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Research paper

A facile preparation of superhydrophobic halloysite-based meshes for efficient oil–water separation

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ABSTRACT

A superhydrophobic halloysite-based mesh was facilely prepared by spraying epoxy/hexadecyltrimethoxysilane-halloysite nanotubes (HDTMS-HNTs) on stainless steel mesh. The as-prepared mesh was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and optical contact angle meter (OCA). The HNTs modified by HDTMS not only enhanced surface roughness, but also endowed hydrophobicity of the mesh. The mesh, with a static water contact angle of 154° and a sliding angle of 1.5°, was applied to separate a series of oil-water mixtures, such as n-hexane-water, isooctane-water and petroleum ether-water, with high separation efficiency of over 98%. The mesh still kept separation efficiency approximately 98.5% even after 25 separation cycles for n-hexane-water mixture separation. More importantly, the mesh is durable enough to withstand heat, chemical and mechanical challenges, such as hot water, strong alkaline, strong acid and sand abrasion, and high hydrostatic pressure. The as-prepared mesh will be a promising material in oil-water separation, because of the simple, economical and easily scalable preparation method and the excellent separation performance in radical oil-water separation.

1. Introduction

With the development of the industrial society, the problems of environment and pollution have been brought to the forefront. The ever-increasing oily sewages in the industrial production and frequent oil spills during oil exploitation and transportation not only lead to serious economic issues, but also pollute the ecosystem severely (Shannon et al., 2008; Ahmadun et al., 2009; Dubansky et al., 2013). Thus, it's urgently demanded to exploit a rapid and effective approach for oil sewage remediation. It is a facile and efficient methods to design new materials with special wettability for oil-water separation, since oil-water separation is affected by interface force. Recently, it has triggered increasing research interest to apply superhydrophobic superoleophilic porous materials to oil-water separation (Wang et al., 2015; Pi et al., 2016; Qing et al., 2017; Zeng et al., 2017; Hou et al., 2018). Since the unique water repellency and oil affinity of these materials, they can separate oil from water effectively by means of filtration or absorption. In addition, a variety of methods to fabricate superhydrophobic and superoleophilic materials have been reported, for example, sol-gel processing (Yang et al., 2010), lithography(Gao et al., 2015), electrostatic spinning (Yohe et al., 2012), chemical etching (Patoway et al., 2015), self-assemble (Shao et al., 2014), chemical vapor deposition (Hsieh et al., 2008) and so on. The limitations of these methods for large-scale fabrication are complex preparation, expensive equipment and long process. Besides, fluorinated acrylic resins were usually used to fabricate superhydrophobic surfaces (Wen et al., 2015; Pi et al., 2016). The long-chain fluorinated alkane can lower the surface energy greatly, and then makes the surface to be superhydrophobic, while its price is high and it will be accumulated in organisms which do harm to the environment and mankind. Therefore, it's highly warranted to find a simple, facile and low-energy method to fabricate a stable, economical and easily scalable superhydrophobic material in rapid oil-water separation.

Halloysite clay is a kind of naturally deposited aluminosilicate material [$Al_2Si_2O_5(OH)_4{\cdot}nH_2O$], which is generally a hollow nanotubular structure as shown in Fig. S1. It is a two-layered (1:1) clay mineral with abundant Si-OH and Al-OH groups (Hou et al., 2017). In addition, the size of HNT varies from 50 to 70 nm in external diameter, 15 nm in lumen diameter and 1 ± 0.5 μm in length (Vergaro et al., 2010). Halloysite nanotubes (HNTs) are far less expensive, eco-friendly and abundant, compared with other nanosized materials, such as carbon nanotubes, boron nitride nanotubes and titanium dioxides

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nanotubes. With the introduction of HNTs, the coating is expected to have better thermal stability and/or fire resistance (Makaremi et al., 2015; Qin et al., 2016). Therefore, Halloysite clay with hydrophobic treatment for developing superhydrophobic materials (Wu et al., 2013; Ma et al., 2017) can open up a new avenue for the application of clay, which is also a promising candidate for oil-water separation.

In this paper, a facile preparation of superhydrophobic meshes was reported by spraying epoxy and HNTs modified by hexadecyltrimethoxysilane (HDTMS) on stainless steel meshes. HNTs were transformed from hydrophilic to hydrophobic with modification of HDTMS. The introduction of epoxy resin could enhance the film-forming property and improve the stability of the coating. Besides, stainless steel meshes are widely applied to oil-water separation for a perfect combination of low cost, favorable mechanical property and easy reuse without squeezing, compared with other substrates, such as sponges, foams and filtration fabrics. Furthermore, spray is one of promising technique in practical production for its easy operation and low cost. The coated mesh has a perfect combination of robust superhydrophobicity, great reusability, excellent water pressure resistance and favorable stability to heat, chemistry and machinery, which is expected to be applied to large-scale oil-water separation, due to the easy, simple, cheap and scalable fabrication method.

2. Experimental section

2.1. Material

Natural HNTs were mined from Yichang, Hubei, China. Hexadecyltrimethoxysilane (HDTMS) was purchased from Aladdin Industrial Corporation. The epoxy resin E-44 was bought from Nantong Xingchen Synthetic Material Incorporation. Ethanolamine was obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. Anhydrous ethanol were supplied from Tianjin Kemiou Chemical Reagent Co., Ltd. Hydrochloric acid (HCl) and acetone were purchased from Tianjin Hongda Chemical Reagent Co., Ltd. Stainless steel meshes were purchased from a local hardware store (Guangzhou, China), and purified by ultrasonic washing with water and acetone for 30 min, respectively, and then completely dried in an oven at 60 °C before use. HNTs were dispersed in 1 mol/L HCl (m/m = 1:20) with magnetic stirring for 24 h at room temperature and then washed with distilled water until the water was neutral and dried in vacuum drying oven at 60 °C. The other chemicals were used as received without any further purification.

2.2. Fabrication of superhydrophobic hybrid epoxy/HDTMS-HNTs coated meshes

Firstly, 1 g HNTs were dispersed in 50 mL ethanol-water (m/m = 19:1) with vigorously stirring and then 2 mL HDTMS was added dropwise into the system. The reaction lasted at 78 °C for 4 h. The resultant HDTMS-HNTs were washed with ethanol and dried in vacuum drying oven at 60 °C. The powder was then milled through a 200-mesh screen. Secondly, stainless steel meshes soaked in ethanol solution with 0.5 wt% γ-(2,3-epoxypropoxy) propytrimethoxysilane for an hour and were dried at 80 °C for an hour. The fabrication process of superhydrophobic halloysite-based mesh is shown in Fig. 1. Epoxy resin E-44, HDTMS-HNTs and ethanolamine with a weight ratio of 1:4:0.16, were added in a mixed solvent of anhydrous ethanol and acetone (v/v = 1:1), with magnetic stirring for 2 h to obtain a stable suspension. Subsequently, the suspension was sprayed onto the mesh by using a spray gun at a distance of 15 cm with the spraying pressure of 0.3 MPa. Finally, the as-prepared mesh was dried in an oven at 120 °C for 2 h.

2.3. Characterization

FT-IR spectra were collected using a Fourier transform infrared spectrometer (PerkinElmer, USA) from standard KBr pellets (1 mg of sample/200 mg of KBr) with 64 scans at 4 cm^{-1} resolution in the 4000–400 cm^{-1} region to characterized the chemical composition of samples. The structures of samples were characterized by X-ray diffraction (XRD) with an X-ray diffractometer (D8 Advance, Bruker) with Cu Kα radiation (λ = 1.5418 Å). The diffractograms were scanned in 2θ ranges from 10 to 70° at a rate of 8 °/min. The surface morphologies of the films were observed by a scanning electron microscopy (SEM, Merlin). In addition, contact angles and sliding angles of water and oil were measured using an optical contact angle measuring device (Data Physics OCA20, Germany) with 5 μL drop of deionized water or oil, respectively. The reported values of contact angles and sliding angles were the average of at least three measurements at different positions on the same mesh. The mechanical stability of the coating was evaluated by taking sand abrasion tests (Milionis et al., 2016; Hou et al., 2017) on the coated mesh surface using sand particles with diameters of 180–280 μm at a height of 18 cm.

2.4. Oil-water separation

A series of oils, including n-hexane, isooctane, petroleum ether, vegetable oil and xylene, were mixed with equal volume of water to form oil-water mixtures. A superhydrophobic mesh was fixed in the miniature separator, of which the diameter is about 2 cm, and then 20 mL of oil-water mixtures were slowly poured into the separator at the speed of 1.2–1.3 mL/s. Oils penetrated the mesh into the beaker quickly while water was stuck in the separator. Gravity was the only driving force during the separation process. The water was collected in the container and weighed. The separation efficiency η was obtained according to $\eta = (m_1/m_0) \times 100\%$, where m_0 and m_1 are the mass of the water before and after the separation, respectively (Pan et al., 2008).

3. Results and discussions

The chemical composition and structure of pure HNTs and HDTMS-HNTs were analyzed by FT-IR and XRD, which were shown in Fig. 2. In the FT-IR spectra (Fig. 2a), the peaks at 3693, 3624 and 911 cm^{-1} were due to the stretching vibration of the inner-surface hydroxyl groups, the stretching vibration of the inner hydroxyl groups and the deformation vibration of the inner-surface hydroxyl groups, respectively. The strong absorption band at 1034 cm^{-1} was associated with Si-O-Si stretching vibration. The peaks at 536 and 469 cm^{-1} were attributed to the deformations vibrations of Al-O-Si and Si-O-Si. Compared to the spectrum of pure HNTs, there were two new peaks appearing at 2922 and 2854 cm^{-1} in that of HDTMS-HNTs, which could be ascribed to the stretching vibrations of aliphatic CH groups. These two news peaks indicated that the HNTs was successfully modified with HDTMS.

The powder XRD patterns of pure HNTs and HDTMS-HNTs, with the standard card of halloysite (JCPDS Card No. 29-1487) were given in Fig. 2b. The diffraction reflections of pure HNTs pattern were clearly observed at 2θ values of 12.35°, 20.03°, 24.95°, 35.05°, 38.14°, 54.41° and 62.23°, corresponding to the reflections of (001), (100), (002), (110), (003), (210) and (300) crystal planes of HNTs, respectively. Its diffraction reflections were consistent with those in the standard card of halloysite, which suggested a high purity of the halloysite clay. After modification of HDTMS, the diffraction reflections of HDTMS-HNTs remained much the same with that of pure HNTs, proving that HDTMS-HNTs retained the crystalline phase of HNTs even after modification of HDTMS.

The surface morphologies of an original mesh and a coated one were analyzed from their respective SEM images. It can be seen that surfaces of original mesh wires were smooth (Fig. 3a and b), whereas quantities of rod-like nanocrystals with 1 ± 0.5 μm in length and 50 to 70 nm in diameter piled up irregularly on surfaces of coated mesh wires (Fig. 3c and d), which constituted binary hierarchical rough structures on the surface of the coated mesh wires. Moreover, the average pore size of the