



Self-indicating and recyclable superhydrophobic membranes for effective oil/water separation in harsh conditions



Shenshen Ouyang, Tao Wang ^{*}, Xueying Jia, Yun Chen, Juming Yao, Sheng Wang ^{*}

Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Zhejiang Sci-Tech University, Hangzhou 310018, China

ARTICLE INFO

Article history:

Received 9 December 2015
Received in revised form 6 February 2016
Accepted 8 February 2016
Available online 11 February 2016

Keywords:

Color indicator
Recyclability
Superhydrophobicity
Oil/water separation
Harsh conditions

ABSTRACT

A durable and renewable superhydrophobic and superoleophilic poly(m-phenyleneisophthalamide)/silicon dioxide (PMIA/SiO₂) membrane was prepared for oil/water separation in harsh conditions, the membrane have a self-indicating capacity when it is to become inoperable. Its nanoroot-shaped micro-nanostructure was achieved by covering each individual electrospun PMIA/SiO₂ nanofiber with a dense silicone nanofilament layer to form a superhydrophobic surface, the water contact angle was more than 150° and the sliding angle was less than 1°. The porous nanofiber network served as a substrate to ensure the high absorption capacity of oils and oil/water separation efficiency, and increase the roughness for hydrophobicity. Its superhydrophobicity, high separation efficiency, and excellent stability and durability in oil/water separations under various extreme conditions, such as high temperature, acid/alkali solutions, and seawater for long periods can be preserved. This behavior is attributed to the robust micro-nanostructure, superior corrosion resistance, and excellent mechanical properties. Congo red in the PMIA substrate acts as a color indicator to indicate superhydrophobic surface failure, and the disabled material can be recovered absolutely by *in-situ* regrowth of silicone nanofilaments. This material is expected to become a highly effective renewable and sustainable material for oil-spill cleanup and recycle.

© 2016 Published by Elsevier Ltd.

1. Introduction

Superhydrophobic and oleophilic materials, which consist of superhydrophobic surfaces and oleophilic substrates, are promising candidates for oil/water separation, because of their high separation and recovery efficiency [1–4]. Superhydrophobic surfaces are usually defined as having a contact angle of water greater than 150°, and a roll angle less than 10°. Various superhydrophobic surfaces have been prepared by methods such as chemical vapor deposition [5], drop-coating [6], spraying [7], electrodeposition [8], and etching [9], to construct rough surfaces with hierarchical micro-nanostructures. Their practical applications are usually limited by complex fabrication procedures, high production costs, weak stability in harsh practical conditions, poor flexibility and recyclability, and the inability for regenerative repair [10]. The choice of a flexible oleophilic substrate with suitable multilevel structures and a stable superhydrophobic surface is challenging for oil/water separation materials to ensure a high carrying capacity, persistent stability, excellent mechanical properties, and a strong bond between the substrate and superhydrophobic surface. Demands for stability are high for oil/water separation in harsh conditions such as strong acid/alkali, sea water, and high temperature environments. This is because

the functional surfaces and the bond with substrates are easily destroyed with irreversible damage. In general, this results in a loss of the functionality in oil/water separation [11,12]. Hence, research into the development of robust, stable, and renewable superhydrophobic and oleophilic materials, which are fit for harsh conditions, is critical for the sustainable development of advanced materials.

The inorganic surface coating for hydrophobic modification is an effective technique to set up functionalization for separation [13,14]. Seeger and coworkers prepared a superhydrophobic surface from silicone nanofilaments (SNs) on glass slides by chemical vapor deposition, which was realized from the dense and entangled arrangement of these filaments with controllable size [15]. Outdoor tests showed that the SN coating retains its superhydrophobic and anti-reflective properties for at least one year [16]. Its chemical durability was tested in various liquid media. Samples annealed at 200 °C showed a good resistance to organic solvents, in neutral and mildly acidic solutions (pH of 3), over at least 6 months, and only retained their superhydrophobicity after short-term exposure (less than 24 h) to strong acidic (pH of 1) and mildly basic (pH above 10) solutions [17]. The team prepared amphiphobic SN coatings by self-assembly of organosilanes with long alkyl groups, and a combination of fluoro-SNs and Krytox liquids for further study [18,19]. They coated the SNs on textile fabrics and found that their tensile strength and color were unaffected by the SN coating, and that the coated fabric remained superhydrophobic after continuous rubbing tests [20]. A superhydrophobic and superoleophilic polyester

^{*} Correspondence authors.

E-mail addresses: Taotao571@hotmail.com (T. Wang), wangsheng571@hotmail.com (S. Wang).

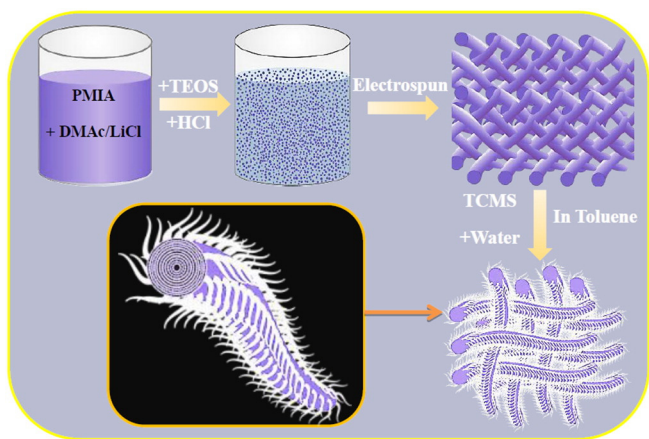


Fig. 1. Schematic diagram showing fabrication of electrospun PMIA/SiO₂-SN membrane with dual micro-nanostructures.

membrane coated with SNs was prepared for oil/water separation and showed excellent reusability, oil/water separation efficiency, and selective oil absorption capacity [21]. Therefore, the SN-superhydrophobic surface combined with a flexible organic polymer is a promising candidate for oil/water separation in harsh conditions. Further research could focus on choosing a polymer substrate with higher stability and mechanical properties, enhanced bonding strength between surface and substrate, and established warning mechanism and recycling method.

We have prepared a robust and durable superhydrophobic superoleophilic poly(*m*-phenyleneisophthalamide)/silicon dioxide (PMIA/SiO₂) membrane with a color indicator and renewability when it is to become invalid for oil/water separation in harsh conditions. The preparation methods are simple, cost-effective, and controllable. The surface of each individual electrospun PMIA/SiO₂ nanofiber was covered with a dense superhydrophobic layer of *in-situ*-grown SN, where the SiO₂ nanoparticles (NPs) on the nanofiber surface act as the seeds, and formed robust dual micro-nanostructures. This structure forms nanoroots with nanofibers as roots and SNs as hairs. The porous structure of the nanofiber network ensures a high oil/water separation efficiency, and increases the SN structure roughness to improve superhydrophobicity. Congo red in the PMIA substrate acts as a color indicator of superhydrophobic surface failure, and the disabled material can be recovered by SN regrowth in the same system. Because of its robust dual micro-nanostructure, superior corrosion resistance, and the excellent mechanical properties of the superhydrophobic SN surface

and PMIA substrate, this material is capable of maintaining a high separation efficiency, remarkable recyclability, and excellent stability and durability under various harsh conditions for extended periods. It is therefore expected to become an ideal sustainable material for efficient oil/water separation in severe practical conditions such as high temperature, acid/alkali solutions, and seawater.

2. Experimental section

2.1. Materials

Commercial PMIA pulp (0.5–3 mm) was provided by Chengdu Boxing Co. Ltd. (China). Dimethylacetamide (DMAC), tetraethyl orthosilicate (TEOS), methyl trichlorosilane (MTS), toluene, ethanol, HCl, and LiCl were purchased from Hangzhou Mike Co. Ltd. (China). Diiodomethane, hexadecane, and all dyestuffs were from Aladdin Co. Ltd. (China). All of the reagents were used as received.

2.2. Methods

2.2.1. Synthesis of PMIA/SiO₂ electrospun membrane (EM)

A certain amount of LiCl was dried in a vacuum dryer at 120 °C for 2 h, and the primed PMIA pulps were treated using methanol, acetone, and ethanol before being dried in a vacuum dryer at 80 °C for 2 h. LiCl (0.85 g) was dissolved in DMAC (10.7 mL) by stirring. The PMIA pulps (1.58 g) were dissolved in LiCl-DMAC solution by stirring at 90 °C to produce a 15 wt.% concentration solution (w/w relative to the entire system). Congo red (25 mg) was added and stirred for 1 h. TEOS (0.4 mL) and HCl solution (0.2 mL, 1 M) were added dropwise and stirred at room temperature for 2 h. The solution (1 mL) was fed through the plastic microtip of a 10 mL syringe. Electrospinning was carried out at a 30 kV applied voltage, with a distance of 10 cm between the collector and the syringe tip, and a solution flow rate of 0.15 mL h⁻¹. All fiber spinning was performed at 25 °C. The resultant composite membrane of PMIA/SiO₂ nanofibers was immersed in water and alcohol for 12 h alternately and dried for 24 h to remove the solvent.

2.2.2. PMIA/SiO₂ casting films (CF)

PMIA solution (15 wt.%) was poured into Teflon dishes and dried at 20 °C. The casting film thickness was controlled by the solution volume and casting area. Post-treatment of the casting films was the same as that of the EM.

2.2.3. *In-situ* growth of SNs

The electrospun/cast PMIA/SiO₂ membrane was immersed in 80 mL toluene with a certain amount of water (15, 20, 30, and 60 μL) and MTS

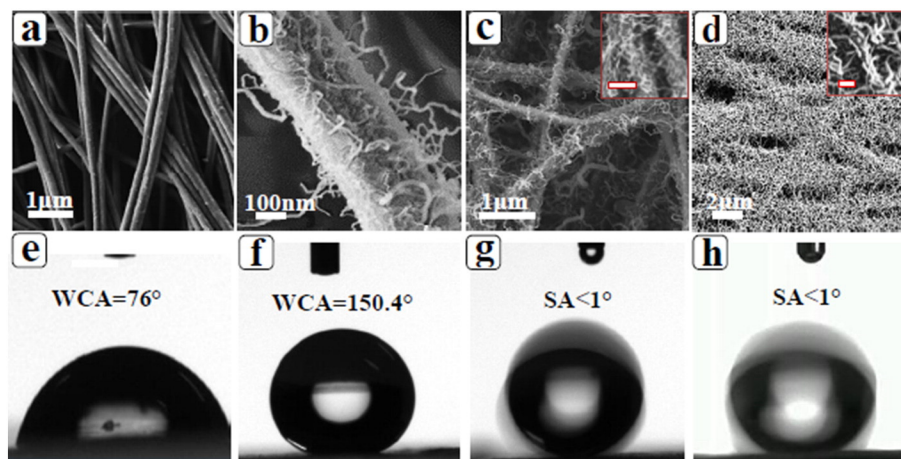


Fig. 2. (a) SEM image of electrospun PMIA/SiO₂ nanofibers without SN. (b–d) SEM images of electrospun EM-SN samples with different SN diameters from 80, 125, and 250 μL MTS and 20 μL water addition in SN growth, and (e–h) corresponding photographs of WCAs. Insets in (c, d) show magnified sample morphology indicated using 200 nm bars.

Download English Version:

<https://daneshyari.com/en/article/7218595>

Download Persian Version:

<https://daneshyari.com/article/7218595>

[Daneshyari.com](https://daneshyari.com)