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Full Length Article

Multifunctional oil-water and immiscible organic liquid separation by micropore arrayed Ti foil

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ABSTRACT

In this work a multifunctional micropore array (size from 5 to 42 μm) was produced by using one-step femtosecond laser microdrilling for oil-water and oil-oil separation. This novel method has many advantages, such as high precision (size error is less than 1 μm), simple operation (one step), extensible function (even complex microstructures) just to name a few. The prepared foil exhibited superhydrophilic and underwater superoleophobic properties, which can be used to separate the light oil (C_8H_{18}) and water mixtures. After heating in dark environment 0.5 h, the prepared foil showed superhydrophobic and underwater superoleophilic properties, and can be used to separate the heavy oil ($C_2H_4Cl_2$) and water mixtures. In addition, the heated sample also showed robust ability to separate the immiscible organic liquid mixtures (formamide and $C_2H_4Cl_2$), exhibiting multifunctional applications. Interestingly, the heated samples would recover its original superhydrophilicity after UV irradiation in ethanol for 1 h. The samples don't contain any fluorinated compounds and display environmental stability even after sonic cleaning and scratch. This work will provide a new insight into the design of intelligent devices for oil/water mixtures separation, organic liquid mixtures separation, and water droplet manipulation.

1. Introduction

Over the past few decades, oil/water separation has received widespread attention due to many important applications in water purification [1], separation emulsions [2], and oil recovery [3]. The traditional separation methods including skimming [4], burning [5], using of chemical dispersants [6] and solidifiers [7], and so on have their own limitations [8], such as (1) skimming methods require strict environment, (2) the burning is easy to cause environment pollution, and (3) dispersants do not reduce the risk to the environment. In order to overcome the disadvantages of traditional methods, researchers have studied a series of functional materials to achieve oil and water separation [9–12]. Fortunately, inspired by Nature, researchers have proposed a novel strategy to construct superhydrophobic/superoleophilic surfaces or underwater superoleophobic surfaces for oil-water separation. For example, Li et al. [13] obtained superhydrophobic and superoleophilic surfaces for oil/water separation by combining electrospinning technology with Ag nanoclusters and surface modification. Zhao et al. [14] prepared the superhydrophobic/superoleophilic porous structure of PDMS sponges by adjusting the weight ratio of the prepolymer to the dimethicone and the size of the NaCl particles. Yong et al. [15] prepared rough superhydrophobic PTFE sheet by femtosecond laser ablation and then generated micropore arrays on rough sheet by a mechanical drilling process to achieve oil-water separation. Li et al. [16] fabricated regular micropore arrays on aluminum foil by the femtosecond laser perforating method and changed the wettability of aluminum foil through PFDTES modification to achieve light/heavy oil-water mixture separation. Yu and co-workers [17] used coating method to change the wetting properties of the stainless steel meshes for oil/water separation. Additionally, Wang's group [18] systematically studied the relationship between surface tension and immiscible organic liquid separation, which established

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important theoretical foundation for organic mixture separation. Although the above methods could achieve oil-water or immiscible organic mixture separation, they still have some disadvantages, such as complex process, special materials, or environmental secondary pollution. In addition, the tunable capability of oil-water or oil-oil mixture separation has not been reported. It is indispensable to develop new functional materials that are environmentally friendly, economical, efficient and reusable, especially self-driven separation membranes, to solve oil-water and oil-oil mixture separation.

Here we fabricated a kind of multifunctional porous titanium foil for oil-water and immiscible organic liquid separation. The foil with regular micropore arrays (size from 5 to 42 µm) was drilled by one-step femtosecond laser irradiation, which is a simple, accurate and efficient processing method. Different separation functions can be achieved through adjusting the wettability of titanium foil. For example, the titanium foil is superhydrophilic and underwater superoleophobic after laser drilling, and can be used for light oil (C_8H_{18}) and water mixtures separation, while the sample is superhydrophobic after heating in dark environment, and can be used to separate the heavy oil ($C_2H_4Cl_2$)/water mixtures and immiscible organic liquid ($C_2H_4Cl_2$ and formamide) mixtures. After UV irradiation in ethanol, the heated Ti foil recovers its original superhydrophilic property. It is worth noting that the Ti foil has excellent durability even after sonic cleaning and scratch.

2. Experimental

2.1. Materials

The titanium foil (25 µm thick) used in our experiment was purchased from New Metal Material Tech. Co., Ltd, Beijing, China. Before laser processing, the Ti foil was cleaned with acetone, ultrasonically with ethanol and distilled water for 10 min, respectively. The 1,2-dichloroethane ($C_2H_4Cl_2$ heavy oil), the normal octane (C_8H_{18} light oil) and the formamide (FA) were chose as the target oil which were purchased from Sinopharm Chemical Reagent Co. Ltd, Shanghai, China. The density of those oil is 1.26 g/cm^3, 0.70 g/cm^3, and 1.13 g/cm^3 respectively.

2.2. Preparation of micropore arrayed titanium foil

A regenerative amplified Ti:sapphire femtosecond laser system (Legend Elite-1K-HE, Coherent, USA) that generates 104 fs pulses at a repetition rate of 1 kHz with a central wavelength of 800 nm was used for the fabrication of the sample. The diameter of laser focal spot was about 20 µm. The micropore size was changed from 5 µm to 42 µm (error is less than 1 µm) through adjusting the laser pulse energy and pulse number. The interval between adjacent pores was kept at 60 µm.

2.3. Instrument and characterization

The pore arrays were observed by a scanning electron microscope (SEM JSM-6700F, JEOL, Tokyo, Japan). Contact angles were measured by using a contact angle system (CA100D, Innuo, Shanghai, China) with a 4 µL water or oil droplet on the treated area (diameter of 20 µm) at ambient temperature. The average values of contact angle were obtained by measuring five drops at different locations on the same surface.

2.4. Oil/water separation experiment

The separation device consists of two cylindrical glass tubes and a conical flask, and then the processed sample was fixed between two glass tubes with a clip. The oil-water mixtures were poured into the upper cylindrical glass tube, and the entire separation process was solely driven by gravity. The oil-water mixture was composed of 10 mL water and 10 mL oil. In order to observe the experimental phenomenon clearly, the water dyed with methyl blue was blue color while the oil dyed with Sudan III exhibited red color for color contrast. The prepared sample showed superhydrophilicity and underwater superoleophobicity. After heating in dark environment for 0.5 h, the treated sample became superhydrophobic and underwater superoleophilic. For separating light oil and water, the prepared titanium foil was fixed at two glass cylindrical tubes. For separation heavy oil and water, the heated sample was used because of its superhydrophobic characteristic so that the heavy oil could penetrate the micropores.

2.5. Oil/oil separation experiment

The experiment device of the oil/oil separation was the same as the oil/water separation experiment. The oil/oil mixture was made of 10 mL $C_2H_4Cl_2$ and 10 mL FA. The $C_2H_4Cl_2$ showed red color while FA displayed blue color through dyeing process, respectively. This separation process only required gravity as driving force.

3. Results and discussion

Regular micropore arrays are obtained on the titanium foil through femtosecond laser perforation method [Fig. 1a]. Fig. 1b is top-view SEM image that shows the surface morphology of the prepared Ti foil. By adjusting the laser pulse energy of 200 µJ, the pores with average diameter of approximately 20 µm is obtained. From the high magnification SEM image [right of Fig. 1b], we can see that the edges of the holes are covered by some nanoparticles [Supporting Information Fig. S1], which contributes to the super wetting property. Additionally, the distribution of the pore size [Fig. 1c] obeys to the normal distribution, which indicates that the pore size are uniformly distributed. The water contact angle (WCA) on the original titanium foil is about ~45° [Fig. 1d], showing that the original surface is hydrophilic. After laser fabrication process, the hierarchical structure on the samples makes the surface more hydrophilic [19,20], and the WCA turns into ~0° [Fig. 1e]. This physical phenomenon can be explained by Eq. (1) [3,16,21,22], derived from the Wenzel model:

$$\cos\theta_{WA}^{'} = r\cos\theta_{WA} \tag{1}$$

where *r* is the roughness factor defined as the ratio of the actual areal of the solid to the projected area on the horizontal plane, and the value of *r* [the specific calculation process is shown in Supporting Information Fig. S2] is always larger than 1, $\theta_{WA}$is the intrinsic WCA on the raw material (smooth surface). Through this formula, the CA can be calculated as ~0.5°. The theoretical calculation and experimental results are consistent within the experimental error range. The original hydrophilic material ($\theta < 90°$) will become more hydrophilic with the roughness increasing [3].

When the processed sample is placed in water, the processed area will be quickly wetted by water due to its superhydrophilicity. The water keeps in micropores and forms a thin water-film at interface. When the oil droplet begins to contact the perforated area, the trapped water will block the oil to penetrate the micropores. In other words, the oil droplet can only contact the upper part of surface, displaying superoleophobicity in water [CAH ~ 3°, Supporting Information Fig. S3]. So, the oil droplet is in Cassie model.[23] And the CA of $C_2H_4Cl_2$ and C_8H_{18} are 153.5° and 150° (Fig. 1f and g), respectively. The fundamental can be described as the following Eq. (2): [19,21,24,25]

$$\cos\theta_{OW}^{'} = f\cos\theta_{OW} + f - 1 \tag{2}$$

In this case, *f* is the ration of the surface of the oil contact to the total rough area, θ_{OW} is the oil contact angle (OCA) on the original surface underwater. After systematic analysis, the value of f and θ_{OW}($C_2H_4Cl_2$) can be obtained as 0.37 and 130° [Fig. S4], respectively. The value of $\theta_{OW}^{'}$ is 150° calculated by the formula (2), which is in perfect agreement with the experimental data (153.5Â°) within the error range.