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JIEC 3441 No. of Pages 10

ARTICLE IN PRESS

Journal of Industrial and Engineering Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Hydrothermal fabrication of robustly superhydrophobic cotton fibers for efficient separation of oil/water mixtures and oil-in-water emulsions

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ARTICLE INFO

Article history:
Received 3 March 2017
Received in revised form 1 May 2017
Accepted 28 May 2017
Available online xxx

Keywords:
Hydrothermal
Superhydrophobic
Cotton fibers assembly
Continuous separation
Emulsion separation mechanism

ABSTRACT

In this study, superhydrophobic and superoleophilic cotton fibers are fabricated by simple one-step hydrothermal route followed by modification with silane. The obtained fibers show selective sorption ability to the oils from water, high sorption capacities, excellent recyclability, and quick sorption rate. The fibers also exhibit outstanding superhydrophobic stability under a variety of corrosive solutions and hot water, which enables it application for the separation of the oils from harsh water environments. Moreover, the superhydrophobic fibers in conjunction with a tube (valid tube area: 0.5 cm^2) that connected to a vacuum system (vacuum pressure: 0.03 MPa) is capable of collecting up to 200 times its self-weight in gasoline within 20 s. The coated fibers can also selectively harvest oils from oil/water mixtures under extreme turbulent condition. More importantly, the coated fibers can separate micron-sized oil droplets from oil-in-water emulsions with a high separation efficiency (transparency for solvent oils: >91%) that is beyond what can be obtained by most traditional separation methods. All these performances make the as-prepared cotton fibers ideally suited for the oil-spill cleanups and water purification.

Introduction

Oil discharges from oil exploration, petroleum refineries, industrial production, and daily life, to water bodies are considered to be one of worldwide environment problems because they have significant impact on water ecosystem and marine organism [1,2]. To resolve these water contamination issues, many methods have been developed, including extracting the oil from water surface [3–5], dispersing the oil into water via using dispersant to facilitate natural degradation [6], and burning the spilled oil in situ [7]. Among these methods, the separation of oil from water with sorbent is one of the most promising methods due to low cost and non-secondary pollution. Thus, developing efficient and inexpensive oil sorbent is vital to alleviate the global scale of oily pollution problem.

The surface of materials with superhydrophobic (water contact angle of >150°) and superoleophilic (oil contact angle of <5°) performances have attracted increasing attention in the field of oil–water separation. Superhydrophobic materials can be obtained via endowing a surface with micro/nanostructures and low surface energy. Currently, various approaches such as dip-coating [8], alkali etching [9], electrodeposition [10], spraying [11], phase separation [12], and hydrothermal method [13], have been developed to obtain superhydrophobic surfaces. Thereinto, hydrothermal method is taken as a simple and effective strategy for fabricating the micro/nanostructured coatings onto the surface of substrates, by which the obtained materials will possess robust superhydrophobic coating due to strong combination between the substrate surface and the coatings. Lately, hydrothermal preparation of superhydrophobic materials for oil–water separation has caused considerable attention of researchers. For example, Zeng et al. fabricated silicalite-1 film consisting of intergrown crystals on porous stainless steel wire by hydrothermal method, which displayed superamphiphilic in air and superoleophobic in water, and the film can effectively collect the oil from oil/water mixture [14]. Chen et al. prepared ZnO nanowires on cellulose filter paper via one-step hydrothermal method, and the coated filter paper showed high separation efficiency in oil/water separation [15]. A robust superhydrophobic TiO_2@fabric composite was prepared

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http://dx.doi.org/10.1016/j.jiec.2017.05.031

Please cite this article in press as: J. Wang, et al., Hydrothermal fabrication of robustly superhydrophobic cotton fibers for efficient separation of oil/water mixtures and oil-in-water emulsions, J. Ind. Eng. Chem. (2017), http://dx.doi.org/10.1016/j.jiec.2017.05.031

though combining one-spot hydrothermal reaction with fluoroalkylsilane modification, demonstrating good anti-UV ability and highly efficient oil–water separation [16]. Despite this, it is still a challenge for researchers to fabricate superhydrophobic and superoleophilic oil sorbents using readily available, inexpensive, and eco-friendly materials so that they can be widely applied in the remediation of the water polluted by oils.

Cotton fibers are a type of renewable resource in nature and easily available agricultural product. Due to low cost, intrinsically high sorption capacity, good biodegradability, and low buoyancy, cotton fibers as oil sorbent is advantageous over many conventional materials [17]. Recently, raw and modified cotton fibers have been evaluated as a promising sorbent for separating oil pollutant from water surface, which exhibits excellent sorption performance [18,19]. Although these studies have been carried out, there is no information on the use of robustly superhydrophobic cotton fibers for the continuous collection of oil from water surface and the separation of the oil droplets in oil-in-water emulsions. Herein, we report a simple one-step hydrothermal method for fabricating durably superhydrophobic and superoleophilic zinc oxide (ZnO)-coated cotton fibers. The functionalized fibers were prepared under facile condition using biodegradable and readily available natural fibers. The superhydrophobicity and superoleophilicity of the fibers enable it to selectively absorb and collect oils from water. The oil sorption capacity of the obtained fibers in various oils was studied, and the fabricated fibers show high oil sorption capacities up to 29.5–52.8 g/g. The recyclability tests indicate that the absorbed oil is easily recovered by a simple vacuum filtration and the coated fibers can be repeatedly used for many times, suggesting excellent recyclability. Furthermore, the in-situ continuous separation of oil pollutants from water surface can be realized with the help of a small amount of ZnO-coated fibers connected to a vacuum pump. Importantly, this modified fibers can also effectively separate micron sized oil-in-water emulsions containing no surfactant, with high separation efficiency. This study provides a simple, facile and inexpensive route toward the fabrication of superhydrophobic and superoleophilic natural fibers, which has potential application in the large scale separation of oil layer on water surface and oil droplets in oil-in-water emulsions.

Materials and methods

Materials

Cotton fibers were purchased from market, Yinchuan, China. Zinc nitrate hexahydrate, acetic acid, and $NH_3 \cdot H_2O$ (analytical grade) were received from Ningxia Yaoyi Chemical Reagent Co. Ltd., China. Dodecyltrimethoxysilane (DTMS, chemically pure) was provided by Nanjin Chengong Organosilicon Co., Ltd., China. Toluene, n-hexane, chloroform, paraffin oil, methanol, ethanol, n-octanol, and THF (analytical grade) were supplied by Sinopharm Chemical Reagent Co., Ltd., China. Gasoline and diesel were provided by the local station, Yinchuan, China.

Preparation process

The fabrication process of superhydrophobic fibers is illustrated in Fig. 1a. $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 M) was dissolved into distilled water (60 mL), and the pH of solution was adjusted to 10 by adding $NH_3 \cdot H_2O$. Cotton fibers were put into the above solution in a reactor, and the reaction system was heated to 90 °C and reacted for 12 h in an oven. After that, the ZnO-coated fibers were took out from the solution, rinsed with distilled water, and then dried to a constant weight. To endow the ZnO-coated fibers with low surface energy, the coated fibers was immersed in DTMS solution (1.5 wt. %) at room temperature for 12 h, and then dried in an oven at 80 °C to constant weight.

Oil sorption performance test

0.1 g of dried sample was put into a stainless steel mesh weighed beforehand and immersed in various oils at room temperature. The mesh was removed from the oil after being immersed into the oils for 5 min to reach sorption saturation, drained several seconds, and wiped with filter paper to remove excess oil from the bottom of the mesh. The oil sorption capacity of the sample was measured by weighing the samples before and after the sorption, and calculated by the following formula:

$$Q = \frac{M_t - M_i}{M_i}$$

where Q is the oil sorption capacity of the sorbents calculated as grams of oil per gram of sample, M_t is the weight of saturated sorbent (g), M_i represents the weight of dried sorbent (g). All oil sorption capacities were tested three times, and an average value was used.

Oil-in-water emulsion was obtained via vigorously stirring the mixture of oil and distilled water (oil/water, 1/10) for 4 h. The separation of micron-sized oil droplets from the above emulsion was carried out by agitating the emulsion containing the coated fibers for a certain time, and then the sorption of oil droplets from milky emulsions will be achieved.

Characterizations

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet NEXUS FTIR spectrometer using KBr pellets. The micrographs of samples were examined using SEM (JSM–5600LV, JEOL). Before SEM observation, all samples were fixed on aluminum studs and coated with gold. Contact angle measurements were carried out using a Krüss DSA 100 (Krüss Company, Ltd., Germany) apparatus at ambient temperature, and the volumes of probing liquids in the measurements were approximately 5 μL. Prior to observation, cotton fiber assembly was flattened with tablet machine. Thermogravimetric analysis (TGA) were carried out on a thermal analyzer (Perkin–Elmer, Norwalk, CT), with the temperature range 25–850 °C and heating rates of 15 °C/min for all the products in nitrogen atmosphere.

Results and discussion

Fabrication and wettability of superhydrophobic fibers

The wettability of the modified fibers was studied by measuring contact angle. As shown in Fig. 1, the water droplets on the surface of original and the modified fibers demonstrate an obvious variation in the wettability. The original fibers exhibit a certain hydrophilic property (Fig. 1b). After the growth of ZnO coating, the coated fibers will be wetted more quickly by water droplet, exhibiting preferable hydrophilicity (Fig. 1c). But, ZnO/DTMS-coated fibers display outstanding water repellency with a water contact angle of 155° (Fig. 1d). Besides, the contact angles of acidic (pH = 1), alkaline (pH = 13), salty (wt. 3.5% NaCl), and Cu solutions (1 M) on the modified fibers are also displayed in Fig. S1. The result indicates that the obtained fibers have good repellency to various corrosive aqueous solutions. Furthermore, the four kinds of corrosive aqueous solution can rapidly bounce off the surface of the fibers without leaving any residual liquid drops after spraying liquid jet Movie S1). In contrast, when toluene and diesel drip on the surface of the modified fibers, they are immediately absorbed

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