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Durability evaluation of superhydrophobic copper foams for long-term oil-water separation

Haiyan Zhu [a], Lin Gao [a], Xinquan Yu [a,*], Caihua Liang [b], Youfa Zhang [a,*]

[a] Jiangsu Key Laboratory of Advanced Metallic Materials, School of Materials Science and Engineering, Southeast University, Nanjing, 211189, PR China
[b] School of Energy and Environment, Southeast University, Nanjing 210096, PR China

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ABSTRACT

Superhydrophobic three-dimensional porous composites with good mechanical stability and high efficiency are promising candidates for oil-water separation application. Hence, several superhydrophobic copper foams were fabricated via the in situ growth of patterned $Cu(OH)_2$ nanoneedles or ZnO nanocrystals (e.g. ZnO nanocones and ZnO nanorods) on the skeleton and followed by chemically modification. All the superhydrophobic copper foams showed efficient oil-water separation ability, especially the samples with ZnO nanorods arrays on the pre-nanostructured skeleton. The durability of superhydrophobic copper foams were then evaluated. Although the superhydrophobic samples kept separation efficiency higher than 95% after cycled evaluation, the pre-roughened copper foams exhibited the best performance against various damage among the samples. Microstructural evolution revealed that the coverage of the copper skeleton became from smooth swelling micro-crystals into rough nano-crystals after the pre-treatment of electrodepositing copper nanoparticles. The rough nanocrystals could not only avoid the formation of loose hierarchical structure, but also improve the binding force between patterned nanorods and the matrix. The fabricated closely-patterned ZnO nanorods could thus remain stable under the damage compared to others, presenting great mechanical robustness. Furthermore, we achieved a long-term efficient oil-water separation using the durable foams by periodic removal of residual oil in nanostructure gaps.

1. Introduction

In recent years, with the development of economy and society, the output of oily wastewater was increasing sharply. The separation of oil-water mixtures was becoming imperative due to its serious threat to environment and human society [1–5].Traditional techniques were employed to remove oil from water, such as in situ burning [6], gravity separation [7], air flotation [8], coalescence and flocculation [9], bioremediation [10], adsorption [11]. But these methods were often suffered from limitations including high costs, complex separation instruments, low separation efficiency, and secondary pollutants, etc. More recently, take inspiration from nature, such as lotus leaves [12] and desert beetle [13], the superwetting materials have been fabricated and used for oil-water separation successfully, which achieved by constructing rough surfaces and modifying with low-surface energy materials [14]. With their high separation efficiency, great selective separation performance, excellent recycling property and environment friendly, superwetting materials have become a research hotspot in the oil-water separation field. In general, there were three types [15] of separation materials which classified as: "oil-removing" type materials [16–18] with superhydrophobic/superoleophilic properties [19] which could filtrate or adsorb oil selectively, "water-removing" type materials [20] with superhydrophilic/superoleophobic properties which could filtrate or adsorb water selectively, and smart separation materials [21–24].

Based on this, various materials including metal meshes, porous sponge materials, fabrics, fluoro-polymers, aerogels, and nanoparticles have been developed to fabricate superwetting materials for oil-water separation. Among numerous separation materials with superwetting property, three-dimensional (3D) porous materials [25] have attracted great attention due to their huge surface area, light weight, and well-developed porous structure, excellent strength, low-cost, and facile preparation processes. In particular, 3D porous metallic materials(e.g., copper foam [26] and nickel foam [27]) compared with those 3D porous organic materials (e.g., polyurethane sponge [28]), did not need mechanical handling (squeezing or compression) to recycle oil or water after one

* Corresponding authors.
E-mail addresses: 101004070@seu.edu.cn, yfzhang@seu.edu.cn (Y. Zhang).

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absorption cycle, which enlarged the application for continuous separation in large-area oily wastewater.

Except for oil-water separation property, the mechanical durability[29] and the durability of oil-water separation for physical abrasion were essential for practical separation application owing to the complex wastewater environment. The durability of superwetting materials were mainly correlated to the stability of their surface structures [30]. The destructive power of the physical abrasion, especially huge flow impact [31] and the abrasion of dirt particles which existed in oily wastewater, could destroy the surface structures of material surfaces, resulting in the separation performance and recyclability degradation or loss. Therefore, it was urgent demand to develop robust superwetting materials for oil-water separation with high separation efficiency, low energy consumption, stable separation abilities and outstanding mechanical durability even in complex environments. Various approaches, e.g., dip-coating [32], vapor-phase deposition [33], in situ synthesis [34] and chemically etching [35], have been used for preparing superwetting surfaces on the skeleton of 3D porous materials. To the best of our knowledge, few reports [26] have systematically investigated the mechanical durability of copper foams with superhydrophobic properties for oil-water separation.

Herein, four kinds of patterned nanostructures ($Cu(OH)_2$ nanoneedles, flower cluster-like ZnO nanocones and patterned ZnO nanorods on smooth micro-crystals closely-patterned ZnO nanorods on rough Cu nanocrystals) on three-dimensional porous copper foam surfaces with robust superhydrophobicity and superoleophilicity were fabricated through different approaches, which mainly involved simple electrodeposition, seed layer growth and low-temperature hydrothermal reaction, and followed by chemical modification. These copper foams showed great mechanical durability after mechanical resistance tests containing water impacting, sandy ethanol washing, sonication in ethanol and continuous oil-water separation. Moreover, all the as-prepared skeleton hierarchical nanostructure copper foams showed efficient and selective oil-water separation ability, which will be promising candidates for practical oil-water separation application under harsh circumstances.

2. Experiments

2.1. Materials

Copper foam (average pore diameter: 450 μm, pore number: 80 PPI) was supplied by Alantum Advanced Technology Materials (Dalian) Co., Ltd., China. 1H,1H,2H,2H-perfluorodecyltriethoxysilane, zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), ethanolamine ($NH_2CH_2CH_2OH$), ethylene glycol monomethyl ether ($CH_3OCH_2CH_2OH$), polyethylene glycol 4000 ($HO(CH_2CH_2O)_nH$), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$), potassium hydroxide(KOH), acetone, and ethanol were obtained from China National Medicines Co., Ltd. All chemicals were used as received without further purification.

2.2. Preparation of nanostructures on copper foams

The copper foams (4 cm × 4 cm × 0.16 cm) were sequentially washed with ethanol, acetone, 1.0 M HCl, and deionized water(DI) for approximately 5 min each under ultrasonication to remove surface oxide and organic contaminants. Finally, the samples were dried at 60 °C.

2.2.1. $Cu(OH)_2$ nanoneedles

The cleaned copper foams were used as the working electrode. The counter electrode was a pure copper sheet (99.9%) and the electrolyte was 1.0 M NaOH aqueous solution. $Cu(OH)_2$ nanoneedles were electrochemically grown at a constant current density of 6 mA/cm^2 for 10 min. After anodization, they were rinsed and dried in a vacuum oven.

2.2.2. ZnO nanocones

Flower cluster-like ZnO nanocones were fabricated on copper foams using a one-step method. Liquid phase growth solution of ZnO nanocones was the 0.25 M alkali zincate ions $[Zn(OH)_4]^{2-}$ solution, which prepared by dropping 20 mL of 4.0 M KOH aqueous solution into 20 mL of 0.5 M $Zn(NO_3)_2{\cdot}6H_2O$ aqueous solution under stirring [36]. Cleaned copper foams were placed in 40 mL of $[Zn(OH)_4]^{2-}$ solution, then sealed in a beaker. After reaction at 35 °C for 8 h, the samples were thoroughly rinsed with DI water and then dried.

2.2.3. ZnO nanorod arrays

Patterned ZnO nanorod arrays were fabricated on smooth copper foams using a two-step process, combining compact seeding layer fabrication on smooth copper foam skeleton and patterned nanorods growth by a solution phase route. At first, the smooth copper foams were coated with precursor seed sol of 0.3 M zinc acetate dihydrate which contained ethylene glycol monomethyl ether, ethanolamine and polyethylene glycol 4000 by dip-coating method, and then high-temperature annealing in an argon atmosphere furnace at 450 °C for 2 h [37]. Next, the patterned ZnO nanorods on seeded copper foams were fabricated. The method was the same as ZnO nanocones, as mentioned previously. After synthesis, the samples were rinsed with DI water and dried in a vacuum oven.

2.2.4. Cu/ZnO nanorod arrays

Closely-patterned ZnO nanorod arrays on rough nanocrystals were fabricated on copper foams via a two-step process, combining simple electrodeposition [38] and ZnO nanorods growth by a two-step route, as illustrated in Scheme 1. First, roughened copper foams (as shown in Fig. A.1) which coated by copper nanoparticles (Cu NPs) was obtained by electrochemically depositing a layer of Cu NPs at a 2.5 V voltage for 300 s at room temperature. The working electrode was copper foam and cathodes were two copper sheets. The electrolyte was an aqueous solution composed of 0.2 M $CuSO_4{\cdot}5H_2O$ and 1.5 M H_2SO_4. Second, closely-patterned ZnO nanorod arrays on roughened copper foams were finally obtained by a two-step route. The fabrication details of ZnO nanorod arrays were same as the patterned ZnO nanorods on smooth copper foams.

2.3. Fabrication of superhydrophobic surfaces

The superhydrophobic copper foams coated with nanocrystals were fabricated by chemical vapor deposition (CVD) technique using 1 mL of 1H,1H,2H,2H-perfluorodecyltriethoxysilane under vacuum conditions at 120 °C for 8 h in a vacuum oven. The superhydrophobic copper foams were finally obtained.

2.4. Characterization

Scanning electron microscopy (SEM) images were taken by a Sirion field-emission scanning electron microscope(FEI-SEM) at 20 kV. X-ray diffraction (XRD) patterns were performed with an X-ray diffractometer model D8-Discover (Bruker) with Cu Kα radiation (λ¼ 1.5418 Å). The static contact angles (SCA) and rolling angles (RA) were measured on an OCA 15Pro machine (Data-Physics, Germany) at ambient temperature. The SCA values were measured from 5.0 μL DI water droplets and averaged five different positions on each sample. 10 μL water droplets were used for