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Synthesis of vertically aligned composite microcone membrane filter for water/oil separation

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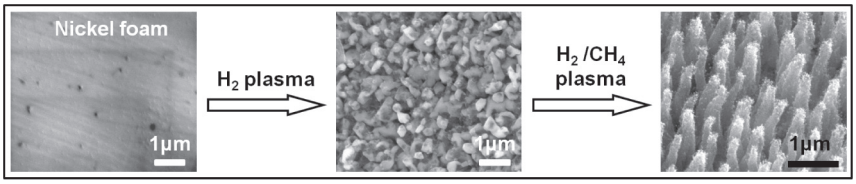
HIGHLIGHTS

- Vertically aligned composite microcone membrane filter was fabricated by self-assembly.
- Water contact angle of the filter is about 175° and the sliding angle is close to 0°.
- Water contact angle of the filter is more than 150° after being exposed to water at a pressure of 10 kPa for 24 h.
- Water can be continuously removed away from the filter by cross-flow filtration.

GRAPHICAL ABSTRACT



Composite microcone arrays were directly synthesized on the surface of nickel foam by microwave plasma enhanced chemical vapor

Composite microcone arrays were directly synthesized on the surface of nickel foam by microwave plasma enhanced chemical vapor deposition.

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ABSTRACT

A simple and efficient strategy is introduced for fabricating a layer of superhydrophobic and superoleophilic membrane on the surface of porous materials by self-assembly, and it is of great interest for the new type separation of oil and water. It is realized in this study by synthesizing an array of vertically aligned composite microcones on the surface of nickel foam by microwave plasma assisted chemical vapor deposition. The hierarchical structure, high aspect ratio, and dual-scale pine tree-like nature of the microcones formed on the nickel foam, which has microscale pores, in combination with the low surface energy of carbon, amplify both the hydrophobicity and the oleophilicity of the membrane. In addition, the membrane exhibits pH-responsivity, and the controllable water permeation can be realized by simply altering the water pH. Given its extremely high hydrophobicity and oleophilicity as well as outstanding mechanical durability, the composite frame can be used as a filter to separate oil/water mixtures and as an intelligent sponge to purify oil-contaminated water with excellent separation efficiency and absorption capacity. It should also be ideal for real world use in various environmental and chemical separation processes.

1. Introduction

Superhydrophobic surfaces are usually defined as surfaces that have a water contact angle (CA) greater than 150° and whose CA hysteresis is low [1–4]. They show intriguing properties such as biomimicking and antisticking characteristics [5], aid in contamination prevention [6], and are water repellent and self-cleaning [7–8]. Thus, they are highly suitable for oil/water separation [9], energy conversion [10], waterproofing electronic devices, and reducing the fluidic resistance in microdevices [11–12]. Among these, oil/water separation has gradually come to play a crucial role in modern society. Oily wastewater is an inevitable byproduct of industrial processes and domestic sewage as well as the direct result of maritime oil leaks, which have become frequent

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[13–14]. It prohibits the cyclic utilization of clean water resources and causes severe environmental problems all over the world. Therefore, it has become necessary to develop economical water purification methods, and significant research efforts are being devoted to do so. A number of researchers have reported that using porous materials that exhibit superhydrophobicity and superoleophilicity would be ideal for effectively separating oil and water [15–16]. This separation process involves the selective absorption or filtration of the oil from the oily water and has several advantages, including high separation efficiency, low operational costs, and environmental friendliness [17]. However, the irreversible fouling of the filtering membrane and the low permeate flux and performance degradation of the membrane material have been widely recognized as the main hurdles to the widespread application of membrane filtration technologies [18]. Therefore, the optimization of porous materials fabricated especially for oil/water separation applications is essential such that the materials exhibit a suitable degree of wettability as well as an ultralow adhesive force, high resistance to oil fouling, high permeate flux, and stable mechanical durability [19–21].

Generally, the CA of a material depends on its surface roughness and the surface energy of the material. Therefore, the surface microstructure must be properly engineered and the surface energy reduced when designing superhydrophobic materials. In order to achieve this goal, researchers have exploited various methods, such as photolithography [22], chemical corrosion [23], and plasma etching [24], to fabricate coarse surfaces and then decorate them using low-surface-energy materials [25]. However, these processes have their own drawbacks in terms of complexity, cost efficiency, and environmental friendliness, which dramatically limit their applicability [26]. Thus, a simple, cost-efficient, and environmentally friendly alternative for fabricating superhydrophobic membranes on the surfaces of various materials is strongly needed.

In this paper, we report the synthesis of a one-layered composite superhydrophobic membrane consisting of uniform microcone pillars on the surface of nickel foam by microwave plasma-assisted chemical vapor deposition (MPACVD). The unique microstructure of this membrane was systematically characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and wettability measurements. The hierarchical structure, high aspect ratio, and dual-scale pine tree-like nature of the microcones formed on the porous nickel foam, which has microscaled pores, in combination with the low surface energy of carbon, amplify both the hydrophobicity and the oleophilicity of the membrane. It was found that the membrane exhibited excellent performance with respect to oil/water separation compared to other materials. It was concluded that the phenomena of superhydrophobicity and superoleophilicity as well as the novel multiscale structure of the composite membrane and the inherent chemical properties of the substrate were responsible for the excellent performance.

2. Experimental section

2.1. Materials

Commercial nickel foam, with thickness of 0.5 mm and pore size of 100–300 μm, was obtained from the market in Harbin, China. Because the size of the object stage is 2 in., the maximum size of substrate is 2 in. Deionized water was purchased from Aladdin Industrial Inc., and used for all experiments. Hydrochloric acid (analytical reagent), acetone, and ethanol were purchased from Beijing Chemical works. N_2 (99.9%), H_2 (99.999%), and CH_4 (99.999%) were purchased from Harbin Liming Co Ltd. Diesel was purchased from Petro China Co Ltd., as a representative of low viscosity oils, and the test emulsion was prepared by ultrasonication and subsequent shaking, diesel and water was set at a volume ratio of 2:1. Oil red O was purchased from Aladdin Industrial Inc. Lubricating oil was purchased from German Wolfsburg Petroleum Chemical Engineering Co., Ltd., which was selected as a representative of high viscosity oil.

2.2. Synthesis of vertically aligned microcone arrays

First of all, the nickel foams was soaked in diluted hydrochloric acid (5% in volume) to wipe off the coating of NiO, and subsequently cleaned by deionized water and dried by N_2. Afterwards, it was cleaned by acetone, ethanol and deionized water respectively, and dried by N_2. The cleaned nickel foams were put in the vacuum chamber of MPACVD system. The nickel foams were directly heated by being immersed in hydrogen plasma; no other heating source was used. The surface temperature of the samples were measured by infrared temperature measurement system. First, nickel foam was treated at 800 °C by hydrogen plasma in a H_2 flow (200 sccm) at the pressure of 120 mbar for 1 min. Then, the power of 2500 W and a ratio of 160/40 sccm for H_2/CH_4 at the temperature/pressure of 600 °C/68 mbar were used to grow microcones on the nickel foam for 3 min. Finally, the sample was cooled rapidly to room temperature in the CVD chamber. The final morphology of the array of the composite microcones, which had a hierarchical structure, formed by self-assembly.

2.3. Characterization

Surface morphology of specimens was examined by a scanning electron microscope (SEM, FEI Helios Nanolab 660i, operated at 1–20 kV). The morphology and microstructure of the samples were studied in detail by transmission electron microscope (TEM, FEI Tecnai G2 F30, operated at 300 kV). The microcones for TEM measurement were scratched from the obtained samples and then dispersed by ultrasonic dispersion. Raman spectra were acquired on a confocal Raman spectroscope (Horiba Jobin–Yvon Lab RAM HR800 System) with 458 nm laser excitation under ambient conditions. Water contact angles (WCA) and oil contact angles (OCA) were measured on an OCA20 system (Data-Physics) under ambient conditions. The WCA values are the averages with corresponding standard deviation that were measured at five different areas on each sample. Optical microscopy images were taken on a Nikon D7100.

3. Results and discussion

3.1. Structure and morphology characterization

The process for fabricating the array of composite microcones on the surface of nickel foam is given in Fig. 1. As shown in Fig. 1(a), commercial nickel foam with thickness of 0.5 mm and pore size of 100–300 μm was used as the template. The use of a thin template with suitable thickness and effective pore size ensured that the obtained composite material exhibited high flux when used for oil/water separation. In addition to showing some fine scratches and protrusions, the high-magnification SEM image shows that the surface of the nickel foam is almost smooth and flat (see Fig. 1(b)). Two key steps were used to synthesize cones on the surface of nickel foam. In step 1, the nickel foam was treated with hydrogen plasma at 800 °C in a H2 flow (200 sccm) at a pressure of 120 mbar for 1 min to promote the formation of catalyst particles. In step 2, a gaseous mixture of CH_4 (40 sccm) and H_2 (160 sccm) was introduced into MPACVD system at the temperature/pressure of 600 °C/68 mbar and the power of 2500 W for synthesizing microcones. The hydrogen plasma is conducive to eliminate the oxide layer and promote the formation of uniformly separated nickel particles [27]. The morphology of the nickel foam, which was treated with hydrogen plasma, is shown in Fig. 1(c). Compared to the untreated surface (see Fig. 1(b)), the treated one is rougher. Further, it contains a large number of catalyst particles. These catalyst particles are separated uniformly on the surface; this is crucial for the fabrication of the composite microcone array. When methane participated in the synthesis reactions, these