Applied Surface Science 435 (2018) 609–616

Contents lists available at ScienceDirect

Applied Surface Science

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

Full length article

Cellulose acetate-based SiO_2/TiO_2 hybrid microsphere composite aerogel films for water-in-oil emulsion separation

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ARTICLE INFO

Article history:
Received 6 May 2017
Received in revised form 22 October 2017
Accepted 15 November 2017

Keywords:
Emulsion separation
Hybrid microsphere
Phase inversion
Aerogel film
Photo-degradation

ABSTRACT

The cellulose acetate (CA)/SiO_2-TiO_2 hybrid microsphere composite aerogel films were successfully fabricated via water vapor-induced phase inversion of CA solution and simultaneous hydrolysis/condensation of 3-aminopropyltrimethoxysilane (APTMS) and tetrabutyl titanate (TBT) at room temperature. Micro-nano hierarchical structure was constructed on the surface of the film. The film could separate nano-sized surfactant-stabilized water-in-oil emulsions only under gravity. The flux of the film for the emulsion separation was up to 667 L m^{-2} h^{-1}, while the separation efficiency was up to 99.99 wt%. Meanwhile, the film exhibited excellent stability during multiple cycles. Moreover, the film performed excellent photo-degradation performance under UV light due to the photocatalytic ability of TiO_2. Facile preparation, good separation and potential biodegradation maked the CA/SiO_2-TiO_2 hybrid microsphere composite aerogel films a candidate in oil/water separation application.

1. Introduction

With the development of global industry and social economy, oily wastewater has become an increasingly serious environmental problem, and has taken severe harm to the human health and ecological environment [1–3]. Some materials are developed with good performance with regard to the separation of oil/water mixture [4–10]. However, the present separation materials are usually based on phase separation mechanism, and effective on immiscible oil/water mixture with a diameter of the dispersing phase more than 150 μm [11]. So it remains challenging on separation of oil/water emulsions, especially surfactant-stabilized oil/water emulsions where there exists without a clear interface between oil and water.

There has been only a few works concerning on the separation of surfactant-stabilized emulsions [12,13]. Zhang et al. first reported an inert solvent-induced phase inversion to prepare a superhydrophobic and superoleophilic poly(vinylidene fluoride) (PVDF) membrane, which can effectively separate both surfactant-free and surfactant-stabilized water-in-oil emulsions with droplet sizes from the micrometer to the nanometer with high separation efficiency (>99.95 wt% of oil purity after filtration) and an extremely high flux (about 2000 L m^{-2} h^{-1}) solely driven by gravity [14]. Following this work, a superhydrophilic and underwater superoleophobic poly (acrylic acid)-grafted PVDF (PAA-g-PVDF) membranes were prepared via salt-induced phase inversion. The PAA-g-PVDF membranes were able to separate surfactant-free and surfactant-stabilized oil-in-water emulsions with droplet sizes from several hundred nanometer to 10 μm with high separation efficiency (water purity infiltrate >99.99 wt%) and high flux (80–2320 L m^{-2} h^{-1}), only on the condition of gravity or 0.3 bar pressure [15]. Recently, bio-based separation materials were focused due to their biodegradability, excellent film-forming properties and easy modification [16–19]. Chaudhary and coworkers fabricated a superhydrophilic agarose/gelatin-based foam membrane through sol-gel method that could separate surfactant-stabilized oil-in-water emulsions under 0.2 bar crossflow pressure. But the permeate flux was only 68.67 L m^{-2} h^{-1} and oil rejection ratio was more than 97.95% [20]. Chen et al. successfully synthesized hydrophilic SiO_2 nanoparticle-modified film by in situ generation of SiO_2 and immerse precipitation phase inversion of CA solution. The surfactant-stabilized oil-in-water emulsions with the droplet sizes in the range of 0.12–23.4 μm can be efficiently separated, with the pure water flux about 435.2 L m^{-2} h^{-1} and 99.8% oil rejection ratio [21]. So far it has a limited success on design of bio-based films for surfactant-stabilized emulsions with a droplet size in the nanoscale. Furthermore, it has been an issue demanding

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https://doi.org/10.1016/j.apsusc.2017.11.123
0169-4332/

Table 1
The characteristics of petroleum ether, diesel and gasoline.

	Density/g cm^{-3}	Viscosity/cP
petroleum ether	0.64	0.30
diesel	0.89	2.5
gasoline	0.82	0.70

an effective way to solve the anti-fouling of the superhydrophobic separation films.

Here we report a facile phase inversion method for the preparation of the CA-based SiO_2/TiO_2 hybrid microsphere composite aerogel film. The film showed effective separation for surfactant-stabilized water-in-oil emulsions with a droplet size in the nanoscale. By means of a simple hydrolysis/condensation reaction, the generated SiO_2 and TiO_2 microspheres provide micro-nanoscale hierarchical structures on the film surface. As a consequence, the films can separate surfactant-stabilized water-in-oil emulsions (the droplet size of about 345 ± 39 nm) with high flux and high separation efficiency only at ordinary pressure. The film exhibited excellent stability during multiple cycles. Moreover, the films performed a fine anti-fouling property. Thus, the excellent films have enormous potential applications for oil/water separation.

2. Experimental

2.1. Materials

Cellulose acetate (CA) and 3-aminopropyltrimethoxysilane (APTMS) were purchased from Aladdin Chemical Co. *N,N*-dimethyl formamide (DMF) was purchased from Tianjin Yongda Chemical Reagent Co., Ltd. (China). Tetrabutyl titanate (TBT) and acetic acid glacial (HAc) were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. (China). Ethanol was purchased from Tianjin FuyuFine Chemical Co., Ltd. (China). Petroleum ether was purchased from Tianjin Yongsheng Fine Chemical Co., Ltd. (China). Diesel and gasoline (grade: 93 octane) were purchased from a gas station (Urumqi, China). The characteristics of these oils were listed in Table 1. Deionized water was used throughout the experiment. All reagents were used as received without further purification.

2.2. Preparation of the aerogel film

The aerogel films with different compositions were prepared by phase inversion method. Typically, CA was dissolved in DMF to obtain 5 wt% of transparent solution. Then 1.84 g TBT was added dropwise to 1.68 g HAc in an ice water bath to form 52.3 wt% of TBT/HAc mixed solution. A transparent casting solution was prepared by mixing 5.0 g 5 wt% of CA solution and 0.23 g 52.3 wt% of TBT/HAc solution, followed by 0.25 g APTMS under stirring for 10 min. Afterwards, the casting solution were poured onto the culture dish with 56 mm diameter on the desiccator under the condition of 33% relative humidity and room temperature to obtain a film after 12 h. Then the film was immersed into deionized water and ethanol, respectively. Finally, the film was dried in room temperature and ordinary pressure. The resultant films were denoted as $CT_{0.5}A_1$, where C, T and A represent CA, TBT and APTMS respectively, while the number represents the weight ratio of TBT to APTMS. CT_1A_1 and $CT_{1.5}A_1$ were prepared by the process above with 0.46 g and 0.69 g 52.3 wt% of TBT/HAc solution respectively. As a control, pure CA film was prepared according to the above procedure except for the absence of TBT/HAC solution and APTMS, and the resultant film was denoted as CT_0A_0.

2.3. Preparation of the water-in-oil emulsions

Surfactant-stabilized water-in-oil emulsions SSE were prepared by mixing water and oil with a volume ratio of 1:120 with Span 80 as an emulsifier under mechanically stirred for 30 min at 3000 r/min. For SSE-1, Span 80 (0.10 g) was added into petroleum ether (120 mL), and mixed with water (1 mL). For SSE-2 and SSE-3, diesel and gasoline was used instead of petroleum ether in SSE-1 respectively. The droplet sizes of SSE-1, SSE-2 and SSE-3 were 330, 367 and 384 nm, respectively. For SSE-4 and SSE-5, 0.15 g Span 80 and 0.20 g Span 80 was added respectively instead of 0.10 g Span 80 in SSE-1. The droplet sizes of SSE-4 and SSE-5 were around 313 nm and 306 nm, respectively. All the emulsions were stable for more than 3 d without demulsification or precipitation occurred.

2.4. Emulsion separation and photocatalytic degradation of organic compounds

The as-prepared aerogel film was fixed between two filter apparatus. The emulsions were poured into the glass tube, and the whole process was driven by gravity only. Finally the filtrates were collected for further test. The flux was determined by evaluating the volume per unit area and per unit time when 5 mL emulsion passed through the film. UV irradiation was provided by a medium pressure mercury lamp (250 W) during photocatalytic degradation process of organic compounds. For the cycling separation, after 5 mL of emulsion passed through the film, the film was placed at ordinary pressure and room temperature for 12 h. Then, the film was used to the next separation according to the same procedure. The procedure was repeated 15 times.

2.5. Characterizations

Apparent densities of the aerogel films were calculated after measuring volume and weight of the films. The porosity, pore size and surface area of the aerogel films were recorded by mercury intrusion test using the Micrometrics Autopore IV 9500 Series (USA). FTIR spectra of the aerogel films were detected by the BRUKER EQINOX55 spectrometer (Germany) with the range of 500–4000 cm^{-1}. The aerogel films were detected by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, USA) with an Al K Alpha X-ray source at a voltage and current of 15 kV and 10 mA. The base pressure in the analyzing chamber was maintained in the order of 10^{-7} Pa. The pass energy was 50.0 eV, and the binding energy was calibrated using contaminant carbon (C1s = 284.6 eV).The microstructure and surface morphology of aerogel films were observed by scanning electron microscopy (SEM, LEO-1430VP, Germany) and transmission electron microscopy (TEM, HitachiH-600, Japan). The elements of the aerogel films were examined by scanning electron microscope-energy dispersive X-ray spectrometer (SEM-EDS, HitachiS-4800, Japan). Contact angles were measured on a JJ2000 B2 machine (Powereach, China) at ambient temperature, where 4 μL water droplets were dropped for observation. The droplet sizes were measured by a nanoparticle size analyzer (Malvern Zetasizer Nano ZS90, the United Kingdom). Oil purity was evaluated by a Karl Fischer titrator (Mettler Toledo DL31/38, Switzerland).

3. Results and discussion

3.1. Hydrolysis/condensation reaction

In the present experiment, we used two modifying agents TBT and APTMS for constructing rough and hydrophobic CA-based materials by sol-gel reaction and water vapor-induced phase inversion. During the modification process of CA by both TBT and APTMS,