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Design and preparation of efficient, stable and superhydrophobic copper foam membrane for selective oil absorption and consecutive oil–water separation

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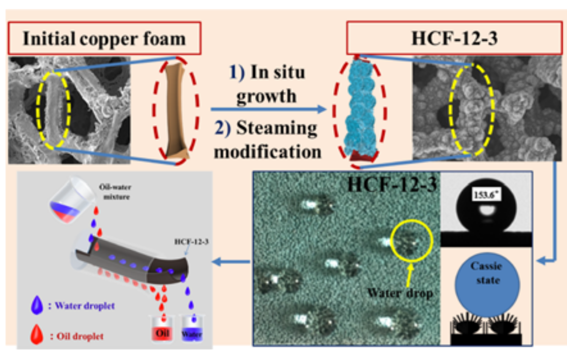
HIGHLIGHTS

- The separation membranes were prepared via in situ self-sacrificial template combining the subsequent steaming modification.
- Steaming modification was characterized by high efficiency, controllability and cheapness.
- The superhydrophobic membranes can be used for oil–water separation and self-cleaning materials.
- Consecutive separation of oil–water mixtures was achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

It is extremely important and challenging to develop an effective device for the continuous separation and recovery of large-scale oil–water mixtures due to their contribution to ecological remediation and contamination control. In this work, a superhydrophobic copper foam with high oil–water separation efficiency was successfully fabricated, which could serve both as oil absorption material and oil–water separation membrane, by in situ self-sacrificial template method combining the subsequent steaming modification. The obtained characterization results present that copper foam possesses large pore structure, micro-/nanoscale two-tier surface roughness, high water contact angle (153.6°), and low sliding angle (4.5°). Experimental results show that as-prepared copper foam could not only rapidly absorb residual oil either on the water surface or underwater, but also separate a series of oils from water, like carbon tetrachloride, trichloromethane, methylbenzene, pump oil and diesel. Furthermore, the separation efficiencies of copper foam on trichloromethane-water and diesel-water mixture were maintained above 96.9% and 90.8% after 10 cycles, respectively. Additionally, as-prepared copper foam exhibits excellent corrosion resistant ability and superior hydrophobic stability. The facile, low-cost and controllable strategy presented herein has a bright future in oil–water separation, and also can be further expanded to prepare various anti-corrosion, self-cleaning and water-proof sport materials.

1. Introduction

Over the past few decades, frequent oil spillage and large amounts of oily wastewater discharged from industrial processes and daily life have

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caused not only severe environmental and ecological damage but also tremendous threats to the human health [1] . In addition, most of the oil spill accidents occurred in the water body (ocean or inland canal) since marine transport is the most common channel for today's oil transportation [2]. Nevertheless, oil spill on the water surface is more emergency than on land since floating oil will spread rapidly with the action of water flow and wind [3]. A lot of efforts have been made to separate the oils/organic solvent from the water surface: chemical dispersion, skimming, combustion, absorption and membrane separation [4, 5]. Among them, absorption and membrane separation are intensively investigated due to the advantage of simple operation and low cost [6]. However, oil-absorbents are often limited by the absorption capacity in the application. Meanwhile, some oil-absorbents, such as acrylate resin and poly vinylidene fluoride (PVDF) aerogel, are difficult to quickly remove the absorbed oil, and the internal structure is susceptible to deterioration, thereby reducing the recyclability [7, 8]. Membrane separation technique, on the other hand, has been considered as a most promising candidate for oil–water separation application which has the features such as high efficiency, continuity and environmental friendly. Although great advances have been achieved in the preparation of oil–water separation membrane, it remains a great challenge to develop a facile, low-cost, and controllable method for the construction of superhydrophobic surface for consecutive oil–water separation.

Superhydrophobic surface is defined by a water contact angle higher than 150° and a contact angle hysteresis of lower than 10° [9, 10]. Inspired by imitating the lotus leaf [11, 12], introducing proper rough surface on the targeted substrates provides a theoretical route for the preparation of superhydrophobic or superoleophilic materials. It is well known that rough micro-/nanostructure could make materials more hydrophobic due to the presence of air cushion between water droplet and substrate. In this respect, some positive results have been achieved. Typically, Jiang et al. [13] reported a concept to biomimetic surfaces with specific wettability through the introduction of surface roughness, and the water contact angle is high up to 148.3° on rough surface which is significantly higher than water contact angle (68.2°) on smooth surface. In recent years, Liu and co-workers [14] prepared superhydrophobic and superoleophilic textile through immobilizing layered double hydroxide (LDH) microcrystals on the microfibers of textile. The as-prepared layered double hydroxide functionalized textile showed a superhydrophobic surface with a water contact angle of 154° and exhibited high oil penetration rate. However, these syntheses are commonly time-consuming and tedious, and the surface morphology is often affected by the interaction force between guest (for example: metal ions and surfactants) and subject (various substrates). Furthermore, the coating layer tend to exfoliate from the membrane interface in practical application due to the weak adhesion, and thus the decrease of separation efficiency and insufficient reusability is inevitable [14]. In recent years, a promising in situ self-sacrificial template method has been developed to synthesize functional nanostructures on a desired substrate, which was a low energy consumption and controllable process in term of the preparation of crystal morphology and structure through the crystal growth kinetic [15]. For example, a assembled CuS nanoflake-built microspheres was synthesized in high yield via a one-pot intermediate crystal self-templating process without surfactant or added templates [16]. Based on the analysis of previous research, it was proposed that building a well-organized coating layer on a substrate could effectively improve the stability of nanostructure via an in situ self-sacrificial template method.

In addition, the low surface energy also is a key factor in achieving superhydrophobicity, which could be accomplished by introducing chemical modifying agents, such as coupling agents and stearic acid. However, organics tend to aggregate on the membrane surface, thereby weakening the surface roughness as well as reducing the permeation of oils [17]. Recently, Ming and co-workers [18] presented a novel method of steaming multiwalled carbon nanotubes (MWCNTs) via acid vapor to achieve surface chemical modification, which is simple, precisely-controllable and environmentally-friendly. Simultaneously, it was put forward that the steaming modification could overcome some of the inevitable, fatal disadvantages existed in solution immersion method. For example, (i) an excess amount of modifying agent is often required for immersing and refluxing the samples, which not only increases the production cost but also pollutes the environment; (ii) the washing and separation of functionalized samples from modifying agent is very tedious process. Hence, this successful chemical modification strategy has provided a significant impetus for the further development and utilization of steaming modification to obtain superhydrophobic surface.

Among different substrate materials used in production, 3D copper foam has attracted widespread concern for their ductility, low density, high specific surface, mechanical strength, moderate cost and environmentally friendliness [19, 20]. Moreover, metal foam could be recycled just by simple washing and drying without a significant impact on its performance. On the other hand, previous studies have shown that silane coupling agent coatings can effectively improve the hydrophobic properties of the material [21]. Note that the use of a silane coupling agent is limited to surface terminated by hydroxyl groups. Then, it has also been proved that silane coupling agent coatings are highly stable under chemical corrosion (such as acidic and basic conditions) and physical abrasion (such as repeated washing) [22, 23]. In addition, 3-methacryloxypropyltrimethoxysilane is a widely used industrial fluoride-free materials. Hence, it is low-cost and environmentally friendly, and could be applied to large-scale real applications.

With this in mind, herein, we take advantage of in situ self-sacrificial template and steaming modification to prepare high-performance oil–water separation membrane. Firstly, coating layer of $Cu_3(PO_4)_2 \cdot H_2O$ nanosheets with a micro-/nanoscale two-tier surface roughness was synthesized by in situ self-sacrificial template employing 3D copper foam as templates. Then, the as-prepared copper foam was modified by 3-methacryloxypropyltrimethoxysilane (KH570) vapor. At the same time, the effects of different surface morphology and modification time on membrane hydrophobicity were studied in detail. With such a simple two-step surface functionalization process, the copper foam membrane exhibited superior characteristics of superhydrophobicity, high selectivity, high separation efficiency, corrosion resistant ability and recyclability. In addition, functional separation channel fabricated by copper foam was used to consecutive separation of oil–water mixture through capillary force and gravity-driven approach. Therefore, this study designs a facile and controllable approach to prepare superhydrophobic copper foam membrane and a new strategy for developing efficient oil–water separation system.

2. Experimental section

2.1. Materials

Several chemicals of dibasic sodium phosphate (Na_2HPO_4), ammonium persulfate ($(NH_4)_2S_2O_8$), hydrochloric acid (HCl), carbon tetrachloride, 3-methacryloxypropyltrimethoxysilane ($CH_2{=}C(CH_3)COOCH_2CH_2CH_2Si(OCH_3)_3$, KH570), trichloromethane, methylbenzene and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. (SCRC). Pump oil and diesel oil were obtained from Sinopec. Deionized water with a resistivity of 18.25 MΩ was used throughout the entire experiment and all reagents were analytically pure and used without further purification. Copper foam was obtained from Suzhou Tai Li Material Technology Co., Ltd., Jiangsu Province, China.

2.2. Preparation of hydrophobic copper foam

The $Cu_3(PO_4)_2 \cdot H_2O$ nanosheets were fabricated on copper foams to achieve desirable surface roughness using an in situ self-sacrificial template method, as illustrated in Scheme 1A. Typically, in order to remove the impurities (such as oxide of copper) in copper foam surface, the purchased copper foam was washed with diluted HCl (3 M) solution for 10