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# A universal copper mesh with on-demand wettability fabricated by pulsed laser ablation for oil/water separation

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ABSTRACT

Oil/water separation by surface wetting has become a research hotspot due to frequent oil spilling accidents and increasing industrial oily waste water. A rapid one-step approach is developed to fabricate copper mesh with high controllability in ambient air. Dynamic pulsed laser ablation directly creates microgrooves on copper mesh decorated with nanoparticles synthesized via the nucleation of laser induced plasma species and air molecules. The single device mesh separates various oil/water mixtures solely by gravity. Pre-wetting by water functionalizes the copper mesh to work in water-removing mode to permeate water and repel oil for light oil/water mixtures. On-demand wettability to oil-removing mode is demonstrated through pre-wetting by oil to permeate oil and repel water in typical heavy oil/water mixtures. Most importantly, the as-prepared copper mesh possesses high separation efficiency above 98% for a series of oil/water mixtures and superior environmental stability which can separate various corrosive materials, such as strong acidic, alkaline and salt solutions. The conditions for the existence of amphiphobicity and effects of surface topography on wettability and separation performance are analyzed in details. The as-prepared mesh can achieve scaling-up production and has potential applications for oil-spilling clean-up and industrial oily waste water treatment.

## 1. Introduction

Oil/water separation has attracted significant attention for environmental, social and economic issues [1,2]. Frequent oil spilling leakage and the discharge of oily waste water have become a challenge that the world faces [3,4]. In response, many researchers are devoted to developing effective and inexpensive approaches for the clean-up of oily polluted water. Various methods have been widely used in oil/water separation, such as centrifugation separation, gravity separation, skimming, air flotation and biological treatment [5–7]. Although these methods are capable of separation, the applicability is restrained by the low separation efficiency, introduction of secondary pollutants, high cost and large size of the set-up [8–10]. In recent years, utilizing desired wettability to design novel materials has attracted increasing interest. Hydrophobic/oleophilic materials (termed as "oil-removing" type of materials) have been developed. Oil quickly penetrates while water is retained at the top of the mesh, demonstrating high selectivity and separation efficiency [11–13]. Nevertheless, oil-fouling of the mesh is a common shortcoming due to their intrinsic oleophilic property, which leads to decreased oil/water separation efficiency. In most occasions, the density of water is higher than that of oil and the water below the oil will form a barrier layer for oil permeation. Recently, functional materials with underwater superoleophobicity (termed as "water-removing" type of materials) have attracted the interest of researchers. This type of new materials has completely opposite wettability to hydrophobic/oleophilic materials and overcomes the problem of oil-fouling effectively [14–16]. Up to date, various materials such as $CaCO_3$ [17], $Cu(OH)_2$ [18], $TiO_2$ [19], poalygorskite [20], ZnO [21,22] and graphene oxide [23], have been studied to gain underwater superoleophobicity.

In comparison, the water-removing type of material has wider application prospects, but it is not suitable for separating heavy oil/water mixtures due to the saturation of heavy oil below water that would hinder water permeation [24–26]. To further overcome this drawback, a universal copper mesh with on-demand wettability should be fabricated, which has both underwater superoleophobicity and underoil superhydrophobicity, named as superamphiphobicity, providing the desired capability of separating both light oil/water and heavy oil/water mixtures by gravity with extremely high separation efficiency. In this work, a superior-performing superamphiphobic copper mesh is fabricated by laser direct writing. The as-prepared copper mesh takes advantage of the liquid-favoring (water or oil) property of high surface

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energy to realize the other liquid's (oil or water) repellency in an oil/water/solid three phase system, which can be applied to effectively separate (> 98%) not only light oil/water mixtures but also heavy oil/water mixtures.

This reliable and facile method can easily construct the dual micro/nano structures which dominate the surface wettability. In addition, the fabricated surface exhibits better recyclability and shelf life with highly stable performance since their homogeneous composition could not suffer from the problem of coat-stripping. The effects of surface structures and the conditions of superamphiphobicity existence are further revealed in this paper. This work may promote the progress of oil/water separation and provide a practical solution for oil-spilling clean-up.

## 2. Experimental

### 2.1. Materials

A 99.99% pure copper sheet with a dimension size of Φ 26 mm (diameter) × 0.1 mm (thickness) is used to fabricate the copper mesh. The different types of oils include commercially available kerosene, heptane, isooctane, 1.2-dichloroethane and dichloromethane. NaCl (10 wt%) is used as the salt solution. HCl (1 M) and NaOH (1 M) are used as acid and base solutions due to their strong corrosiveness to metals, respectively. Plastic tubes and red ink used in the experiments was commercially purchased.

### 2.2. Production of copper mesh

The fabrication of underwater/oil superamphiphobic copper mesh was performed by pulsed fiber laser (1064 nm, 100 ns). Firstly, a copper sheet was cleaned in alcohol ultrasonic bath at ambient temperature. Then, holes were ablated in the copper sheet with a focused laser beam to obtain the copper mesh. Subsequently, the copper mesh surface was scanned line-by-line by laser, resulting in diverse surface topography solely by controlling laser scanning repetition time and pitch. The repetition time of laser scanning ranges from 5 to 15 with an interval of 5 times, and the pitch size of laser scanning ranges from 0.1 to 0.4 mm with an interval of 0.05 mm. The laser spot diameter incident upon the copper surface was focused to approximately 0.05 mm. The pulsed laser power was about 24 W, the fluence was set about 61.16 $J/cm^2$ and the laser scanning speed was typically fixed at 1000 mm/s. Finally, the copper mesh was cleaned by ultrasonication.

### 2.3. Oil/water separation

The copper mesh was fixed between two transparent tubes with a diameter of 20 mm. Several types of oils were employed in this work, including kerosene, isooctane, heptane, 1.2-dichloroethane and dichloromethane. When the density of water was greater than oil, the copper was pre-wetted by a small amount of water before the separation process. Otherwise, the copper mesh was pre-wetted by oil. Then, the oil/water mixture was poured into the tube with the filter and the driving force for separation was gravity. In order to observe the separation process more clearly, the water was colored with red ink.

### 2.4. Characterization

The morphological structures of the copper mesh surfaces were analyzed by field emission scanning electron microscope (FESEM, SU-70). The water and oil contact angles were measured with a DSA25 apparatus at room temperature. The volumes of the individual water and oil droplets were 2 μL. Kerosene and 1.2-dichloroethane were used as the main detecting oils. In order to ensure the accuracy of results, average values were measured in five different points on the same surface.

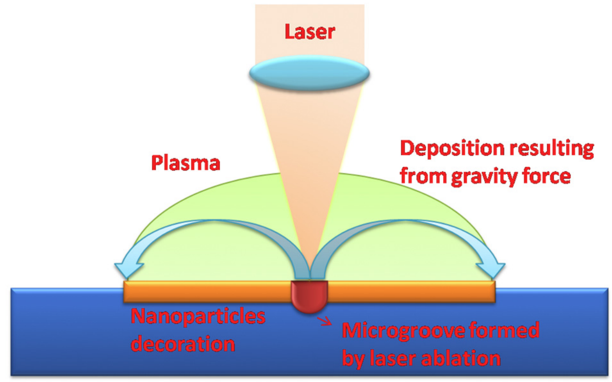


**Fig. 1.** Pulsed laser ablation dynamics to generate micro/nanostructures and deposition of nanoparticles on the copper surface due to the gravity force.

## 3. Results and discussion

Laser ablation is an effective method to remove substrate materials and synthesize nanoparticles [27,28]. Fig. 1 shows the generation of nanoparticles during laser ablation. The process includes the formation of plasma, the generation of the shock wave, the expansion of the plasma plume and the dynamic growth of nanoparticles [29,30]. The dynamics of the materials' ejection and nucleation are two dominant factors of the nanoparticles' formation [31]. When the fluence is high enough, laser can induce the materials' breakdown and the plasma generation through the irradiation of copper [32]. The plasma plume has high pressure and high temperature, and consists of laser induced energetic species, such as atoms, clusters and particulates. During laser ablation, these plasma species can be ejected out from the copper surface anisotropically and possess high kinetic energy due to the strong recoil pressure generated during the plasma formation [33]. Then, the air molecules promote the nucleation of the species, leading to the generation and aggregation of nanoparticles. Due to the gravitational force acting on the nanoparticles, these nanoparticles are deposited onto the copper surface. The micro/nano dual structures are generated by laser ablation.

Fig. 2 shows the SEM images of the as-prepared copper mesh at different scale bars. After the laser ablation, the original smooth copper sheet possesses numerous regularly arranged square holes with 0.3 mm pitch and 0.1 mm side length. The criss cross grooves and plenty of sputtered nanoparticles deposited on the mesh surface result from the laser ablation. The micro/nano dual structure is one of the main factors of surface wettability [34], which is advantageous to capture water (or oil) and repel oil (or water).

The wettability of copper mesh was comprehensively evaluated by a contact angle measurement system. As known, the wetting behavior of solid surface depends on both their surface energy and geometrical structures. Fig. 3(a) and (c) show that the as-prepared copper mesh is superhydrophilic and superoleophilic simultaneously. When an oil (kerosene) droplet touches the surface, it rapidly spreads out, resulting in a contact angle close to 0°. This is ascribed to the cooperative effect of the high surface energy and multi-scale structures. Nevertheless, the copper mesh once immersed in water or oil has its wetting behavior significantly changed. As can be seen in Fig. 3(b) and (d), both the underwater oil droplet and the underoil water droplet are quasi-spherical with high contact angles of 163.98° and 159.09°, respectively. In addition, Fig. 3(e) shows the underwater oil contact angle and underoil water contact angles for different oils are all above 150°, indicating that the copper mesh is underwater superoleophobic and underoil superhydrophobic for various oils. This particular wettability is attributed to two main reasons: i) The surface pattern can be easily filled by water and oil without any trapped air due to the superamphiphilicity of the copper mesh; and ii) When the surface pattern is filled with a liquid, the