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Fabrication of novel superhydrophilic and underwater superoleophobic hierarchically structured ceramic membrane and its separation performance of oily wastewater

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ABSTRACT

Hierarchically engineered asymmetric ceramic membrane is successfully fabricated, and special wettability is endowed to the membrane by introducing superhydrophilic and underwater superoleophobic silica nanoparticles through dip-coating technology onto the active separation layer. Effect of reaction temperature on the wettability of the silica nanoparticles is discussed. It has been found that the hydrophilicity of the silica increases with increasing the temperature and superhydrophilicity can be obtained when the temperature reaches to 60 °C. Underwater oil contact measurements are performed using a series of oils and it turns out the as-prepared material bear excellent oil repellency towards various oil droplets. Separation performance of the membrane for oily wastewater treatment was investigated. It has been revealed that the as-prepared membrane can successfully separate the oil contaminated wastewater within one step under a small applied pressure (0.1 MPa) with oil rejection coefficient $R > 99.95\%$, indicating an extremely high separation efficiency.

1. Introduction

Oily wastewater widely exists in many industrial applications, such as metallurgical, coking, mechanical processing, petroleum exploitation and refinery [1]. The further treatment for oily wastewater is an essential and important process to eliminate oil pollution. Conventional techniques for oil/water separation such as gravity separation, coagulation and flotation suffer from the limits of complex operation process, energy-cost and low efficiency and are not applicable to separating oil/water emulsions, especially for those with droplet below a micron in size [2]. Membrane separation process has been proven to be an effective and environmental approach to deal with oily wastewater thanks to its high oil removal efficiency, easy regeneration access and small compact influence on the environment [3,4]. Currently, organic membranes [5,6], inorganic membranes [7,8] and inorganic-organic composite membranes [9–11] are most frequently used in oily wastewater treatment. Unfortunately, severe fouling issues produced during separation reduce the efficiency and the lifetime of the membranes, thus restricting the popularized practical applications of membrane technology [3]. Therefore, the development of membranes with excellent antifouling properties for removal of large amounts of organic contaminants from oily wastewater is highly desired yet challenging.

Two factors are considered to be the primary reasons causing membrane fouling issue: oily contaminant absorbed on the membrane surface and the concentration polarization [12]. An enhancement of the hydrophilicity of the membrane surface is believed to be able to effectively mitigate the membrane fouling problem [13]. Generally speaking, the wettabilities of solid surfaces are usually governed by the chemical compositions which determine the surface free energy, and the surface morphology which is related to the surface roughness [14]. Thus, approaches to enhance the hydrophilicity of membranes are usually on the basis of introducing hydrophilic chemical components onto the membrane surface [15] and improving the surface roughness. Numerous authors have elaborated hydrophilic membranes [13,16] for oily wastewater treatment in an attempt to enhance the antifouling performances. Cohen et al. [17] formulated antifouling ceramic-supported polymer (CSP) ultrafiltration membranes by introducing hydrophilic poly(vinylpyrrolidone) (PVP) onto the surface of ceramic membrane supports for treatment of synthetic microemulsions. It was found that the CSP membrane demonstrated excellent antifouling property and higher oil rejection compared to the native membrane. Chang et al. [18] modified commercial Al_2O_3 microfiltration membranes with the nano-sized ZrO_2 particles by in situ hydrolysis of $ZrCl_4$ to separate engine oil-water emulsion. It turned out the modified coating enhanced the hydrophilicity of the membrane and contributed to reducing the

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membrane fouling of oil droplets to a large extent. Even more noteworthy is that the rapid development of functional materials with special wettabilities has offered a brand new conception for developing advanced separation membranes [19–22].

Based on theoretical predictions, functional surfaces with contrary wettability towards water and oil has been generally developed on various substrates through an appropriate combination of surface energy and surface roughness to deal with oily wastewater [23,24]. Typically, two types of substrates are mainly involved: adsorbing materials, such as textiles [25], foams, and sponges [26]; filtration materials, such as metal meshes [27] and polymeric membranes [28]. However, most of the techniques for fabricating super-wetting or super-antiwetting surfaces make use of polymeric substrates [14,24,29], which usually suffer from the limits of poor stability under sever conditions, weak environmental adaptability and low loading capacity [1,11,30]. Consequently, they are not applicable to practical application with a large separation capacity. To address these challenges, the development of all-inorganic membranes with superhydrophilicity and underwater ultralow adhesive superoleophobicity [31,32] is highly desirable.

Herein, we reported a facile method to fabricate hierarchical ceramic membrane with superhydrophilicities and underwater superoleophobicities for high-efficiency oil/water emulsions separation. Completely different from the conventional approach of using organic membrane as the substrate to achieve special wettability as reported previously, all-inorganic ceramic membrane was used for the first time as the substrate to achieve superhydrophilic and underwater superoleophobic properties, which displays longer service life than polymeric membrane and stronger anti-fouling ability than the general ceramic membranes. Instead of traditional particle size-sieving, the mechanism of the as-prepared ceramic membrane for separation of oil/water emulsions is based on the different wettability towards oil and water, as shown in Fig. 1. As a consequence, the membrane can separate the wastewater under a small applied pressure (0.1 MPa), with extremely high separation efficiency (oil rejection coefficient rate $>99.95\%$ after one-time separation) and relatively high flux. Most importantly, the excellent separation performance of the membrane and its outstanding antifouling property indicate great potential for practical applications.

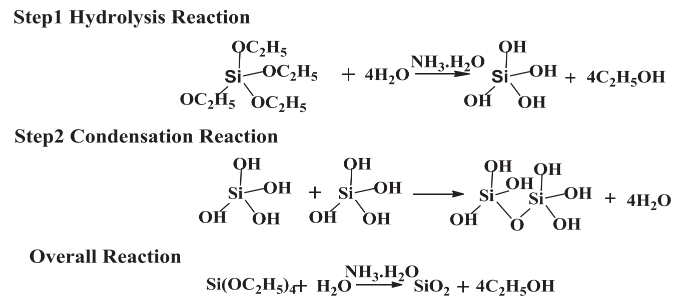

Fig. 2. The reaction mechanism diagram of the preparation of silica sol via Stöber process.

2. Experiment

2.1. Materials

The raw materials utilized for fabrication of the membrane support (kaolin, quartz, alumina oxide, corn starch) were obtained in Aladdin Chemistry Co., Ltd. China. All these starting materials were used without further purification Polyvinyl alcohol (PVA) was supplied by Ke Long Chemical Reagent Co., Ltd. China. Polyethylene glycol (PEG, Mn=6000), carboxymethylcellulose (CMC), Tetraethylorthosilicate(TEOS), ammonia (25–28% aqueous solution), and absolute ethanol, were obtained in Aladdin Chemistry Co., Ltd. Oily wastewater was supplied by an oilfield in China.

2.2. Fabrication of the hierarchical membrane

The membrane support was prepared by mixing the raw materials (30 wt% kaolin, 30 wt% alumina oxide, 20 wt% quartz, 20 wt% corn starch) in a ball mill at 45 rpm for 0.5 h, and the resultant mixture was then sieved using a 30 mesh standard screen. In this composition, different materials contribute to different functions during the support elaboration. Kaolin endows the membrane low plasticity, quartz increases the thermal stability, alumina oxide provides the mechanical strength, and corn starch acts as the pore forming agents. Subsequently, 6 wt% of PVA was added as the binding agent and the mixture was grind and dried in an oven at 60 °C alternately to obtain a uniform mixture. A requisite amount of powder was filled in a home-made stainless steel mold to be pressed at a pressure of 25 MPa to elaborate a disk shaped membrane. The obtained membrane (30 mm diameter and

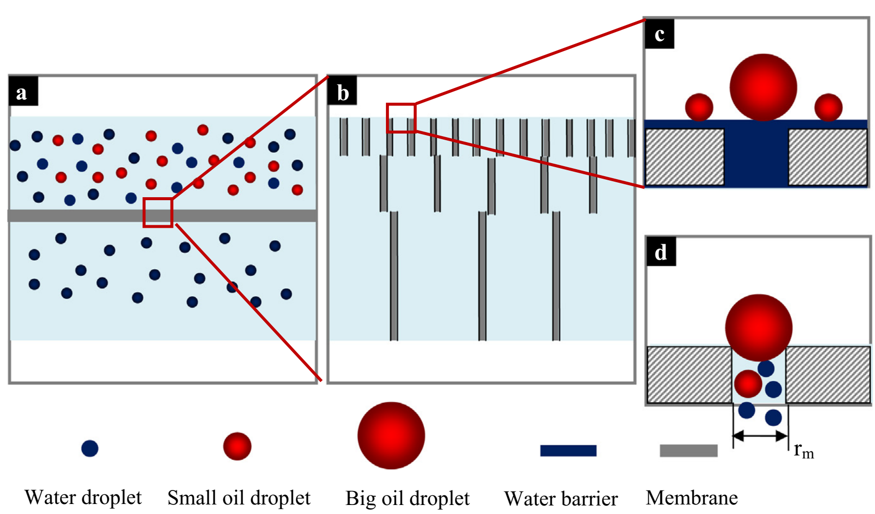

Fig. 1. (a) Schematic of water-in-oil emulsion separation process through a membrane; (b) Idealized schematic of a hierarchical membrane showing skin layer with small pores, support layer with larger pores and intermediate layer between them; (c) Close-up diagram of rejected oil droplets by a water barrier due to superhydrophilicity of the membrane; (d) Close-up diagram of traditional size-sieving separation mechanism of membrane.