataphysics OCA15, Germany), with the shape of the droplet being determined by the Young-Laplace equation. Measurements were conducted at five different positions on the same sample for consistency. The adhesive force between the water droplets and the patterned surface was measured using a high sensitivity microelectromechanical balance system (Dataphysics DCAT11, Germany). A 4 μL water droplet was suspended from a copper ring, and the patterned surface was placed on the balance table. The table was moved upward at a constant speed of 0.01 mm s\(^{-1}\) until the patterned surface came into contact with the water droplet. Then, the table was moved downward. The force increased gradually until it reached its maximum value, and the droplet was then pulled away from the patterned surface until the contact force was sharply reduced to zero.
5.2.3 Measurement of the water collection properties.

A fog flow consisting of tiny water droplets was generated using an ultrasonic humidifier and captured on sample surfaces. A bottle was placed under the sample for collecting the water droplets. The whole process was recorded using an optical microscope and its CCD components. The water collection efficiency was calculated using the formula: \( \eta = \frac{V}{St} \), where \( V \) is the volume of collected water in \( \text{m}^3 \), \( S \) is the fog capture area in \( \text{m}^2 \), and \( t \) is the collection time.

5.3. Results and Discussion

![Schematic illustration of the construction of the Stenocara beetle-inspired functional surface with a superhydrophilic/superhydrophobic pattern.](image)

Figure 5.1. Schematic illustration of the construction of the Stenocara beetle-inspired functional surface with a superhydrophilic/superhydrophobic pattern. (a) A clean substrate with hydrophilicity was prepared. (b) A superhydrophobic silica polydimethylsiloxane (PDMS) aerogel coating was sprayed on the substrate. (c) Platinum (Pt) was deposited on
the superhydrophobic substrate by using the PLD approach and patterned stainless steel meshes as masks. (d) The patterned superhydrophilic/superhydrophobic surface was obtained, where the black square regions were superhydrophilic, and the white regions were superhydrophobic.

In recent years, two-dimensional superwettatable patterned surfaces have been attracting great attention because of their practical applications in droplet/protein manipulation, fluidic devices, synthesis template, anti-bioadhesion and water collection. Pulsed laser deposition (PLD) is a versatile and effective approach to conducting two-dimensional patterned surfaces. Here, the PLD technique was adopted to fabricate Stenocara beetle-inspired functional two-dimensional surfaces with superhydrophilic/superhydrophobic patterns. The fabrication of a superhydrophilic pattern on a superhydrophobic surface involves two main steps (Figure 5.1): (i) preparing a clean substrate and spraying a superhydrophobic coating on its surface (Figure 5.1a-b), (ii) coating Pt on the superhydrophobic surface by using PLD and stainless steel meshes as masks, resulting in the Stenocara beetle-inspired ordered superhydrophilic/superhydrophobic patterns as shown in Figure 5.1c-d.

Table 5.1. Hydrophilic areas of different surfaces and the percentage of the total hydrophilic area with respect to the total surface area.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Area of pattern (mm²)</th>
<th>Distance (D) (mm)</th>
<th>Number of patterns (N)</th>
<th>Total area of patterns (mm²)</th>
<th>Percentage of superhydrophilic area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superhydrophilic</td>
<td>225</td>
<td>0</td>
<td>1</td>
<td>225</td>
<td>100</td>
</tr>
<tr>
<td>Superhydrophobic</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$S150$</td>
<td>0.0108</td>
<td>0.053</td>
<td>95*95</td>
<td>97.47</td>
<td>43.3</td>
</tr>
<tr>
<td>$S200$</td>
<td>0.0056</td>
<td>0.053</td>
<td>117*117</td>
<td>76.66</td>
<td>34.1</td>
</tr>
<tr>
<td>$S300$</td>
<td>0.0028</td>
<td>0.053</td>
<td>141*141</td>
<td>55.67</td>
<td>24.7</td>
</tr>
</tbody>
</table>

177, 178 fluidic devices, 179-181 synthesis template, 182-184 anti-bioadhesion and water collection. 132
Figure 5.2. Surface microstructures and the corresponding wettability with a tilted angle of 0°, 90°, and 180° of different samples. (a) The silica PDMS-coated surfaces exhibited rough microstructures and superhydrophobicity with a small sliding angle. (b) After fully depositing hydrophilic Pt nanoparticles on the silica PDMS-coated surfaces through the PLD approach, the water contact angle was changed from about 157° to nearly 0°, showing superhydrophilicity. (c-e) The resultant S150, S200, and S300 samples presented bio-inspired patterned superhydrophilic/superhydrophobic surfaces with macroscopical high adhesive superhydrophobicity. Water droplets were firmly pinned on the patterned surfaces and did not roll off, even when the patterned surfaces were tilted vertically or turned upside down. This implies that the Pt-coated superhydrophilic square micro-regions...
on the superhydrophobic substrate played a vital role in the strong adhesion. (c) S150 sample, (d) S200 sample, (e) S300 sample. The water droplet is about 4 μL.

The surface microstructures and the corresponding water contact angle images of the as-prepared samples are presented in Figure 5.2. For the silica PDMS aerogel particle-coated sample, its surface exhibited a rough microstructure. Water droplets deposited on its surface form almost perfect spheres, demonstrating the superhydrophobicity with a water contact angle of about 157° and a sliding angle < 1°. This can be attributed to the cooperation of the low surface free energy PDMS coating and rough microstructures. Furthermore, the water droplet is hardly able to stick to the silica PDMS-coated surfaces, allowing water droplets to roll off quite easily (Figure 5.2a). After fully depositing Pt on the silica PDMS-coated surfaces through the PLD approach, the case is just contrary. The surface wettability of was changed from superhydrophobicity to superhydrophilicity with a water contact angle of nearly 0° (Figure 5.2b), which can be attributed the inherent hydrophilic characteristic of Pt particles. In order to mimic the superhydrophilic/superhydrophobic patterns of the Stenocara beetle, Pt nanoparticles were deposited on the silica PDMS-coated superhydrophobic surfaces using patterned stainless steel meshes as masks through the PLD approach. The mesh numbers of the stainless-steel masks are #150, #200, and #300, and the resultant samples are denoted as S150, S200, and S300, respectively (Figure 5.2c-e). After depositing Pt nanoparticles on the superhydrophobic surfaces with masks, all the resultant patterned samples showed superhydrophobicity with water contact angles of more than 150°. However, in contrast to the silica PDMS-coated superhydrophobic surfaces with a small sliding angle, water droplets were firmly pinned on the patterned surfaces and did not roll off their surfaces, even when the patterned surfaces were tilted vertically or turned upside down, showing a
high contact angle hysteresis (Figure 5.2c-e). This can be attributed the bio-inspired patterned surfaces possess the square micro-regions coated with superhydrophilic Pt nanoparticles and all other linear micro-regions with superhydrophobicity.\textsuperscript{36} The single Pt-coated micro-square sizes on the S150, S200, and S300 patterned surfaces are approximately 104×104, 75×75, and 53×53 μm\textsuperscript{2}, respectively. The separation distance between the dark square micro-regions is about 53 μm for all patterned samples. The ratio of the superhydrophilic area on the superhydrophobic surfaces for S150, S200, and S300 is about 43.3%, 34.1%, and 24.7%, respectively (Table 4.1). Therefore, the resultant bio-inspired surfaces exhibited the patterned superhydrophilic/superhydrophobic characteristic, which is similar to the Stenocara beetle in nature. This demonstrated that micro-patterned Pt-coating is a facile and versatile avenue for the construction of the superhydrophilic state on a superhydrophobic surface.

Figure 5.3. (a-h) In situ and direct observation of the water vapor condensation, water droplet growth, and roll of water droplets on the S200 sample with Stenocara beetle-inspired superhydrophilic/superhydrophobic patterned surfaces. Tiny water drops grew and coalesced quickly on the S200 surface (a-e). Through a series of droplets coalescence, water droplets jump out off the surface (f-h).
In order to investigate the water harvesting behaviour of the resultant Stenocara beetle-inspired superhydrophilic/superhydrophobic patterned surfaces, optical microscope was used to in situ record the water collection processes. Figure 5.3 shows the representative water harvesting process on the S200 sample with patterned superhydrophilic/superhydrophobic surfaces. When water vapor was sprayed on the patterned surface, tiny water droplets were formed or condensed immediately (less than 1 s) on the Pt-coated superhydrophilic square regions. Arising from the high adhesive property of the resultant patterned sample, water droplets with spherical shape can pin on the Stenocara beetle-inspired surfaces. When the droplets reach a critical value, they will roll off quite easily, demonstrating the effective water harvesting property.

Figure 5.4. (a-e) Enlarged in situ observation of the coalescence and growth of water droplets on the Stenocara beetle-inspired S200 sample surface. Tiny water drops coalesced to a small droplet (a-b), and then the small droplet grew (b-c). When it touched the surrounding small droplets, they coalesced again to a big droplet (c-e). (f-j) Schematic illustration of enlarged in situ observation of the coalescence and growth of water drops on S200 sample surface.
Further fundamental investigations of the water droplet growth process would be useful for the understandings on the water harvesting mechanism of Stenocara beetle-inspired superhydrophilic/superhydrophobic patterned surfaces. Magnified processes of the condensation and coalescence of water droplet growth are shown in Figure 5.4. Condensed tiny droplets on the Pt-coated superhydrophilic square regions coalesced rapidly with neighboring tiny water droplets, which were pinned on Stenocara beetle-inspired patterned surfaces. Accompanied by the growth of water droplets, the coalescence happened more frequently between the neighboring water droplets, leading to the formation of big droplets. The big droplets then merged with the neighboring small and big water droplets, leaving a fresh patterned surface for the new tiny water droplet condensation from water vapor. Finally, when a big droplet reached a certain size, it rolled off quickly due to the gravity. The rolled water droplet will also take away the droplets on its rolling path, which continuously release the fresh patterned surface for water harvesting. The Stenocara beetle-inspired superhydrophilic/superhydrophobic patterned surfaces offered vast prospects for high-speed water harvesting. This also implied that the water harvesting speed could be enhanced greatly by the addition of mechanical vibration to the effect of gravity.\textsuperscript{190}
Figure 5.5. Schematic illustration of the set-up used to measure the water collection efficiency of different surfaces.

In order to investigate the water harvesting efficiency of the obtained samples, an experimental apparatus was constructed, and the schematic representation was shown in Figure 5.5. A flow of fog, consisting of tiny water droplets, was generated using an ultrasonic humidifier, and the fog was captured on sample surfaces. A bottle was placed under the sample for collecting water droplets. The whole process was recorded by an optical microscope with charge-coupled display (CCD) components.
Figure 5.6. Water harvesting efficiency and droplet critical rolling off diameter on different surfaces, including a superhydrophilic surface (SHL), a superhydrophobic surface (SHB), and Stenocara beetle-inspired patterned surfaces S150, S200, and S300.

The water collection efficiency was calculated using the formula: $\eta = \frac{V}{St}$, where $V$ is the volume of collected water, $S$ is the fog capture area, and $t$ is the collection time. It was demonstrated that the water harvesting efficiency of the resultant Stenocara beetle-inspired patterned surfaces was superior to that of the single superhydrophobic or superhydrophilic surfaces (Figure 5.6). For the silica PDMS-coated superhydrophobic surface and the Pt nanoparticles-coated superhydrophilic surface, the water harvesting efficiency is about 3 g cm$^{-2}$ h$^{-1}$ and 4.1 g cm$^{-2}$ h$^{-1}$, respectively. For the Stenocara beetle-inspired superwettable patterned samples, the water harvesting efficiency is increased with the decrease of the percentage of Pt-coated superhydrophilic square regions. The maximum water harvesting efficiency of the resultant patterned surfaces can reach about...
5.3 g cm$^{-2}$ h$^{-1}$, which is 1.8 times higher than that of the reported star-shaped patterned surfaces.\textsuperscript{132} Furthermore, the water harvesting efficiency is a parabolic relationship with superhydrophilic density in which the maximum efficiency reach is at 24.7% superhydrophilic. Obviously, the higher superhydrophilic density can enhance the water condensation. However, the optimized lower superhydrophilic density improves the droplet removal, which plays a role in water harvesting efficiency.

Figure 5.7. Time dependence of the size of the single water droplet condensed on the superhydrophobic (SHB) surface and on the Stenocara beetle-inspired superhydrophilic/superhydrophobic patterned surfaces (S150, S200, and S300) until it rolls off of the surface.
The water harvesting process based on the principles of wettability usually consisted of the following three steps, the condensation of water vapor, the growth of water droplets, and the roll off of droplets. Gravity is the easiest and most convenient driving force for the removal of droplets. Therefore, fast vapor condensation, high-speed growth, large sized droplets, and quick removal of droplets are the key elements to achieve highly efficient water harvesting. On the one hand, in order to allow tiny fog droplets to condense and form water droplets easily, the nucleation region should ideally be superhydrophilic. On the other hand, the coalescence of neighboring water droplets is decisive if the droplets are to grow fast and reach a critical size quickly, in addition to the self-growth of the individual droplets. This required that the water harvesting surfaces possess both superhydrophilicity and superhydrophobicity, as well as very strong adhesion. For the silica PDMS-coated surface, the superhydrophobic property hindered the condensation and the coalescence of tiny water droplets, resulting in the slow increases in the water droplet size (Figure 5.7). For the Pt nanoparticles-coated superhydrophilic surface, the condensed water droplets can grow very big, but the droplets take a long time to fall off because of the very strong adhesion of the surface (Figure 5.8). The water droplet sizes can increase quickly and frequently on the Stenocara beetle-inspired
superhydrophilic/superhydrophobic patterned surfaces, demonstrating the superior water harvesting efficiency. According to the World Health Organization, the minimum water requirement to sustain life is about 2.5 L per person per day under moderate climatic conditions. In this work, if the size of the Stenocara beetle-inspired superwettable patterned sample S300 is 1 m², 53 L fresh water can harvest in 1 hour with a normal fog velocity at 45~50 cm/s, which can meet the basic water requirement for more than 20 people. Moreover, the present fog collector could be produced on a larger scale, which has a promising application potential in an arid region with high incidence of fog.

Figure 5.9. (a) The image shows droplets of water, 12M HCl, and 1M NaOH on the superhydrophilic patterned superhydrophobic surface. (b) Mechanical durability of the sample under abrasion processes using 400-grit sandpaper.

The chemical stability and mechanical durability of the superhydrophilic patterned superhydrophobic surface are crucial for the practical applications. The S300 samples are rinsed using a 12 M HCl solution (pH = 1) and 1M NaOH solution (pH = 14) for 10 mins, respectively. After that, water, HCl and NaOH contact angle of the S300 remain greater than 150° (shown in the Figure 5.9a). The superhydrophilic patterned superhydrophobic surface showed superior chemical durability, with the ability to be unaffected by any acid or base solution. Furthermore, we have conducted the sandpaper abrasion experiment. The
S300 sample was abraded using a 400-grid sandpaper with 20 g loading weight on it for 10 times, as shown in Figure 5.9b. The water contact angle remains at greater than 150°. The water harvesting efficiency of S300 sample after chemical and physical durability tests did not affect our results significantly.

5.4 Conclusions

In this chapter, Stenocara beetle-inspired superhydrophilic/superhydrophobic patterned surfaces were fabricated on the silica PDMS-coated superhydrophobic surfaces through the PLD technique with a mask. The resultant superwettable patterned samples exhibited superior water harvesting efficiency in comparison with the silica PDMS-coated superhydrophobic surface and the Pt nanoparticles-coated superhydrophilic surface. Both the size and the percentage of the Pt-coated superhydrophilic square regions on the patterned surface have an important effect on water harvesting efficiency. Furthermore, the present approach proved to be a versatile and effective strategy for the construction of superwettable patterned surfaces with water harvesting in a large scale, which provides a potential avenue to relieve the growing global water crisis.
Chapter 6 Galinstan Heart beating effect at room temperature

6.1 Introduction

Heartbeat power the functions of organs and cells is paramount to living beings. Heartbeat rate and contractions of the heart as well as continuous beating at proper rate keeps alive. However, if the beating stops or heart beats randomly, it causes disastrous and fatal consequences. Electric shocks can often retrigger the beating again. The heat beating rate varies mainly with the size of hearts. This requires the discharge process to adjust its rate to ensure the heart to beat and contract at an appropriate speed for organs to function properly.

Soft matters are ideal materials for the design of next-generation flexible and artificial intelligent robots or devices. The ultimate goal for a soft intelligent robot is to be capable of mimicking all the physical motions of living beings such as the flow of liquid or gas, a stretch of body parts etc. to function in various environments. Beating mercury observed in 1873 is one of the interesting oscillations in electrochemical systems. A few recent attempts on liquid metals reveal that the liquid metals can be deformed greatly which mimic the stretch motion of being’s body, can move directionally or rotationally either on its own axis of a droplet or in a circle through the electro-chemical process.
The liquid metals are fluids and are of high electrical conductivity\textsuperscript{213, 214} and good surface tension tuneability in various solvents rendering them ideal platforms for electrochemical control of their states. To date, the one of the most suitable soft matter that can serve these purposes seems to be the room temperature liquid metals, particularly Ga and its alloys, as they are low-toxic as compared to liquid Hg\textsuperscript{215}.

Some experiments reported so far have demonstrated that it is possible to mimic these functionalities to some extents through mechanical, electrochemical or optical control, even though they are far from full capability and flexibility of that of living beings\textsuperscript{216, 217}. It is a great ambition to add a heartbeat function in any soft devices or Robots which can play the vital role to power their components like the heart in living beings. However, the great challenge is that “heart” should beat constantly (to mimic living being’s heartbeat) and must operate in a controllable way. This is the paramount goal of manipulation at will for physical motions in soft matters.

Here, we report our discovery of voltage-induced heart beating phenomenon in room temperature liquid metal galinstan by designing a novel type of electrode. We report that the liquid metal droplets with different weight/sizes can beat constantly, and the beating rates are controllable by voltage. The rate of galinstan heartbeat can be the same as that of living beings. Our findings offer the great promise of practical applications of liquid metal for a new generation of soft robots powered by beating hearts.

6.2 Experiments

6.2.1 Chemicals
Galinstan with 62% Ga, 22% In, and 16% Sn by volume was purchased from Alfa Aesar. 0.5 mol/L NaOH solution was adjusted with a solid 99% NaOH capsule and deionized water. The deionized water was prepared by Purelab Ultra Elga.

6.2.2 Beating of Galinstan heart

40, 120 180 and 240 µL galinstan droplets were placed in a glass vessel (diameter of 9 cm) with 0.5 mol/L NaOH solutions at room temperature. A piece of blue reference paper was placed under the vessel. A copper wire anode was connected to a graphite ring, which had an inner diameter of 10 mm and an outer diameter is 30 mm. The galinstan droplet was placed in the graphite ring and touched its inner wall. A copper wire cathode was placed in the solution. The applied DC voltages were supplied from 0 to 5 V by a GW laboratory DC power supply, model GPS-1850. A camera was placed over the vessel and recorded the whole process of the experiment via 1080p, 30 frame-per-second (fps) video.

6.2.3 Footprint Measurements

The analysis was performed using the open-source IMAGEJ software with the spatial scale calibrated to the in-image standard using a piece of blue reference paper placed under the vessel. Automated image-recognition analysis was performed with the TRACKMATE plugin using a LOG detector filtered by contrast. The trajectories were manually checked frame-by-frame and where necessary, the ellipse dimension and position were corrected slightly. The camera was timed to film the droplet when the power supply was switched on and recorded the process of droplet oscillation. The distances were measured from the obtained photographic series, in which the displacement distance was defined as
the distance between the geometric centre of the galinstan droplet and centre of the electrode.

6.3 Results and discussion

Figure 6.1. Diagram of the experimental setup before the external DC voltage was applied.

The experimental set-up is sketched in Figure 6.1. A graphite ring and the electrolyte were placed in an insulated and transparent glass Petri dish, and a droplet of liquid galinstan was put inside the graphite ring. Two copper wires, each with a diameter of 0.5 mm, acted as the two electrodes. The cathode was inserted into the electrolyte, while the anode was in contact with the surface of the graphite ring electrode. The applied voltage and the volume of galinstan were altered to control the beating activity in 0.5 M NaOH solution.
Figure 6.2. The series of photographs captured from the video show the basic cycle as the 40 µL drop as it shapeshifts, displaces and alters diameter, reminiscent of a heartbeat.

To understand the mechanism, it is useful to consider the repetitive heartbeat (Figure 6.2) in five steps: contact, oxidation, loss of contact, etching and downhill drift. A liquid metal droplet placed in the graphite ring electrode touches the inner wall of the ring when an external voltage is applied, positive charges are induced to the graphite and the liquid metal via the anode as they are in contact each other. (Figure 6.2 Δt = 0 ms) This can result in two consequences: 1) repulsion between liquid metal and graphite due to Column charge repulsion. This leads to the droplet being pushed away from the graphite; 2) oxidation of liquid metal into Ga2O3 which in turn lead to the significant deformation and extension of the droplet due to the significant reduction of surface tension of galinstan.142 Both charge repulsion and extension drive the droplet to spread into a film-like form and move away from the inner wall of graphite (Figure 6.2 Δt = 60 ms). This proceeds until the pancake-shaped galinstan loses contact with the edges of the electrode (Figure 6.2 Δt = 180 ms). Therefore, the droplet is detached from the graphite, which cuts the connection between the droplet and the external power supply. The apparent diameter of the metal component begins to shrink, since without the applied voltage, hydroxyl ions can etch the oxide layer surrounding the liquid metal surface219 leading to the recovery of a state with high surface tension.142, 220 (Figure 6.2 Δt = 300 ms) After reach a certain size, the liquid metal then instantly changes back to a spherical droplet. Then the galinstan droplet moves back to the
graphite electrode due to gravity and reach the inner well of graphite, completing its first cycle of the beating. (Figure 6.2 Δt = 480 ms) It will then repeat the same process as the first cycle of the beating.

![Graph showing the motion of a galinstan drop](image)

Figure 6.3. The motion of 40 µL galinstan drop in the alkaline solution (0.5 mol/L NaOH aq.), when DC voltages of 3 V is applied at room temperature. The vertical coordinate Distance denotes the distance between the geometric centre of the top-view of the liquid metal to the closest point on the inner edge of the graphite electrode. The vertical coordinate Area denotes the top view footprint area of the liquid metal droplet.

For the 0.5 M NaOH solution, no beating was observed at 3 V. (Figure 6.3) Thus, a threshold voltage of at least 4 V is required to initiate the reaction and sustain the oscillation. Figure 6.4 and 6.5 show the changes in the top-view area of a 40 µL galinstan droplet and the distance between the geometric centre of the top-view of the droplet and the inner wall of the graphite ring electrode under 4 and 5 V applied voltage, respectively.
The horizontal coordinate refers to the time from when the voltage was switched on. The vertical coordinate for the upper graph represents the distance between the geometric centre of the top-view of the droplet and the inner wall of the ring, and the vertical coordinate for the lower graph represents the top-view area of the droplet. In order to analyse a large number of photographic frames in the experiment, and accurately extract the beating frequency, we took advantage of automatic image-recognition and tracking algorithms.\textsuperscript{218} The voltage causes the drop to self-actuate on sufficiently flat surfaces ($\theta < 0.5^\circ$) and a stable periodic motion is obtained.

![Graph of distance and area over time](image)

Figure 6.4. The beating phenomenon for 40 $\mu$L galinstan drop in the alkaline solution (0.5 mol/L NaOH aq.), when DC voltages of 4 V is applied at room temperature.
Figure 6.5. The beating phenomenon for 40 μL galinstan drop in the alkaline solution (0.5 mol/L NaOH aq.), when DC voltages of 5 V is applied at room temperature.

The galinstan drop also undergoes a shape-shifting transition during the cycle, changing cross sectional area as it spreads. As with the displacement, the transformation is caused by the formation of the oxide layer.\textsuperscript{142} It was observed that the changes in area (or deformation) peaks quickly after the droplet is pushed away from graphite and the liquid metal recovers its shape slowly. The galinstan drop under 5 V requires more time to return to their spherical form (Figure 6.5) indicating there is a voltage-dependent time associated with the shape transformation from oblate to a spherical form. The beating rates or the oscillation frequencies are about 1.31 and 1.69 Hz for the 40 μL droplet at 4 and 5 V, respectively.
In addition to the dominant electrochemical and mechanical effects, we directly verified that the drop also has a small net charge, and experiences Coulomb repulsion after the drop is detached to the graphite electrode. This is clear because inserting a wire into the system as an additional control electrode can either repulse or attract the drop without physical contact. Furthermore, the drop is able to induce mirror currents in a nearby neutral copper wire. Given the high conductivity and fast electronic response, the liquid metal can be treated as an ideal conductor under electrostatic equilibrium such that Maxwell’s equation $\nabla \cdot \mathbf{E} = 0$ applies. The mechanism for the electromagnetic repulsion is then analogous to the motion of metallic electrostatic bells, the most famous example being Benjamin Franklin’s bell designed to detect an approaching thunderstorm. This necessitates that any residual charge is redistributed at the surface, producing a dipole that balances the external potential. In the electrolyte, this involves forming the electrical-double layer (EDL) on the liquid metal, structured with negative hydroxyl groups terminating the metal-oxide counterbalanced by external positive ions, providing a capacitance that leads to a long-lived charge on the drop for several seconds.
Figure 6.6. (a) Under a constant applied DC voltage of 4 V, regular oscillations can be observed for the 120. (b) Chaotic motions can occur for the 120 µL drop under 5 V applied voltages, or once the stabilizing voltage is removed.

Both regular and irregular oscillations can be observed in galinstan heart beating, as shown in Figure 6.6. Figure 6.6a shows the regular oscillations for 120 µL galinstan drop under 4 V applied voltages with the frequency of 0.74 Hz. However, the drop exhibits chaotic trajectories with no well-defined periodicity while the 5 V voltage was switched on. The following mechanisms are responsible for the heart beating effect with irregular bouncing back and forth. For large volume droplets at high voltages, the drop tends to be flat instead of being spherical due to gravity as its heavy weight overcomes its surface tension. The relative flat drop leads to the fact that of liquid metal are more areas at the
edge in contact with inner wall of graphite. Under the positive charging, the edge areas and graphite both charged positively are repulsed each other. This causes the liquid drop moves away from graphite along the direction where the repulsion force is maximum (depending on where the positive charges accumulate at maximum). Simultaneously, the droplet gets flatter due to the fast formation of Ga$_2$O$_3$. It’s difficult that the droplet detaches from the graphite ring electrode. The droplet may touch multi-positions on the inside wall of the graphite ring electrode, which lead to an irregular shape with irregular beating (Figure 6.6b).

### 6.4 Conclusions

In summary, a new and easily accessible heart beating phenomenon has been discovered by using low-toxic galinstan under electrical filed in a graphite ring. The continuous reversible deformation is dominated by a surface oxide and electrical field effect. The liquid metal droplet was moving in the horizontal direction with a range of beating frequency from 0.74 to 1.69 Hz. These findings represent a significant step forward to adding new functionality for dynamic fluid controllers, stretchable electronics$^{222}$ and composite materials$^{223}$ using mechanically robust liquid metals$^{224}$. 
Chapter 7 A Novel Liquid Metal Patterning Technique: Voltage Induced Non-Contact Electrochemical Lithography at Room Temperature

7.1 Introduction

Room temperature gallium based liquid metals are set to play a significant role in various applications due to their high electrical and thermal conductivity, negligible vapor pressure, and low viscosity.\cite{213,224-231} Most importantly, they are less toxic as compared to mercury. Novel phenomena characteristic of gallium and gallium based alloys include giant deformation and transformation caused by significant changes in the surface tension of liquid metals due to the formation or removal of oxide on the liquid metal surface under the application of a voltage.\cite{141,142,145,232} Recently intensive research efforts on these new phenomena have led to the development of emerging applications, including liquid metal enabled pumps,\cite{145,233} tunable antennas,\cite{25,26,28,234} microelectromechanical system (MEMS) devices,\cite{23,32,235-237} and liquid metal robots.\cite{200,216,217,238} We have recently demonstrated spontaneous fast deformation and solidification in supercooled liquid gallium induced by both voltage and nucleation on the electrode.\cite{232}

Patterning of liquid metals has attracted intense interest for applications such as microfluidic electrodes,\cite{239-241} sensors,\cite{200,242,243} stretchable electronics,\cite{244-248} and reconfigurable circuits.\cite{23,222} Two-dimensional (2D) patterning of liquid metals can be
enabled through methods such as masked deposition,\textsuperscript{249} direct laser patterning,\textsuperscript{250} inkjet printing,\textsuperscript{251} and conventional lithography.\textsuperscript{252} The three-dimensional (3D) shaping of liquid metals through the processes of injection molding\textsuperscript{253} and 3D printing\textsuperscript{254, 255} are restricted by the requirement for a mold and the size of the pattern, respectively. These techniques for 2D and 3D liquid metal patterning are usually costly or inflexible, due to the need to produce a mask or mold to shape the material. Here, we propose a new patterning method, voltage induced electrochemical lithography for liquid metals at room temperature, which is non-contact, maskless, and material-reusable.

Liquid metals have very high surface tension and usually form a spheroidal ball on a substrate. Gallium-based liquid metal has an oxide skin under ambient conditions. This oxide skin encircles the liquid metal and wets the substrate surface, which enables the liquid metal to be molded into non-equilibrium shapes. Through removing the oxide skin, a thin sheet of liquid metal is able to be greatly deformed and transformed into a spherical liquid metal drop in water or NaCl solution.\textsuperscript{141} Inspired by this phenomenon, we propose that, by applying a voltage to an electrode above the surface of a liquid metal film, a physical hole can be created underneath the tip of the electrode. Such an ability to form a hole in liquid metal is the most important step to creating any pattern in a liquid metal. In this chapter, we demonstrate voltage induced electrochemical lithography for liquid metals at room temperature. We report that the hole size and its formation speed can be controlled by the amplitude of the voltage and the concentration of the solution. Using this novel non-contact lithographic technique for liquid metal, we have successfully patterned the liquid metal in various shapes, such as circular and polygonal holes, and formed letters of the alphabet and complicated patterns with different sizes. Our findings offer a new liquid
metal patterning technique for further development of liquid metal applications in electronics, optics, and microfluidics.

7.2 Experimental Section

The galinstan (62% Ga, 22% In, and 16% Sn by weight) was purchased from Alfa Aesar. The alloy has a low melting point (10.7 °C). The galinstan films were prepared on an insulated, transparent vessel. About 20-50 μL of galinstan was put into the vessel to form a liquid metal film. NaCl solutions were adjusted using 99% NaCl and deionized water. The deionized water was prepared by Purelab Ultra Elga. The liquid metal hole formation processes were recorded using a video camera. In the experiments, about 30 mL of 0.01 mol/L NaCl solution is added to the vessel. A copper wire anode (0.1 mm in diameter and 7 cm in length) is placed above the top center of the liquid metal film at a distance h.

The voltage was generated by a GW laboratory DC power supply, model GPS-1850. A video camera was placed over the vessel and recorded the whole process of the experiment via 33fps video. Analysis was performed using the open-source ImageJ software with the spatial scale calibrated to an in-image standard, using a piece of blue reference paper placed under the vessel. The camera was timed to record the liquid metal when the power supply was switched on and off.

Three conductive polymer electrodes in geometric shapes were fabricated by using a 3D printer (Me3D, Australia). The conductive polylactic acid (PLA)-based filament was purchased from BlackMagic3D with resistance of 0.6 ohm cm and 220 °C printing
temperature. The 3D geometric pattern images were drawn by using 3D Builder, and were printed in a few minutes for each conductive polymer (CP) electrode. The electrodes had a diameter or side lengths of 20 mm for the circle, triangle, and square, and a thickness of 2 mm with height $h = 3$ mm. Then, slim cylinders with a diameter of 1.3 mm and height of 50 mm were printed to connect with the geometric pattern.

### 7.3 Results and Discussion
Figure 7.1. (a) Schematic diagram of the experimental set-up without an applied voltage when the galinstan film is prepared on the glass substrate in the NaCl solution or distilled water. Schematic diagram of the enlarged cross-section of the liquid metal film (b) before and (c) after the voltage is applied.

As shown in Figure 7.1a, an insulated vessel is adopted to accommodate the galinstan film and electrolyte solution. The galinstan film was prepared on the vessel bottom in air. A thin layer of oxide was formed on the liquid metal surface as a result of oxidation. A copper ring cathode is placed in contact with the liquid metal film, while the other copper-wire anode is placed above the liquid metal at a certain distance \((h)\) in the surrounding electrolyte solution.

We now discuss the mechanism for the hole formation in the liquid metal. The whole liquid metal surface is fully covered by an oxide layer, including the interface regions between the vessel surface and the liquid metal. When a voltage is applied to the electrode tip, which is positioned above the liquid metal, the local oxide surface layer in both interface regions between the liquid metal and electrolyte as well as between the vessel surface and the liquid metal underneath the tip will be quickly reduced. The liquid metal has a very large surface tension and doesn’t wet the vessel surface. As a result, the exposed liquid metal deforms rapidly and curves inward at the interface because of the capillary effect. This process takes place in the center of the top surface of the liquid metal below the tip and spreads uniformly outward, creating a hole in the liquid metal film (see Figure 7.1b and c). The hole size and the hole formation speed depend on the speed of the redox reaction, which is determined by the amplitude of the voltage on the tip, the tip distance, and the electrolyte concentration.
First, we investigated the effect of the voltage on the hole formation in the liquid metal using various voltages \((v)\) of 0 to 18 V. In addition, different electrode spacings were investigated, since the distance \((d)\) between the tip of the electrode wire and the liquid metal film directly affects the electrical field strength. We note the fact that an acid or a base solution can remove the oxide layer from the liquid metal film, causing the liquid metal to take on a spheroidal shape in the solution due to the high surface tension of the liquid metal.\(^{20,139}\) Therefore, we adopted a neutral solution (NaCl) for all our experiments. We have investigated the effects of short pulses or continuous voltage, the electrode distance, and the solution concentration on the voltage-induced non-contact electrochemical lithography effect.

![Figure 7.2](image)

Figure 7.2. Photographs of the hole formation phenomenon in the liquid metal. These snapshots are images of a hole formed in the liquid metal film over one 12 V pulse of applied DC voltage.
We demonstrate the results for the smallest and the largest sizes of the holes that are formed and their spreading speeds under different conditions. We have observed the following main results: 1) A threshold voltage is needed to form a hole in the liquid metal. 2) The speed of the hole formation \( r_f \) as well as the maximum size of the hole \( R_{\text{hole}} \) is proportional to the applied voltage and the NaCl concentration for a fixed distance \( d \), and they are inversely proportional to \( d \). Here, the speed of the hole formation, \( r_f \), is defined as the rate of increase of the hole’s diameter in mm per second. 3) The hole formation is irreversible. Snapshots for the hole formation process for \( v = 12 \) V are shown in Figure 7.2.

Figure 7.3. (a) Different diameters of the holes under different 1-second single pulse voltages.
Figure 7.3 illustrates the evolution of the hole formation in the liquid metal film by a short pulse of 12 V DC voltage, obtained by quickly switching the power supply on and off, with $d = 1$ mm in 0.01 mol/L NaCl. According to our observations, as soon as the voltage is applied, a hole is instantly formed and quickly spreads with a uniform omnidirectional speed, and the formation stops immediately once the applied voltage is removed. The diameters of the holes as a function of time ($t$) for different pulse voltages are shown in Figure 7.3. The final hole sizes increase monotonically with the applied pulsed voltages. The threshold voltage for hole-formation is 6 V. For $v = 12$ V, the hole size is about 9.5 mm at $t = 0.4$ s, and it becomes 15.2 mm after $t = 1$ s. The hole size can reach 25 mm for $v = 18$ V and $t = 1$ s.

Figure 7.4a illustrates the evolution of the hole formation by a continuous applied DC voltage with $d = 1$ mm in 0.01 mol/L NaCl. The final diameter of the hole is proportional to the amplitude of the applied voltage. In the case of high voltages ($v > 6$ V), as soon as the continuous voltage is applied, a hole is instantly formed in the liquid metal, and it quickly reaches its final size in less than 5 s and then remains unchanged with time, even when the voltage is switched off. For low voltages ($v = 3$ and 6 V), the hole size increases quickly with time (for $t < 10$ s), then grows linearly for $t > 20$ s. For $v = 3$ and 6 V, the hole size increases to 7.6 and 15.7 mm at 20 s, respectively, then linearly increases up to 21.7 and 24.3 mm at the speed of 0.12 and 0.07 mm/s, respectively, up to 140 s. For high voltages of 9-18 V, the hole size quickly increases and reaches its final size of 25.3, 30.7, 31.2, and 32.1 mm, respectively in less than 20 s.
Figure 7.4. (a) Diameters of the holes formed under different constant voltages. The distance between the tip and the liquid metal film is fixed at 1 mm, and 0.01 mol/L NaCl
solution was used in this case. (b) An enlargement from (a) of the hole evolution process within 0.3 seconds.

Figure 7.4b shows the hole diameter vs. time within the first 0.3 s under various continuous voltages. For \( v > 3 \) V, the hole sizes increase with time. For \( v = 3 \) V, no hole is formed until \( t > 3 \) s. Interestingly, for \( v = 6 \) V, we observed that the hole size increases from 0.7 mm for \( t = 0.1 \) s to 3.1 mm for \( t = 0.3 \) s.

![Graph showing hole diameter vs. time](image)

Figure 7.5. The hole formation velocity within 0.3 seconds of the application of voltage.

The hole formation speed is an important parameter for potential applications of liquid metal electrochemical lithography, as shown in Figure 7.5. It is observed that the speeds, \( r_t \), are greater than 60 mm/s for \( t < 0.1 \) s when \( v > 12 \) V. The speeds decrease to 15 - 40
mm/s for \( t > 0.2 \) s for \( v > 6 \) V. The speeds drop to zero for \( t > 5 \) s and \( v > 12 \) V, \( t > 50 \) s for \( v = 9 \) V, and \( t > 100 \) s for \( v = 6 \) V, respectively (see Figure 7.5).

![Figure 7.6](image)

Figure 7.6. Final diameters of the holes vs. anode tip distance from the liquid metal at various DC voltages.

We also investigated the irreversible hole formation under different tip distances \( d \). The experiments were conducted for several typical distances \((d = 1, 3, \text{ and } 6 \text{ mm})\) for a fixed solution of 0.01 mol/L NaCl. We observed that the larger the \( h \) is, the smaller the hole size will be (Figure 7.6). The final diameter of the holes for \( v = 3, 6, 9, \text{ and } 12 \) V and \( d = 1 \) mm is reduced to 21.7, 24.3, 26.5, and 30.6 mm, respectively, and further decreases to 9.5, 17.4, 19.7 and 25.1 mm for the tip distance \( d = 3 \) mm. We note that no holes can be
formed when $h \geq 6 \text{ mm}$ and $v < 6 \text{ V}$. This indicates that the electric field strength generated between the tip and liquid metal surface is too weak to create a hole.

Figure 7.7. Diameters of the holes vs. time for solutions with different concentrations in 9 V DC voltage. Inset shows longer time.

The hole formation was further examined using different solution concentrations for a fixed $d = 1 \text{ mm}$ and a fixed voltage of 9 V (Figure 7.7). The hole sizes increase with the concentration. For $t = 1 \text{ s}$, the hole sizes are 0, 10.6, 12.3, and 22.6 mm for $t = 1 \text{ s}$, and they increase to 5.2, 18.6, 23.0, and 25.9 mm for $t = 4 \text{ s}$ for the solution concentrations of 0 (deionized water), 0.005, 0.01, and 0.02 mol/L, respectively. We found that the higher the solution concentration is, the quicker the holes will reach their final maximum sizes.
We briefly summarize the effects of the applied voltage, the tip distance, and the solution concentration on the hole formation process: A threshold voltage is required to form a hole in the liquid metal; the hole formation speed and the final size are proportional to the voltage and the NaCl concentration; and they are inversely proportional to the tip distance.

The irreversible hole formation that we have observed offers us a novel approach to non-contact electrochemical lithography for liquid metals. It affords great versatility in the hole formation approach to patterns in surface engineering of liquid metals. To demonstrate applications of the non-contact patterning process for liquid metals, we carried out experiments with continuous and pulsed voltages. Three patterning methods were demonstrated, which are the electrochemical dot matrix printing method, the electrochemical “writing” method, and the electrochemical movable type printing method. It is noteworthy that all these methods are non-contact.
Figure 7.8. Three characters, ‘UOW’, and a stick-figure were formed by discontinuous electrochemical lithography.

Figure 7.8 presents examples of different patterns achieved using a single electrode tip, consisting of a Cu wire on top of the liquid metal film, and a 2 V constant voltage, with a 0.01 mol/L NaCl solution. The copper wire was put into the solution and slowly brought close to the liquid metal surface. After reaching a certain distance, a hole or a dot is formed in the liquid metal, and then the copper wire tip was retracted immediately to avoid further expansion of the hole. Each hole/dot formed in the liquid metal was about 2 mm in diameter. By purposefully arranging the hole/dot positions we can form any patterns that we choose. Patterns in the form of ‘U’, ‘O’, ‘W’, and a stick-figure were produced using the dot matrix method, as shown in Figure 7.8.

Figure 7.9. Left: A ‘Crop Circle’ like the pattern is also formed by discontinuous electrochemical lithography in one of our attempts (Right: the pattern of the referenced Crop Circle).
Furthermore, in our new approach, we can also use a pulsed voltage to implement a dot matrix approach to patterning. This method mimics the laser engraving method. It is well known that, for laser engraving, a laser beam is directed to draw a 2D vector, which evaporates the surface material dot by dot, forming any desired pattern on a solid surface. A ‘Crop Circle’ pattern was produced by this discontinuous electrochemical dot matrix approach (Figure 7.9).

![Figure 7.10. Snapshots of “UOW” logo formed by using a continuous writing method.](image)

In addition to the above described electrochemical dot matrix patterning process, a continuous electrochemical “writing” method with a constant voltage was employed. The electrode tip distance to the liquid metal surface and the applied voltage remain unchanged during the patterning process. Figure 7.10 shows the “UOW” logo formed by using a continuous writing method.
Figure 7.11. (a-c) Three typical basic shapes of patterns were formed by using the corresponding geometric shaped CP electrodes, including (a) a circle, (b) a triangle, and (c) a square.

We now demonstrate the third new electro-chemical patterning method for liquid metal, which is movable type printing. The principle for this method is that the pattern of the electrode determines the pattern of the liquid metal. CP electrodes in the shapes of a circle, triangle, and square were fabricated by using a 3D printer. These CP electrodes with geometric shapes were immersed in the solution and placed close to the liquid metal surface. As soon as a pulsed voltage is applied, a pattern that is the same as the geometric shape of the CP electrode is formed very quickly in the liquid metal. We also found that the sizes of the patterns are almost the same as for the CP electrodes. Figure 7.11 shows the patterning process with and without an applied voltage. The above demonstrated new electrochemical patterning methods are unique for liquid metal patterning. They are non-contact, maskless, and incur no loss of materials.
We summarize the applicable conditions of the method as follows. 1) The higher voltage and solution concentration, the larger hole size and higher formation speed. 2) The closer the tip is placed on the liquid metal film, the larger the hole size will be. 3) The higher conductivity of the anode wire, the faster of the formation speed. According to our observations, patterning performance would be influenced when the anode tip is close to the rim of the copper ring (less than 2 mm). However, when using a low-conductivity anode wire, hole creation process would not affect the neighbouring patterns. So, the low-conductivity anode is beneficial for patterning multiple crosses or complex patterns. Future studies should be aimed to create micron size resolution patterns by reducing the thickness of the liquid metal film using low-conductivity anode thin wires, and tuning other experiments conditions such as voltages, distances and solution concentrations.

7.4 Conclusions

In summary, non-contact, maskless electrochemical lithography technique was developed for liquid metal at room temperature. The ability to form a hole in liquid metal is the most important step in creating any pattern on it. We have investigated the effects of the voltage, the tip distance to the liquid metal surface in a solution, and the electrolyte concentration on the hole formation process for liquid metal. The hole sizes can be formed in the range from submillimeters to above 30 mm with the highest formation speed above 76 mm/s for high voltages and concentrations. Various patterns have been fabricated using three different approaches: electrochemical dot matrix printing, “writing”, and movable type printing. This method has the potential to enable applications of film-based liquid metal systems in the areas of patterning, optics, and microelectromechanical systems, such
as for smart windows, mirrors, switches, transport mechanisms, reconfigurable circuit boards, etc.
Chapter 8 Discovery of room temperature penetration and wall climbing effects for liquid metals

8.1 Introduction

Liquids that crawl up the sides of a container, or penetrate through a porous solid or a “wall” are the two of the three fascinating macroscopic phenomena that are well known in superfluids such as liquid helium.256-258 It is zero viscosity that endows the liquid helium superfluid with zero flow resistance or frictionless flow, leading to these amazing properties. Nevertheless, these fascinating properties emerge only in the so-called quantum states or quantum fluids at extremely low temperatures of almost zero Kelvin. Room temperature penetrating and wall climbing effects for liquids have not been realized so far. In this paper, we demonstrate that liquid metals such as gallium and its alloys also possess these superfluid-like dual properties. We present our experimental observations on both the wall climbing and penetration phenomena that mimic superfluids, which are realized at room temperature.

Nontoxic liquid metals, such as liquid gallium and its eutectic alloys, are attracting great attention from both industry and academia due to their unique properties. In our experiments, we have used a liquid metal gallium alloy (galinstan: 62 wt % Ga, 22 wt % In, and 16 wt % Sn) with a low melting point of 10.7 °C. Room temperature gallium-base liquid metals have some unique properties, such negligible vapor pressure,138 large surface tension,253 low toxicity,215 high electrical conductivity214 and thermal conductivity.138
Especially its low viscosity is thousands times less than honey or similar with the viscosity of water. These properties provide a powerful way to utilize room temperature liquid metal for the applications and fluid dynamics explorations.

We first highlight some typical fascinating physical and electrochemical properties of liquid gallium and its alloys under the application of a voltage at room temperature, including the following: 1) giant deformation of liquid metal droplets in acid and base solutions; 2) self-rotation; 3) locomotion; 4) spontaneous fast deformation and solidification in the supercooled state; and 5) the electro-hydrodynamic shooting phenomenon of a liquid metal stream, 6) electrochemical lithography for liquid metals, 7) liquid metal phagocytosis and 8) liquid metal triggered wire oscillartor. It is noteworthy that the surface tension of liquid gallium and its alloys is quite high (~500 mJ/m²), and therefore, they appear to be superlyophobic and do not wet most solids. When a layer of oxide, e.g., Ga₂O₃, is formed, however, due to the electrochemical reactions in acid or base solutions, the surface tension is then reduced significantly and can reach a near-zero value under an applied-voltage. It has been well accepted that it is the extremely low surface tension that plays the key role in the giant deformation effect in liquid metals. Inspired by the near-zero surface tension phenomenon, we have investigated liquid metal’s possible abilities to climb walls and penetrate through porous materials with the help of both voltage and gravity.

We now discuss the physics and chemistry of both phenomena for liquid metals. The flow of any liquid is determined by two main factors: its viscosity and its surface tension. For zero viscosity, the flow is frictionless, as is seen in superfluids such as liquid helium. If the surface tension of a liquid is near zero, its contact angle with a solid has to be near...
zero, which is regarded as a super-wetting state. For liquid metal, the near-zero surface tension due to the surface oxidation by an applied voltage in an acid or a base solution causes the liquid metal to spread very easily on the surface of a solid or any interface, in order to maintain its near-zero contact angle. This process enables the liquid metal with near-zero surface tension to keep moving when in contact with a solid surface, regardless of the size of the contact area. The galinstan is quite heavy (~6.359 g/cm³), and hence, the gravity factor can also contribute to maintaining its flow. We assume a solid material with an appropriate porosity in which all voids are interconnected, such that when a droplet of liquid metal is placed on its surface, the liquid metal remains stationary on the surface and will not penetrate through the solid due to its large surface tension. When its surface tension is significantly reduced to near-zero, however, the droplet will start to move into the solid and keeps flowing inside the interconnected voids until it finally penetrates through the solid and drips down under the force of gravity.

The near-zero surface tension can also cause the liquid metal to climb up the side of a solid wall. This is also driven by the zero-contact-angle state, whenever the liquid metal makes contact with a solid surface such as the wall of a container. Nevertheless, the liquid metal can only reach a certain height, which is limited by its weight. If the driving force overcomes gravity, the liquid metal can crawl over the top edge of the container and continues to flow down along the outside of the container.

8.2 Experimental section

8.2.1 Materials preparation
Galinstan with 99.99% purity was purchased from Alfa Aesar. The concentrations of 0.25 - 1 mol/L NaOH solutions were adjusted with a solid 99% NaOH capsule and deionized water. The deionized water was prepared by Purelab Ultra Elga. Three kinds of sponges with different pore sizes and thicknesses were used. Plastic holders were fabricated by using a 3D printer (Me3D, Australia). Other various porous materials such as plastic mesh, fiber mesh, metal mesh, and wiper paper were studied in our experiments.

### 8.2.2 Penetration effect.

A container of 1 mol/L NaOH solution was prepared at room temperature. The sponge was fixed in a plastic holder, which was put into the container. After a 150 μL droplet of galinstan was set on the sponge, two copper wires with a diameter of 0.5 mm were connected to the electrolyte and the galinstan. The applied DC voltages were supplied from 0 to 20 V by a GW laboratory DC power supply (model GPS-1850). A camera was placed in front of the container and recorded the whole process of the experiment with 1080p, 33 frames-per-second (fps) video.

### 8.2.3 Wall climbing effect.

A container of 1 mol/L NaOH solution was prepared at room temperature. A small transparent container was immersed in the solution and placed in the container. A given amount of galinstan was initially placed in the small container. Two copper wires with a diameter of 0.5 mm were connected to the electrolyte and the galinstan. The applied DC voltages were supplied from 0 to 20 V by a GW laboratory DC power supply (model GPS-1850). A camera was placed in front of the container and recorded the whole process of the experiment with 1080p, 33 frames-per-second (fps) video.
8.3 Results and discussion

![Figure 8.1](image)

Figure 8.1. The penetration effect of the galinstan through voltage control in an electrolyte. Schematic diagram of a galinstan droplet on a sponge before (a) and after (b) the voltage is applied.

The experimental setup for the penetration effect is shown in Figure 8.1a and b. A plastic holder with a fixed sponge was immersed in the NaOH electrolyte. A 150 μL galinstan droplet was set on top of the sponge and was also immersed in the electrolyte. A copper anode wire was inserted into the galinstan droplet, and a copper cathode was placed in the electrolyte. To investigate the applied-voltage effect, a DC power supply with 2.5 V to 15 V applied voltage was employed. NaOH solutions with different concentrations of 0.25, 0.5, and 1 mol/L were tested. To demonstrate the robustness of the penetration effect, we have performed the experiment using sponges with different average pore sizes of ~150 (sponge A), ~350 (sponge B), and ~550 μm (sponge C), as shown in Figure 8.2a-c. The
penetration effect for different thicknesses of these sponges was also investigated. Furthermore, various porous materials, such as plastic and metal meshes, as well as wiper papers, were studied in our experiments. The volume of the galinstan used was fixed at 150 μL for all experiments.

Figure 8.2. Photographs and optical microscope images of (a) sponge A, (b) sponge B, and (c) sponge C.
We first demonstrate our observations on the liquid metal's penetration effect. A galinstan droplet was placed on the top surface of a sponge. The galinstan droplet remains stationary when no voltage is applied. Remarkably, when a voltage is applied, the penetration effect can be observed immediately. Snapshots of the effect are shown in Figure 8.3. The experiment was conducted under 10 V, in a 0.5 mol/L NaOH solution with a sponge 7.5 mm thick. Upon application of the voltage, the droplet immediately merges into the sponge, quickly (2 s) leaks out from the bottom of the sponge, and then continuously drips down to the bottom of the container. This process continues as long as the voltage is maintained, and it is stopped either by turning off the applied voltage, or because the galinstan droplet has run out.
Figure 8.4. Reference diagram of liquid metal penetration effect under different voltages and concentrations of electrolyte. Squares indicate that the liquid metal can penetrate the sponges; triangles show that the liquid metal can’t penetrate the sponges. The green regions indicate that the liquid metal can penetrate all the tested sponges, and the red region indicates that the liquid metal can’t penetrate any of the tested sponges.

To understand the mechanism behind the penetration effect in sponges, it is useful to consider under what conditions the liquid metal can penetrate a sponge, such as the pore
size of the sponge, the applied voltage, and the concentration of the electrolyte solution (as shown in Figure 8.4).

We observed that for the green-area conditions, as shown in Figure 8.4, the liquid metal is able to penetrate all the sponges. For conditions in the un-shaded area, penetration can take place for sponges B and C. For larger voltages and low concentration (red area in Figure 8.4), however, no penetration is observed, which is likely due to the rapid reaction that produces excessive oxide in the droplet.

![Diffusion speed of the penetration effect for sponges A, B, and C under different solution concentrations and applied voltages.](image)

Figure 8.5. Diffusion speed of the penetration effect for sponges A, B, and C under different solution concentrations and applied voltages.
It should be noted that, under the right conditions, the maximum volume of the galinstan that can penetrate through a sponge is unlimited, as long as the liquid galinstan is supplied continuously. We found that the penetration speed increases with increasing pore size of the sponge for all conditions. For sponge A, the penetration speeds are 0.1 mm/s for 2.5 V in the 0.25 mol/L NaOH solution and 0.34 mm/s for 10 V in the 1 mol/L NaOH solution. The penetration speeds for sponges B and C are in the range of 0.3 - 1.9 and 2.5 - 7.5 mm/s, respectively (Figure 8.5).
Figure 8.6. Snapshots of the penetration effect for (a) a sponge A, (b) a sponge B and (c) a sponge C 7.5 mm in thickness with 10 V applied voltage in 1 mol/L NaOH solution.

Figure 8.7. Snapshots of the penetration effect for a sponge C 7.5 mm in thickness with 2.5 V applied voltage in 0.25 mol/L NaOH solution.

A few typical snapshots showing the penetration effect under different conditions for different sponges are given in the Figure 8.6 and 8.7.
Figure 8.8. Photographs and optical microscope images of (a) plastic mesh, (b) fiber mesh, (c) metal mesh, and (d) wiper paper.
The robustness of the penetration effect has been further investigated using wiper paper, and plastic and metallic meshes with different pore sizes, as shown in Figure 8.8. Apparently, as compared to thick sponges, the galinstan droplet can penetrate through all the porous materials very easily and leaks out from the other side. Snapshots showing galinstan penetrating through a fabric mesh with pore size of ~0.75 mm are shown in Figure 8.9. A few typical snapshots showing the penetration effect under different conditions for wiper papers, plastic (pore size of ~280 μm) and metallic (pore size of ~45 μm) meshes are given in the Figure 8.10.

Figure 8.9. Snapshots of the penetration effect process for a ~0.75 mm-pore size fabric mesh with 5 V applied voltage in 1 mol/L NaOH solution.
Figure 8.10. Snapshots of the penetration effect for (a) a plastic mesh (pore size of ~280 μm), (b) a metallic mesh (pore size of ~45 μm) and (c) a piece of wiper paper with 5 V applied voltage in 1 mol/L NaOH solution.
We now demonstrate the second fascinating phenomenon, which is the wall-climbing effect. Galinstan was added into a small cup, such that a specific value of height $h$ was obtained, with the height $h$ defined as the distance from the top edge of the cup to the beginning of contact between the galinstan and the cup's wall. The liquid metal remains static inside the small cup without an applied voltage. As soon as the voltage is applied, however, the liquid metal deforms due to the significant decrease in its surface tension to near-zero, which drives the liquid metal to keep moving or deforming. Since the only free space for the galinstan to move to is the region in between the container wall and the liquid metal (as shown in Figure 8.11a), the liquid metal is forced to move up along the inner wall of the small cup, resulting in the so called “wall climbing” effect, which appears to be against gravity. If the driving force overcomes the gravity, the liquid metal can reach the top edge and eventually flow down the outside of the cup (Figure 8.11b). Two typical images for this effect with and without an applied voltage are shown in Figure 8.12a and b. The wall climbing process continues if the voltage continues to be applied. It stops when
gravity overcomes the climbing force. This process ends instantly once the applied voltage is removed.

Figure 8.12. The edge of the small cup has been magnified on the left side. Snapshots of the wall-climbing effect process (a) before and (b) after 10 V applied voltage in 1 mol/L NaOH solution.

So far, we have demonstrated two fascinating effects for the liquid metal: the penetration and the wall-climbing effects at room temperature. Both effects mimic what
has been seen in liquid helium superfluid. Nevertheless, the underlying physics for both effects in liquid metal is quite different from that for the liquid helium superfluid. The dual effect in the liquid helium superfluid stems from the quantum phase transition from the normal liquid state to a Bose-Eisenstein condensate (BEC). The BEC results in zero viscosity, which causes the frictionless flow of liquid helium at extremely low temperatures. The dual effect, however, can amazingly occur in liquid metal at room temperature without undergoing the BEC phase transition, but with near-zero surface tension induced by certain applied voltages.

Furthermore, we have monitored the dripping process through porous materials with and without cutting off the applied voltage. We have found that once the voltage is removed, the liquid droplet stops penetrating into porous materials and pops back up to the surface due to the recovery of the large surface tension of galinstan. Simultaneously, the drips extending down into the solution break up very quickly and are re-shaped into spherical droplets. The dripping phenomenon in our experiment was purely driven by gravity, which is different from a previously reported similar effect that uses a pumping method to help the flow/dripping of the liquid metal.\textsuperscript{142}

### 8.4 Conclusions

We discovered that liquid metal is capable of penetrating through a porous material and climbing up the sides of a container at room temperature. We have demonstrated the penetration effect in sponges with different pore sizes and thicknesses, as well as other porous materials such as wiper paper, and plastic and metallic meshes. The penetration speed depends on the concentration of the electrolyte solution, the applied voltage, and the
pore size of the sponge or other porous material. The key physics is that there is a giant reduction of the surface tension of the liquid metal to near-zero, induced by the applied voltage. The near-zero surface tension guarantees a zero contact angle between the liquid metal and the solid surface. This drives the liquid metal to diffuse into the porous material, keep moving out of the material, and drip down by gravity. The wall-climbing effect was also presented. Our findings offer new opportunities for novel microfluidic applications and could promote further exploration for more exotic fluidic states of liquid metals.
Chapter 9 Conclusions

In this doctoral work, emerging wettability applications of water, oil, and liquid metals have been studied. The novel materials with superior wettability properties have been developed for high effective oil/water separation and water harvesting. Voltage-induced novel phenomena such as heart beating effect, penetration effect, wall-climbing effect and liquid metal patterning of have been studied for room-temperature liquid metal galinstan. Their potential application has also been discussed.

Conclusions can be made as follows:

(1) A novel superhydrophilic and underwater superoleophobic NiO/Ni mesh has been developed, which shows superior oil/water separation in harsh environments. It can separate different oil-water mixtures with and without sand or soil, with > 99% separation efficiency and up to $5.4 \times 10^4 \text{ L m}^{-2} \text{ h}^{-1}$ permeate flux. The mesh is reusable and durable, and its superior performance can be easily recovered by a very short heat treatment that is only needed for sticky oils.

(2) Stenocara beetle-inspired superhydrophilic/superhydrophobic patterned surfaces were fabricated on the silica PDMS-coated superhydrophobic surfaces through the PLD technique with a mask. The resultant superwetttable patterned samples exhibited superior water harvesting efficiency. Both the size and the percentage of the Pt-coated superhydrophilic square regions on the patterned surface have an important effect on water harvesting efficiency.
(3) A new and easily accessible heart beating phenomenon has been discovered by using low-toxic galinstan under electrical filed in a graphite ring. The continuous reversible deformation is dominated by a surface oxide and electrical field effect. The liquid metal droplet was moving in the horizontal direction with range of beating frequency from 0.74 to 1.69 Hz.

(4) Non-contact, maskless electrochemical lithography technique was developed for liquid metal at room temperature. The hole sizes can be formed in the range from submillimeters to above 30 mm with the highest formation speed above 76 mm/s for high voltages and concentrations. Various patterns have been fabricated using three different approaches: electrochemical dot matrix printing, “writing”, and movable type printing.

(5) We discovered that liquid metal is capable of penetrating through a porous material and climbing up the sides of a container at room temperature. We have demonstrated the penetration effect in sponges with different pore sizes and thicknesses, as well as other porous materials such as wiper paper, and plastic and metallic meshes. The key physics is that there is a giant reduction of the surface tension of the liquid metal to near-zero, induced by the applied voltage. This drives the liquid metal to diffuse into the porous material, keep moving out of the material, and drip down by gravity. The wall-climbing effect was also presented.
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Appendix

Appendix A: Publications

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