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Full Length Article

Construction of caterpillar-like cobalt-nickel hydroxide/carbon cloth hierarchical architecture with reversible wettability towards on-demand oil-water separation

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ABSTRACT

Superwettability materials have focused considerable interest of researchers due to their extensive applications like oil/water separation. Currently, the development of materials with controllable wettability for efficient on-demand oil/water separation is highly desired. In this work, we constructed caterpillar-like cobalt-nickel hydroxide/carbon cloth hierarchical architecture via *in situ* hydrothermal growth. Interestingly, this hierarchical architecture shows reversible wettability after immersing in stearic acid ethanol solution and tetrahydrofuran, which can be used for efficient on-demand oil/water separation. This hierarchical architecture is proved to have excellent environmental and mechanical durability. Moreover, the fluid-based gating and liquid-infusion-interface mechanism are presented to explain oil/water separation process. The caterpillar-like cobalt-nickel hydroxide/carbon cloth with low cost and simple preparation shows a promising prospect in the application of efficient on-demand oil/water separation.

1. Introduction

In decade years, large quantities of oily wastewater produced from oil spills, our daily life and industrial processes caused tremendous threats on environment and human health [1–3]. Usually, conventional oily water treatment methods including skimming, gravity processing, ultrasonic separation, air flotation, membrane filtration, electro-coalescence, and biological treatment, suffer from limitations of low separation efficiency, highly energy-consuming, generation of secondary pollutants, and high costs [4,5]. Thus, it is of great significance to develop new materials or methods for oil/water separation. Recently, materials with special wettability have drawn considerable interests from researchers [6]. Wettability is a fundamental property of solid surface, which can be ascribed to combination of surface micro/nano hierarchical structures and surface chemistry composition [7]. Wettability of solid surface is currently a hot topic and plays a important role in industry, agriculture, and daily life [8,9]. Notably, the superwetting materials are suitable for high-efficiency oil/water separation due to interfacial energy difference of oil and water [10–12].

Nature provides a source of inspiration for scientists and engineers to design new technologies and advanced materials [13–16]. Undergo billions of years of evolution and natural selection, natural materials not only exhibit perfect micro/nano structures but also bear fascinating properties in responding and adapting to changes in their environment [17–19]. Inspired by "lotus effect", a superhydrophobic/superoleophilic mesh was first fabricated for oil/water separation via a spray-and-dry method by Jiang et al. in 2004 [7]. Subsequently, a large number of superhydrophobic materials have been fabricated for oil/water separation. Guo et al. designed a superhydrophobic polydopamine@SiO_2 coated cotton fabric through copolymerization reaction and trimethyl silyl modified process for oil/water separation [20]. Kong et al. reported a superhydrophobic phosphor-copper mesh by surface modification with 1-dodecanethiol on highly dense ordered Cu_2O nanorods for oil/water separation [21]. However, such "oil removal materials" are more suitable for heavy oil ($\rho_{oil} > \rho_{water}$)/water separation. Inspired by fish scale, superhydrophilic/underwater superoleophobic materials have been also fabricated for light oil ($\rho_{oil} < \rho_{water}$)/water separation [22]. We previously reported a superhydrophilic/underwater superoleophobic membrane via thermal oxidation of Cu mesh and one-step coordinated assembly of Fe(III)-CMC

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chelate hydrogel for oil/water separation [23]. A underwater superoleophobic membrane was prepared via coating graphene oxide on mesh after subsequent O_2 plasma treatments by Sun et al., such membrane shows good oil/water separation performance [24]. Unfortunately, underwater superoleophobic materials are unable to separate heavy oil/water mixtures for the accumulated oil layer between water and membrane. Thus, a superhydrophobic or superhydrophilic/underwater superoleophobic materials are incompetent for on-demand oil/water separation.

Switchable wettability materials (such light, heat, and pH response smart materials) hold great promising for on-demand oil/water separation. For example, Tian et al. reported an aligned ZnO nanorod array-coated stainless steel mesh, the wettability of mesh can be switch by storage in the dark and UV light irradiation [25]. Raturi et al. fabricated ZnO nanowires-coated stainless steel mesh, the wettability of mesh can be switched from superhydrophilic to superhydrophobic by annealing at 300 °C alternatively under H_2 and O_2 environment [26]. Cheng et al. reported a pH-controllable membrane via assembling the responsive HS(CH2)10COOH molecules on the $Cu(OH)_2$ nanorod structured copper mesh for on-demand oil/water separation [27]. The fabrication of such smart materials, however, are time-consuming, complex, and costly. Consequently, it is highly desirable to develop simple and cost-effective strategy for fabricating materials with controllable wettability for efficient on-demand oil/water separation.

Herein, we constructed caterpillar-like cobalt-nickel hydroxide/carbon cloth hierarchical architecture via *in situ* hydrothermal growth. The surface wettability switching between superhydrophobicity and superhydrophilicity can be easily manipulated by immersing in stearic acid ethanol solution and THF for short time, and thus can be used for on-demand oil/water separation. In addition, the as-prepared material has excellent environmental and mechanical durability. Such material that easy operation and cost-effective may provide great potential application in on-demand oil/water separation.

2. Experimental section

2.1. Materials and chemicals

The fibers cloth were obtained from abandoned cotton shirt. (The compositional, morphology and wettability analysis regarding the cotton shirt were provided in supporting information section: Figs. S1–4.) Cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$, AR), nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$, AR), hexadecyltrimethyl ammonium bromide (CTAB, 99%), urea (AR, 99%), tetrahydrofuran (AR, 99%, THF), methylene blue (≥70.0%, MB), petroleum ether (AR, bp 90–120 °C) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). The absolute alcohol (AR, 99.7%), methanol (AR, 99.7%), hydrochloric acid (HCl, AR, 36–38%) and sodium stearate (96%), sodium chloride (NaCl, 99.5%), ammonia solution (NH_3 H_2O, AR, 25–28%), toluene (≥99.5%), 1,2-Dichloroethane (≥99.5%), hexane (> 99%), chloroform (> 99%), acetone (≥99.5%) were received from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Soybean oil was obtained from local supermarket. Diesel was purchased from China Petroleum & Chemical Corporation. All chemicals were in analytical purity and used in the experiments directly without any further purification.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apsusc.2018.08.161.

2.2. Characterization methods

X-ray photoelectron spectroscopy (XPS) were estimated by a Kratos Axis Ultra DLD spectrometer equipped with an Al Kα X-ray source (1486.6 eV), survey scan range was 0–1360 eV with the step size 1.000 eV and sweeps number of 5, and survey spectra were recorded with a pass energy of 100 eV, and high resolution spectra with a pass energy of 20 eV. The samples were observed under the Scanning Electron Microscopy (SEM, JSM-7001F, JEOL, Japan) and Field Emission Scanning Electron Microscope (FESEM, ZEISS MERLIN VP compact, Germany). Contact angles (CA) were measured on a contact angle meter (KSV, CM200, Finland). All the CAs measurements were used about 5 μL water or oil.

2.3. Preparation of samples

The abandoned cotton shirt (fibers cloths, FC) was cut into small pieces and washed with absolute ethanol. Subsequently, fibers cloth pieces were loaded porcelain boat placing in a tube furnace to carbonize at 500 °C for 2 h with a ramping rate of 5 °C/min under flowing N_2. Finally, carbon cloths (CC) were washed with HCl (6 wt%) and deionized water.

The caterpillar-like cobalt-nickel hydroxide/carbon cloth hierarchical architecture were fabricated by *in situ* hydrothermal growth, as described previously, [28] typically, 5 mmol $CoCl_2{\cdot}6H_2O$, 2.5 mmol $NiCl_2{\cdot}6H_2O$, 2 mmol CTAB, 9 mmol urea were dissolved into 50 mL of deionized water with stirring for 30 min to form a transparent pink solution. After that, the solution was then transferred to a Teflon-lined stainless steel autoclave and a pieces of CC was placed into solution keeping at 100 °C for the designed time (3, 6, 9, 12 h). During hydrothermal process, the surface of CC was covered with cobalt-nickel hydroxide (Abbreviated as CNH-X/CC, X represented hydrothermal time). The CNH-X/CC were rinsed with deionized water and absolute ethanol by ultrasonication, and drying at 60 °C for 2 h. The CNH-X/CC were putted in 0.1 mol L^{-1} alcohol solution of sodium stearate setting in a water bath oscillator (100 rmp) for 1 h to obtain (super)hydrophobic CNH/CC. Similarly, the wettability was reverted to superhydrophilicity/underwater superoleophobicity by immersion in THF for 30 min.

2.4. Oil/water separation experiments

The superhydrophobic or superhydrophilic CNH/CC was fixed by two Teflon holders, and two glass tubes with diameter of 20 mm were fixed on each side. As a proof of concept, hexane and dichloroethane were chosen as representative light oil and heavy oil, respectively. The other types of oil (petroleum ether, toluene, diesel oil, soybean oil, chloroform) were also tested. The mixture of oils and MB aqueous solution (20 mL:20 mL) were poured into glass tube. The separation process was solely driven by gravity.

2.5. The environmental and mechanical durability of the samples

The environmental durability of superhydrophobic CNH/CC was evaluated by WCA, the WCA measurements were used about 5 μL water with pH ranging 1–14, and salty water (1–5 wt% NaCl solution). The superhydrophobic CNH/CC was treated by different solvents (methanol, ethanol, toluene, acetone, chloroform) for more than 1 h, and then conducted WCA measurements.

The superhydrophilic CNH/CC were first immersed in water with pH ranging 1–14 for more than 1 h, then conduct oil CA measurements underwater. The salt resistance was tested by conducting oil CA measurements in salty water (1–5 wt% NaCl solution). The mechanical durability of superhydrophilic CNH/CC was tested by water impacting. Briefly, water was introduced to the surface of superhydrophilic CNH/CC with a gradient of about 45° from a height of about 40 cm with a flow rate of 2.5 m/s for about 2.5 h, and then conduct oil CA measurements underwater.