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Smart ZIF-L Mesh Films with Switchable Superwettability Synthesized via a Rapid Energy-Saving Process

Ting Chen^a, Allana Lewis^a, Zhipeng Chen^a, Xianfeng Fan^a, Norbert Radacsi^a, Andrea J. C. Semiao^b, Huanting Wang^c, and Yi Huang^{a,*}

^aSchool of Engineering, Institute for Materials & Processes, The University of Edinburgh, Robert Stevenson Road, Edinburgh, EH9 3FB, UK

^bSchool of Engineering, Institute for Infrastructure and Environment, The University of Edinburgh, Thomas Bayes Road, Edinburgh, EH9 3FG, UK

^cDepartment of Chemical Engineering, Monash University, Clayton, Victoria, 3800 Australia.

Corresponding author: Yi Huang, E-mail: Yi.Huang@ed.ac.uk

Highlights

- Ultra-facile fabrication of intelligent zeolitic imidazolate framework (ZIF)-L mesh films at ambient conditions
- Unique, superwetting ZIF-L surface consists of oriented two-dimensional ZIF-L nanoplates
- Switchable oil/water separation was easily achieved on various smart ZIF-L meshes without additional chemical or heat treatment
- Highly-efficient separation of various oil/water mixtures with excellent long-term cyclic separation performance
- Satisfactory stability in harsh conditions, e.g., in concentrated acid, base and salt solutions

Abstract

Smart materials with unique surface wetting properties have attracted considerable interest, particularly for oil/water separation, where oil can cause severe environmental damage. Despite

the considerable progress made in the past decade, critical challenges remain in scaling up, as smart materials are either expensive to fabricate or involve complicated, energy-intensive, and/or time-consuming production processes. In this work, an ultra-facile approach to fabricate hierarchical Zeolitic Imidazolate Framework-L (ZIF-L) mesh films with switchable superwettability for efficient oil/water separation was reported for the first time. A thick, continuous layer of well-intergrown ZIF-L nanoplates with an average aspect ratio of ~25 was successfully synthesized on various stainless steel (SS) meshes at ambient conditions. The ZIF-L mesh films exhibited extraordinary in-air superamphiphilic, underwater superoleophobic and underoil superhydrophobic properties, and showed outstanding performance in solely-gravity-driven oil/water mixture separation. Interestingly, a prewetting-induced switchable permeation function was found for the hierarchical ZIF-L surface, truly achieving “oil-blocking” and “water-blocking” separation. The ZIF-L mesh films demonstrated superior cyclic separation performance for a variety of oil/water mixtures with separation efficiencies above 99.99% and satisfactory chemical and mechanical stabilities even in harsh conditions. Their rapid and energy-efficient fabrication is therefore highly promising for cost-efficient and large-scale production for widespread applications in oil/water separation.

Graphical Abstract

Keywords: ZIF-L mesh, switchable superwettability, ultra-facile, energy-efficient, oil/water separation

1. Introduction

Oily wastewater generated from various industrial processes and frequent oil spill accidents have become pressing environmental concern, posing severe threats to both the global ecosystem and human health.^[1,2] Sustainable oil/water separation is hence urgently required. Conventional techniques, such as flotation,^[3] centrifugation,^[4] and coagulation,^[5] have been widely applied to alleviate current oil contamination concerns. However, they have inevitably suffered from either high-energy consumption, low separation efficiency, or secondary pollution. Therefore, the development of cost-effective, energy-efficient, and environmentally friendly approaches to address these environmental and economic challenges has been very demanding. Membrane separation technology has rapidly developed during the past decades due to its economic efficiency, infrastructure agility, and operational simplicity. It is widely employed for water purification.^[6,7] Recently, bioinspired membranes with rationally designed smart surfaces have been recognized as attractive candidates for highly-efficient oil/water separation.^[8,9] By adopting nanofabrication processes, bioinspired polymer-based membranes^[10] and inorganic/ceramic-based membranes with superwetting surfaces have been reported for efficient oil/water separation.^[11] However, it has been very challenging to alleviate limitations associated with the intrinsic physicochemical properties of the membrane materials as well as the thermodynamic nature of the manufacturing processes. For instance, polymeric membranes suffer from long-standing chemical stability issues,^[12] while ceramic membranes usually involve complex and energy-intensive fabrication processes.^[13] Moreover, they both have severe fouling problems, which greatly hinder their reusability and large-scale applications. In the recent decade, metallic-based meshes with low cost and long-term durability have been regarded as an effective alternative.^[14] A wide range of techniques have been developed to impart superwetting properties onto mesh surfaces, including chemical etching,^[15] electrochemical anodization,^[16] plasma treatments,^[17] grafting of hydrophilic polymers^[18] and

deposition of inorganic materials.^[19] However, most of these involve expensive/toxic chemicals, sophisticated devices, or high synthesis temperatures in the manufacturing process, creating potential scaling up, economic or environmental concerns.^[20] Thus, there is an immediate need for an energy-effective, scalable, and environmentally friendly approach to fabricate intelligent mesh-supported membranes/films with tunable superwetting properties.

With the concept of introducing different affinities towards oil and water, both superhydrophobic-superoleophilic and superhydrophilic-superoleophobic materials are expected to be useful for oil/water separation.^[21] In the past decade, superhydrophobic-superoleophilic membranes have been extensively studied and used to remove oil from aqueous mixtures, but they usually suffer from structural fouling due to the adsorption of oils onto the intrinsically oleophilic surfaces.^[22,23] Superhydrophilic-superoleophobic surfaces, on the other hand, are free from the oil contamination problems due to their intrinsic oil-repellent properties.^[24] However, it is highly challenging to construct such materials since a superoleophobic surface inherently exhibits superhydrophobicity.^[25] To tackle this challenge, underwater superoleophobic surfaces which are inspired by fish scales have been fabricated.^[26,27] superhydrophilic surfaces with micro/nano-hierarchical architectures can trap abundant water in the rough surfaces, forming a water barrier between the oils and membrane surface and thus generating underwater superoleophobicity.^[28,29] A wide range of materials, such as metal hydroxide,^[30] graphene oxide,^[31] TiO₂ nanoparticles,^[32] and polyaniline nanowire,^[33] have been employed to prepare underwater superoleophobic membranes with excellent oil/water separation efficiency. Very recently, intelligent materials with a switchable wetting surface have been reported with a promising performance in treating various types of oil/water mixtures.^[34-38] The special wettability of the smart surfaces was usually switchable between superhydrophobicity-superoleophilicity and superhydrophilicity-superoleophobicity once the external driving force, such as heat,^[34] electricity,^[35] gas,^[36] pH variation^[37] or light irradiation,^[38] was applied. However, the preparation of these intelligent materials usually is

very complex and energy-consuming. As switchable oil/water separation requires additional heat or chemical treatment of the surface, the separation procedure can be further complicated, and excess energy consumption could be necessary. Therefore, it is very challenging to fabricate such intelligent surfaces for a more sustainable oil/water separation.

Metal-organic frameworks (MOFs), a class of multifunctional crystalline materials, are of great interest in their application as intelligent membrane material due to their beneficial characteristics such as unique chemical versatility, flexible structural design, and abundant functionalities.^[39,40] MOF-based membranes have displayed promising performances in a wide range of applications, such as catalysis,^[41] gas storage,^[42] and gas adsorption.^[43] Among them, zeolitic imidazolate frameworks (ZIFs) are a typical type of MOFs with topologies analogous to those known for zeolites.^[44] In recent years, both the crystalline form and amorphous form of ZIFs have been extensively studied due to their tunable pore structure and functional properties. For instance, Wang et al.^[45] demonstrated the synthesis of a continuous nanoporous carbon composite membrane through the direct carbonization of ZIF-L film on a porous alumina. The membrane exhibited a narrow micropore size distribution and a high H₂ permeance. Tsapatsis et al.^[46] reported the immediate amorphization of ZIF-L using a scanning electron beam. The obtained amorphous ZIF-L exhibited significantly improved water stability. Because of the good stability under humid environments, ZIFs have also been attracting particular attention for liquid separation.^[47,48]

In this work, we demonstrated for the first time a low-cost, energy-effective, and scalable approach to grow ZIF-L nanoplates on various stainless steel meshes at room temperature and ambient pressure. The as-synthesized ZIF-L meshes with extremely rough micro-/nano-hierarchical surface structures exhibited outstanding in-air superamphiphilic, underwater superoleophobic and underoil superhydrophobic properties. Such special superwetting property towards oil and water molecules achieved switchable oil/water mixtures separation without applying any external driving force or chemical treatment. The energy-efficient, time-saving,

and environmentally friendly fabrication process developed in this work has great potential to scale up the manufacturing of ZIF-based films for widespread applications in mixture liquid separation.

2. Experimental section

2.1 Materials

2-methylimidazole (2-mim; 99%) was purchased from Sigma-Aldrich Company Ltd. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 98%), methylene blue and oil red O were obtained from Alfa Aesar. Stainless steel meshes (200 mesh/77 μm ; 270 mesh/58 μm ; 325 mesh/42 μm ; 400 mesh/34 μm) were purchased from The Mesh Company (Warrington) Ltd. All other solvents as well as oils used in the oil/water separation experiments were supplied by Fisher Scientific UK Ltd and were used as received.

2.2 Rapid room-temperature fabrication of ZIF-L coated meshes

Stainless steel meshes with a size of 4 cm $\times$ 4 cm were sequentially cleaned ultrasonically in acetone, ethanol, and deionized (DI) water to remove surface impurities, followed by soaking in 0.1 M hydrochloric acid solution and then rinsing by DI water to remove surface oxide. The ZIF-L coated mesh was fabricated simply following a pre-seeding and secondary growth process. The synthesis solution was prepared according to a previous study with small modifications. Typically, aqueous solutions of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2-methylimidazole were mixed ($V:V = 1:1$) and stirred for 30 minutes at room temperature ($\sim 25^\circ\text{C}$). A piece of cleaned stainless steel mesh was then vertically placed in the synthesis solution for 15 minutes. After that, the seeded mesh was vertically immersed in the freshly-prepared synthesis solution under room temperature for secondary growth. After 1 h, the mesh was removed and washed with deionized water repeatedly. After room temperature drying, the ZIF-L coated mesh was then ready for oil/water mixture separation tests.

2.3 Switchable oil/water separation

The oil/water separation performance of the ZIF-L coated mesh was tested by conducting a series of gravity-driven oil/water mixture separation experiments. Oil/water mixtures were prepared by simply mixing water with the oil(s). For better observation, water was dyed with methylene blue and oils were dyed with oil red O. A home-made separation apparatus was designed for gravity-driven oil/water mixture separation experiments. The mesh was placed between two identical glass tubes with a diameter of 25 mm and then sealed firmly with clamps. In a separation test, the oil/water mixture was poured directly onto the mesh. The permeate was collected, and its real-time flux was monitored at the same time. In a switchable oil/water separation test, the mesh was firstly pre-wetted with water by simply pouring ~50 mL of deionized water onto the mesh surface. Then a mixture of water and cyclohexane was poured into the top funnel, and the permeated water was collected in a beaker, realizing the “oil-blocking” separation. After that, the mesh was gently shaken in methanol using tweezers and kept soaking for 30 min, followed by air drying for 5 min. The cleaned mesh was then fixed in the separation apparatus and pre-wetted with oil by pouring ~50 mL of dichloromethane onto the mesh surface. A mixture of dichloromethane and water was then poured into the top funnel, and the permeated dichloromethane was collected, realizing the “water-blocking” separation.

2.4 Characterizations

The surface morphology of the ZIF-L coated mesh was characterized by using a JEOS JSM-IT100 Scanning Electron Microscope (SEM). The crystalline structure of the synthesized ZIF-L was determined by X-ray diffractometer (XRD, Bruker D8 Advance) with Cu K α radiation in a 2θ range of $4.0^\circ \sim 40.0^\circ$. Contact angle (CA) measurements were performed on the First Ten Angstroms (FTA 32) instrument. For underwater and underoil contact angle measurements, a transparent rectangular container prefilling with water or oil was used. The ZIF-L mesh films were then soaked horizontally in the water. An oil or water droplet was gently placed onto the mesh film surface using a home-made curved needle. The residual oil content in the permeate solutions was characterized by an OCMA-220 oil content analyzer.

3. Results and Discussion

3.1. ZIF-L mesh film fabrication and characterizations

The hierarchical ZIF-L mesh films were fabricated using a fast seeding and secondary growth process, as displayed in the schematic diagram in Fig. 1a. After dip-coating in the synthesis solution at room temperature ($25\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$) for 15 min, the stainless steel mesh (size 400) which initially had a smooth surface (Fig. 1b,c) was covered by a thin layer of ZIF-L seeds (Fig. 1d). Then, a new synthesis solution with the same composition was prepared and used to promote the fast secondary growth of ZIF-L film at room temperature. The seeded stainless steel mesh was placed vertically in the reactor. After only 1 h of synthesis, the mesh surface was uniformly covered by ZIF-L nanoplates (Fig. 1e), forming a very rough surface. The XRD pattern of the powder collected at the bottom of the reactor showed characteristic ZIF-L diffraction patterns,^[49] and XRD pattern of the ZIF-L mesh film further confirms that the mesh surface is composed of a thin layer of ZIF-L crystals. (Fig. S1) After secondary growth, the average mesh aperture size was decreased from $34\text{ }\mu\text{m}$ to $\sim 25\text{ }\mu\text{m}$ (Fig. 1e). The cross-sectional SEM image of the mesh wire revealed that the ZIF-L nanoplates with an average length of $\sim 5\text{ }\mu\text{m}$ have vertically grown on the mesh surface (Fig. 1f). A high-magnification SEM image again confirmed that the mesh surface was fully covered by well-intergrown ZIF-L nanoplates with an average thickness of $\sim 200\text{ nm}$ (Fig. 1g). Abundant micro- and nano-sized pores were observed on the continuous, hierarchical ZIF-L mesh film. With further increase of the secondary growth time, the mesh surface morphology showed no significant change except the effective aperture size which decreased from 34 down to $\sim 22\text{ }\mu\text{m}$ after 6 h of secondary growth due to bigger ZIF-L crystals forming on the mesh wires. Therefore, the effective aperture size of the ZIF-L mesh film can be readily adjusted by merely controlling the ZIF-L growth time (Fig. S2). However, the underwater oil contact angle (OCA) of the ZIF-L meshes did not

improve with higher secondary growth time (i.e., > 1 h), indicating that short reaction time was sufficient to fabricate a ZIF-L mesh with the excellent underwater superoleophobic property. By using different mesh films (e.g., mesh sizes 200, 270, and 325), very similar ZIF-L structures were fabricated on the mesh surfaces (Fig. S3). It is worthwhile mentioning that ZIF-L membranes/coatings have been successfully formed on anodic aluminum oxide (AAO)^[49] and polymer substrates.^[48] For example, Zhong et al. have successfully prepared oriented two-dimensional zeolitic imidazolate framework-L membranes on an AAO support.^[49] Very recently, Bruggen et al. reported a two-step deposition of ZIF-Ls on 3D printed polyamide membranes.^[50] However, to the best of the authors' knowledge, it is the first time that the unique hierarchical ZIF-L structure with switchable transport function was easily fabricated on the metal surface (stainless steel in this work) under ambient conditions.

In the fabrication process, mesh seeding was a crucial step for the growth of continuous and dense ZIF-L nanoplates on the mesh surface. Without pre-seeding, no ZIF-L nanoplates were formed on the surface after one-hour direct growth (Fig. S4a,b). Minimum growth time of 7 h was found necessary to have adequate ZIF-L coverage on mesh wires in the absence of seeds, which was significantly longer than that required in the presence of seeds (Fig. S4c-f). The slow crystallization was attributed to the unfavorable nucleation and crystal growth on the unseeded mesh surface. Therefore, a longer growth time was required to form a continuous ZIF-L coating on the surface. In contrast, in the presence of seeds, ZIF-L nucleation and crystallization was more favorable and much faster on the mesh surface. It has been reported that the existing seeds can considerably lower the activation energies associated with nucleation and subsequent crystallization, making the synthesis system more favorable for fast crystal growth at ambient conditions.^[40,49] In this work, by applying seeding, a thick and continuous ZIF-L nanoplate film was successfully formed on the metal surface under one hour at room temperature.

The wettabilities of the bare stainless steel mesh and the ZIF-L nanoplate meshes were characterized using contact angle measurements. The bare mesh exhibited in-air hydrophobicity

and oleophilicity with a water contact angle (WCA) of $\sim 117^\circ$ and an OCA of $\sim 0^\circ$ (Fig. S5a,b). After ZIF-L growth, the mesh surface became hydrophilic with a low WCA of $\sim 20^\circ$ (Fig. 2a). Underwater wettabilities were explored by immersing mesh in water and performing oil contact angle measurements. The underwater OCA of the clean mesh was $\sim 65^\circ$ (Fig. S5c). After growing ZIF-L nanoplates on the surface, however, the mesh showed an underwater OCA of $\sim 156^\circ$, suggesting an outstanding underwater superoleophobic surface was formed (Fig. 2b). Similar to many other works,^[34-38] the obtained superwetable meshes preferentially allowed the permeation of water while blocking the oil phase, achieving the “oil-blocking” separation of “water-rich” oil/water mixtures. On the other hand, the mesh surface was superoleophilic in air, as oil droplets quickly spread out once contacting the surface (Fig. 2c). It was expected that such in-air superoleophilic surfaces could efficiently adsorb oil molecules in their nano/microstructures and form a repulsive oil film to the water phase, exhibiting underoil superhydrophobic behavior. The underoil wettability of the ZIF-L coated mesh was examined by immersing it into a representative oil, cyclohexane. The results confirmed that the ZIF-L mesh exhibited excellent underoil superhydrophobicity with an underoil WCA of $\sim 160^\circ$ (Fig. 2d), while the bare mesh only showed an underoil WCA of $\sim 135^\circ$ (Fig. S5d).

Once prewetted with an oil phase, these intelligent surfaces favored oil permeation but rejected water, achieving “water-blocking” separation of “oil-rich” aqueous mixtures. Fig. 2e,g display images of underwater oil droplets (dyed with Oil red O) and underoil water droplets (dyed with methylene blue) on the ZIF-L mesh film, respectively. In both analyses, the oil or water droplets can easily roll over on the mesh surface while retaining the same size, suggesting ultralow surface oil-adhesion and water-adhesion properties, respectively.

The sketches in Fig. 2f,h diagrammatically explain the underwater and underoil wetting mechanisms of the hierarchical ZIF-L mesh surface, respectively. Contact angles in the oil/water/solid three-phase environment can be illustrated by the modified Cassie model,^[8,9] as shown in the following equation:

$$\cos \theta' = r_f f \cos \theta + f - 1 \quad (1)$$

where θ and θ' represent the underwater oil contact angle (or underoil water contact angle) of an ideal smooth surface and a rough surface, respectively. r_f is the non-dimensional surface factor, which refers to the ratio of the surface area to the projected area; f is area fraction of the underwater (or underoil) solid surface contact with oil (or water). In our case, the closely packed 2-dimensional ZIF-L nanoplates generated extremely rough surface, resulting in a sharp decrease in the area fraction, f , thus significantly increasing underwater oil contact angles (or underoil water contact angles). To further explore the surface wettability of the ZIF-L coated mesh, underwater contact angles of a series of oils (Fig. 2i) and underoil water contact angles in different oils (Fig. 2j) were measured. According to these Figures, our mesh films have indeed exhibited excellent underwater superoleophobicity for various oils with all OCAs higher than 155° . Meanwhile, the mesh film also displayed extraordinary superhydrophobicity under different oil phases with WCAs close to 160° .

3.2. Oil/water separation

In this work, a series of gravity-driven oil/water separation tests were carried out because the superior superwetting properties of our ZIF-L coated mesh films allowed the separation driven solely by gravity. Their separation principle was schematically illustrated in Fig. 3a. Briefly, when prewetted with water, the water molecules preferentially permeated through the mesh film while the oil molecules were rejected completely and remained on top of the surface, due to its underwater superoleophobicity as well as ultralow oil-adhesion property. In contrast, when prewetted with oil, our ZIF-L mesh film preferentially allowed the permeation of oil, while rejected water above the surface because of its superior underoil superhydrophobic property. Fig. 3b showed the photographs of the ZIF-L coated mesh at a different stage in a switchable oil/water separation test. Firstly, a mixture of oil red-dyed cyclohexane and methylene blue-dyed water ($\rho_{\text{water}} > \rho_{\text{oil}}$) was poured onto the water-prewetted mesh, triggering

“oil-blocking” separation as cyclohexane was rejected above the mesh surface despite being in contact with the surface at the beginning (Video S1). After a simple cleaning with methanol and a fast air drying, the ZIF-L mesh was prewetted with cyclohexane. Then, a mixture of water and dichloromethane ($\rho_{oil} > \rho_{water}$) was poured into the top funnel. It was observed that only dichloromethane permeated through the mesh while the water was completely blocked (Video S2), confirming that the separation was successfully switched to the “water-blocking” separation mode. All the separation processes were solely driven by gravity, and no external pressure was applied. Note, the switchable separation performance of our mesh film was realized by merely changing the prewetting media before the tests. No expensive chemical or heat treatment was required, confirming that the switchable separation using our ZIF-L mesh was highly energy- and time-effective.

The separation performance of the mesh towards a series of oil/water mixtures was also explored in this work. The permeate flux (F) of the mesh was calculated from the volume of the permeation in unit time, according to:

$$F = V / A \cdot t \quad (2)$$

Where V is the volume of the filtrate (L), A is the effective filtration area of the mesh (m^2), and t is the permeation time (h). The separation efficiency (R) was calculated using the following equation:

$$R(\%) = \left(1 - \frac{C_p}{C_0} \right) \times 100 \quad (3)$$

where C_p is the residual oil concentration in the collected filtrate, C_0 is the original oil concentration in the feed oil/water mixture.

As presented in Fig. 4a, the separation efficiencies of ZIF-L mesh film (size 400) for all oils tested in this work were above 99.99% (or more precisely less than ~30 ppm of oil content in the filtrate) with an averaged permeate flux as high as $\sim 1.35 \times 10^5 \text{ L m}^{-2} \text{ h}^{-1}$, suggesting the mesh was capable of realizing highly-efficient separation of various types of oil/water mixtures. The

influence of the secondary ZIF-L growth time on the mesh separation performance was also studied. As shown in Fig. 4b, all ZIF-L coated meshes showed excellent separation performance with an oil rejection above 99.99%. However, it was found that with the increase of the secondary growth time, the permeation flux declined from $\sim 1.35 \times 10^5$ down to 0.86×10^5 L m⁻² h⁻¹. This decrease in flux was caused by a thicker and denser ZIF-L nanoplates film formed on the mesh wires, resulting in the decrease in the aperture size and consequently a reduced water permeation through the mesh (Fig. S2).

The separation performances of the mesh with different mesh numbers were also examined. As shown in Fig. 4c, the permeate flux increased while the separation efficiency slightly decreased from 99.99% to 99.55% when a smaller mesh number was used. It is worthwhile mentioning that our results showed that excellent oil/water separation could be obtained on mesh 200, which had open apertures of 77 μ m in size. To the best of our knowledge, this is the largest mesh aperture size used for meshed-based oil/water separation in the literature. We ascribed this superior performance to the extraordinary superwetting property endowed by the unique hierarchical ZIF-L structure. Additionally, the use of a large-aperture mesh with low cost and improved mechanical strength has great potential in reducing capital investment and is of great importance in designing large-scale applications with this membrane.

“Water-blocking” separation performance of the ZIF-L coated mesh was also studied using different types of oil/water mixtures. The “water-blocking” separation is suitable for the separation of heavy oil/water mixtures, in which the density of oil is greater than that of water (such as dichloromethane, trichloromethane, bromobenzene, and carbontetrachloride, and tetrachloroethane). Although there are limited cases of heavy oil/water mixtures reported, the separation of heavy oils is still significant and should not be ignored. It was revealed that the oil prewetted mesh exhibited superior separation performance towards all the tested oil-enriched mixtures (Fig. S6). The results confirmed that the ZIF-L coated mesh was capable of realizing the highly-efficient separation of various types of oil/water mixtures under both water-

removal and oil-removal modes. As compared to those “single-separation” mesh materials, our ZIF-L mesh films with switchable separation function were more cost-effective and easy-to-use, and thereby they are more promising for economic on-demand oil/water separation. Finally, long-term cyclic separation tests were performed in order to test the stability of the separation performance. At least 50 cycles of oil/water separation were randomly tested for over 6 months. As shown in Fig. 4d, an oil rejection rate greater than 99.98 % was obtained for all 50 cycles, and the water flux maintained higher than $\sim 1.24 \times 10^5 \text{ L m}^{-2} \text{ h}^{-1}$. SEM images of the mesh film after 50 cycles (Fig. S7) showed that a fully coverage of ZIF-L was maintained on the mesh surface, suggesting that our ZIF-L mesh films were highly stable after a short period of intense tests.

3.3. Separation mechanism

To further understand the prewetting induced switchable separation mechanism, four schematic models were displayed in Fig. 5a-d. Theoretically, the intrusion pressure (Δp), which refers to the pressure that the mesh can hold before the onset of oil permeation, can be determined as follows:

$$\Delta p = \frac{2\gamma}{R} = \frac{-l\gamma \cos \theta}{A} \quad (4)$$

Where γ is the interfacial tension, R is the radius of the meniscus, l is the perimeter of the mesh pore, A is the area of the pore and θ is the advancing contact angle on the mesh surface. When water (or oil) is in contact with the mesh surface, θ is nearly 0° due to the superamphiphilicity of the mesh surface in air. Thus, the intrusion pressure (Δp) is negative ($\Delta p < 0$) according to Equation 4, suggesting water (or oil) can freely permeate through the mesh film (Fig. 5a,c). When the mesh is prewetted by water (or oil), abundant water (or oil) molecules are trapped into the submicron- and nanoscale structures, forming a layer of water (or oil) barrier against oil (or water). At this time, θ is greater than 90° and $\Delta p > 0$, indicating the mesh can withstand a certain height of oil (or aqueous) phase on top (Fig. 5b,d). Above analyses clearly explain the

excellent reversibility between superhydrophilicity/underwater superoleophobicity and superoleophobicity/underoil superhydrophobicity of our unique hierarchical ZIF-L mesh films. The experimental intrusion pressure (Δp_e) was evaluated by measuring the maximum height of the oil column that the mesh can support (Fig. 5e) and calculated according to the following equation:

$$\Delta p_e = \rho g h_{\max} \quad (5)$$

Where Δp_e is the experimental intrusion pressure, ρ is the density of the test oil (or water), g is the acceleration of gravity, and $h_{\max}$ is the maximum height of the oil (or water) phase that the mesh can support before the onset of oil permeation (or water permeation). In this work, the Δp_e was estimated using different oils. As shown in Fig. 5f, our ZIF-L meshes displayed an intrusion pressure of ~2.0 kPa, which was higher than most of the reported values (Table S1).

3.4. Chemical and hydrothermal stabilities

Industrial oily wastewater usually exists under different pH environments (either acidic or basic) and contains specific concentrations of salts (e.g., NaCl). Therefore, satisfactory structural stability of the mesh in these harsh environments is essential for long-term industrial applications. In this work, mesh stability was systematically evaluated by monitoring the wettability change of the mesh surface under different conditions. As shown in Fig. 5g, our ZIF-L meshes showed satisfactory stability under different pH conditions with both underwater oil and underoil water contact angles higher than 150°. The corresponding SEM images further confirmed that the hierarchical ZIF-L nanostructure was mostly retained after soaking in a strongly acidic HCl or basic NaOH aqueous environment for 6 h at room temperature (Fig. S8). Furthermore, the stability of the mesh against aqueous salt solutions was studied by immersing the mesh in different NaCl solutions (up to 10 wt% in water) for a period of 6 h at room temperature. According to the results, our ZIF-L mesh exhibited satisfactory stability in all salt solutions. Both underwater oil and underoil water contact angles were retained above 150° (Fig.

S9a). SEM images confirmed that the ZIF-L meshes displayed excellent chemical stability at low salt concentrations (Fig. S9b,c). However, they still showed satisfactory stability at extremely high salt concentrations (10 wt%), although a change of surface morphology was observed. (Fig. S9d,e). The stability of ZIF-L mesh films under both acidic and basic conditions was examined by soaking the as-synthesized samples in an acidic HCl solution ($\text{pH} = 4$) and a basic NaOH solution ($\text{pH} = 14$) for 6 h, respectively. As shown in Fig. S10, both mesh samples still retained characteristic ZIF-L X-ray diffraction patterns, although lower intensity was observed in the sample after strong acid treatment. The results underscored that our ZIF-L mesh films exhibited better structural stability under basic conditions. However, it is worthwhile mentioning that the ZIF-L amorphization in both stability studies has not significantly influenced the overall hierarchical morphology of the intergrown ZIF-L layer (Fig. S8) and also their separation performance. Long-term stability of our ZIF-L meshes was further studied by exposing them in wet air with a relative humidity (RH) of around 60 % at room temperature for 6 months and further soaking the mesh sample under DI water for 7 days. As suggested by the XRD results in Fig. S10 and SEM images in Fig. S11a,b, ZIF-L nanoplate structure was well retained on the mesh surface after stored in wet air for 6 months, while significant water dissolution was observed after soaking in water for 7 days which was consistent to the results reported previously.^[46] However, the liquid water soaked sample still exhibited almost a complete coverage of thinner, flexible nanosheet materials, forming similar hierarchical roughness on the mesh surface (Fig. S11a,b). According to above results, it's critically important to tackle the weak long-term hydrostability of ZIF materials in aqueous solutions, although they have shown excellent stability in wet air over a period of 6 months. Relevant works are currently ongoing in our labs.

Last but not least, the facile fabrication process developed in this work was highly energy-efficient and time-effective compared with those reported in other works. Fig. 5h and Table S1 summarized some recent synthesis conditions of mesh-based materials. It is evident that either

a long synthesis time (>2 h) or a high-temperature pre- (or post-) treatment (>100 °C) was inevitably involved. In fact, in many studies, the high-temperature calcination (up to ~550 °C) step was essential to activate or regenerate the as-synthesized materials before applying for oil/water separation. In this work, our synthesis was completed in one hour under ambient conditions (25 °C and atmospheric pressure). Meanwhile, the separation efficiency and flux of our ZIF-L mesh films were superior as compared to previously reported mesh films (Fig. S12). The obtained ZIF-L meshes showed intelligent prewetting-induced switchable separation function and satisfactory chemical stability in harsh environments. From the energy consumption and economic point of views, our fabrication method is highly promising for the low-cost and energy-effective production of ZIF-based membranes/films for many other important practical applications, e.g., natural gas purification or CO₂ capture from flue gases.

4. Conclusions

Novel ZIF-L nanoplates coated stainless steel mesh films with hierarchical porous structures have been successfully fabricated via a rapid seeding and secondary growth process under ambient conditions, i.e., 1 h at 25 °C and 101 kPa. The as-synthesized meshes showed extraordinary in-air superamphiphilicity, underwater superoleophobicity, and underoil superhydrophobicity. The intelligent ZIF-L mesh films exhibited switchable superwetting properties and demonstrated superior separation performance for immiscible oil/water mixture separation with a permeation flux as high as $\sim 1.35 \times 10^5 \text{ L m}^{-2} \text{ h}^{-1}$ and an oil (or water) rejection rate of above 99.99%. The oil (or water) intrusion pressure was found up to ~2.0 kPa, which is higher than most reported values for mesh-based materials. The low-cost, energy-efficient, and time-saving fabrication route reported in the present work is of vital importance in rapid and economical mass production of ZIF-based materials.

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Declaration of Competing Interest

The authors declare no conflict of interests.

Appendix A. Supplementary data

Supplementary data to this article can be found online.

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Fig. 1. Fabrication and morphology of the ZIF-L coated mesh. a) Schematic illustration of the fabrication process of ZIF-L coated meshes. SEM image of b) the pristine stainless steel mesh, c) an enlarged view of the pristine stainless steel mesh surface, d) the ZIF-L seeded mesh wire, e) the ZIF-L coated mesh, f) a cross-sectional view of the ZIF-L film, and g) a close top-view of the intergrown ZIF-L nanoplates on the mesh wire.

Fig. 2. Surface wetting performance of the ZIF-L coated mesh. a) In-air water contact angle, b) underwater oil (cyclohexane) contact angle, c) in-air oil contact angle, d) underoil water contact angle, e) underwater oil droplets (chloroform) on the ZIF-L coated mesh, f) schematic illustration of oil wetting on the ZIF-L coated mesh with a micro-hierarchical structure in water, g) under-oil water droplets on the ZIF-L coated mesh, h) schematic illustration of water wetting on the ZIF-L coated mesh with a micro/nano-hierarchical structure in oil, i) underwater oil contact angles of various oils, and j) underoil water contact angle under different oils.

Fig. 3. Switchable separation process of the ZIF-L coated mesh. a) Schematic illustration of the prewetting induced switchable separation property of the ZIF-L coated mesh and b) photographs of one cycle of the switchable gravity-driven oil/water separation process. When prewetted by water, the mesh works under the “oil-blocking” mode, and thus oil (cyclohexane, dyed with Oil red) was rejected. When prewetted by oil (cyclohexane), the mesh switches to the “water-blocking” mode: water (dyed with methyl blue) was rejected while oil can permeate through the mesh film. In water-blocking separation, a heavier oil, dichloromethane (dyed with Oil red), was used for better visualization.

Fig. 4. Oil/water separation performance of the ZIF-L coated mesh. a) Permeate flux and separation efficiency of the ZIF-L coated mesh for a series of oil/water mixtures, b) the influence of growth time of ZIF-L on the separation performance, c) permeate flux and separation efficiency of mesh with different mesh numbers, and d) permeate flux and separation efficiency variations of the ZIF-L coated mesh in a cyclic test.

Fig. 5. Schematic illustration of the liquid-wetting modes on the hierarchical ZIF-L coated mesh. a) The mesh showed superhydrophilicity in air, and water can permeate through the mesh because $\Delta p < 0$; b) the mesh displayed underwater superoleophobicity because water was trapped between the ZIF-L nanosheets, and oil can be sustained because $\Delta p > 0$; c) the mesh was superoleophilic in air and was permeable to oil because $\Delta p < 0$; d) the mesh was superhydrophobic underoil because oil was trapped between the ZIF-L nanosheets, and water cannot pass through because $\Delta p > 0$; e) oil column (cyclohexane) above the ZIF-L coated mesh; f) the intrusion pressure (Δp_e) of the ZIF-L coated mesh for a series of oils; g) wettability of the mesh in an acidic and alkaline environment; and h) comparison of the reported fabrication conditions (temperature and time) of superwetting meshes.

Supplementary materials

Smart ZIF-L Mesh Films with Switchable Superwettability Synthesized via a Rapid Energy-Saving Process

Ting Chen^a, Allana Lewis^a, Zhipeng Chen^a, Xianfeng Fan^a, Norbert Radacsi^a, Andrea J. C. Semiao^b, Huanting Wang^c and Yi Huang^{a,*}

^aSchool of Engineering, Institute for Materials & Processes, The University of Edinburgh, Robert Stevenson Road, Edinburgh, EH9 3FB, UK

^bSchool of Engineering, Institute for Infrastructure and Environment, The University of Edinburgh, Thomas Bayes Road, Edinburgh, EH9 3FG, UK

^cDepartment of Chemical Engineering, Monash University, Clayton, Victoria, 3800 Australia.

Corresponding author: Yi Huang, E-mail: Yi.Huang@ed.ac.uk

Supplementary Text

The “water-blocking” separation test of the ZIF-L coated mesh

The “water-blocking” separation of oil/water mixtures was performed by placing the ZIF-L coated mesh between two identical glass vessels and fixed with clamps. Then around 50 mL of oil (dichloromethane) was poured onto the mesh surface to pre-wet the mesh. After that, 100 mL of oil/water mixture was poured into the top vessel. All the separations were driven by gravity.

The oil flux was calculated using the following equation:

$$F = V / A \cdot t \quad (1)$$

Where V is the volume of the filtrate (L), A is the effective filtration area of the mesh (m^2), and t is the permeation time (h). The rejection rate (η) was defined as:

$$\eta = \frac{m_1}{m_0} \times 100\% \quad (2)$$

where η is the rejection rate, m_1 is the mass of oil before the separation, and m_0 is the mass of oil after the separation.

Figure S1. The XRD patterns of the stainless steel (SS) mesh support, ZIF-L SS mesh film, and the as-synthesized ZIF-L powder. The inset shows a enlarged view of the XRD patterns in the 2θ range of $9 \sim 25^\circ$.

As shown in Figure S1, it is clear that the ZIF-L coated SS mesh shows the characteristic peaks of ZIF-L, confirming that the mesh is coated by a layer of ZIF-L nanoplates. Note, the peaks are weak as compared to those of the as-synthesized ZIF-L powder. This is reasonable because the intensity of the XRD patterns of ZIF-L coating is proportional to its mass content in the sample. In our mesh film sample, the stainless-steel mesh support provided the most weight and therefore, significantly affected the intensity of ZIF-L XRD patterns.

Figure S2. SEM images of ZIF-L coated meshes synthesized after different secondary growth time. a) 2 h, b) 3 h, c) 4 h, d) 5 h, e) 6 h, and f) the influence of secondary growth time on the effective aperture size as well as the underwater oil contact angle of the membrane.

Figure S3. SEM images of bare stainless steel meshes with a different mesh number. a) Mesh 200/77 μm ; b) mesh 270/58 μm , c) mesh 325/42 μm , d) ZIF-L coated mesh 200/77 μm , e) ZIF-L coated mesh 270/58 μm , and f) ZIF-L coated mesh 325/42 μm .

Figure S4. SEM images of the mesh surface after direct growth in ZIF-L synthesis solution. a) and b): 1 h direct growth, c) and d): 6 h direct growth, and e) and f): 7 h direct growth. a), c) and e) are low-magnification SEM images, while b), d), and f) are high-magnification SEM images.

Figure S5. Surface wetting properties of the bare stainless steel mesh 400. a) water contact in the air, b) oil contact in the air, c) underwater oil contact, and d) underoil water contact.

Figure S6. “Water-blocking” separation performance of the ZIF-L coated mesh towards different types of oil/water mixtures.

Figure S7. (a) low-magnification and (b) a high-magnification SEM images of the mesh surface after 50 cycles of oil/water separation.

Figure S8. SEM images of ZIF-L coated mesh film after soaked in an acidic and alkaline environment. a) and b): ZIF-L coated mesh film after soaked in acidic HCl solution (pH = 4) for 6 h, c) and d): the ZIF-L coated mesh film after soaked in basic NaOH solution (pH = 14) for 6 h, and b) and d) are high-magnification views of the mesh surface.

Figure S9. Stability of the ZIF-L coated mesh film in aqueous salt solutions. a) Underoil water contact angle and underwater oil contact angles of ZIF-L mesh after soaked in NaCl solutions with different concentrations, b) SEM image and c) a high-magnification view of the mesh surface after soaking in 8 wt% NaCl solution for 6 h, and d) SEM image and e) a high-magnification view of the mesh surface after soaking in a 10 wt% NaCl solution for 6 h.

Figure S10. XRD patterns of the ZIF-L mesh films after soaked in acidic HCl solution (pH = 4), in basic NaOH solution (pH = 14), in 10 wt% NaCl solution for 6 h, in wet air (~60% RH) for 6 months, and DI water for 7 days.

Figure S11. SEM images of ZIF-L coated mesh film after stored in saturated vapor and water environment. a) and b): ZIF-L coated mesh film after storing in wet air (~60% RH) for 6 months, c) and d): ZIF-L coated mesh film after soaking in water for 7 days, and b) and d) are high-magnification views of the mesh surface.

Figure S12. Separation performance comparison (separation efficiency and flux) of previously reported mesh films for oil/water separation.

A comparison on the flux and separation efficiency was summarized and showed in the Figure S12. As shown in Figure S12, the separation efficiency and flux of our ZIF-L mesh films are at the top-right corner suggesting a superior separation performance was achieved as compared previously reported mesh films. However, it is worth noting that the materials synthesis process reported in this work is much less energy intensive, because our best ZIF-L mesh films were successfully produced at room temperature within 1.5 hours including seeding and drying time.

Table S1. Comparison of previously reported superwetting meshes for efficient oil/water separation with this work

Substrate	Material	Temperature, °C	Time, h	Separation efficiency	Flux, $\times 10^4$ L m ⁻² h ⁻¹	Intrusion pressure, kPa	Ref
Stainless steel mesh	ZIF-8	100	2 ~ 37	>99.90%	18.0	~ 0.95	(47)
Wire mesh	Graphene oxide	90	2 ~3	>98.00%	N/A	N/A	(31)
Wire mesh	Cellulose hydrogel	100	>5	>98.90%	1.29	1.94	(18)
Stainless steel mesh	POSS hybrid acrylic	80	~10.5	>99.00%	N/A	4.11	(23)
Stainless steel mesh	UiO-66	120	~36	>99.99%	12.7	2.93	(29)
Copper mesh	CuO	200	~4	>99.97%	0.4	N/A	(15)
Ti mesh	TiO ₂	350	>7	>99.20%	~ 1.7	0.85	(51)
Stainless steel mesh	TiO ₂	400	~4	99.90%	1.36	1.70	(52)
Copper mesh	Silica	500	~2	>99.99%	N/A	N/A	(53)
Stainless steel mesh	PDMS	550	>2	>99.00%	8	3.46	(54)
Copper mesh	TiO ₂ /CuO	550	>7	>99.99%	8	N/A	(19)
Stainless steel mesh	BiVO ₄	550	>17	>98.60%	N/A	N/A	(55)
Stainless steel mesh	MFI	550	~33	>99.00%	>1.4	0.96	(56)
Stainless steel mesh	MFI	550	~37	>99.00%	>8	N/A	(57)
Stainless steel mesh	CeO ₂ /Co ₃ O ₄	350	~39	>99.99%	~ 0.14	N/A	(58)
Stainless steel mesh	ZIF-L	25	1	>99.99%	~ 13.5	~ 2.0	This work
Stainless steel mesh	ZIF-L	50	<1	>99.99%	~ 13.5	~ 2.0	This work