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Superhydrophilic and underwater superoleophobic modified chitosan-coated mesh for oil/water separation

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ABSTRACT

To develop an effective and simple approaches for the cleaning-up of the oily wastewater, a superhydrophilic and underwater superoleophobic mesh that can be applied to separate oil/water mixtures is prepared by spraying chitosan–silica nanoparticles–glutaraldehyde composite on the stainless steel mesh. The mesh can separate a series of different oil/water mixtures with >99.0% separation efficiency in the harsh environment such as acidic, saline or alkaline conditions, making it promising for practical oil/water separation applications.

1. Introduction

Because of industrial oily wastewater production growth and frequent oil spill accidents, demand for development of effective and simple approaches for oil/water separation has risen. Design of advanced materials with desirable wettability have stimulated many interests because oil/water separation is governed by the special interfacial phenomena [1–3]. Inspired by nature (e.g. fish scales), enormous artificial hydrophilic and underwater superoleophobic materials have been fabricated via hydrophilic surface modification on base materials. These hydrophilic and underwater superoleophobic materials have many advantages compared to traditional hydrophobic and oleophilic materials. First, they can effectively avoid or reduce external fouling. Then, the water barrier is easy to form between the hydrophilic and underwater superoleophobic membranes and the oil phase. However, they cannot long remain stable in complex environments such as acidic, alkaline, or hyper-saline conditions. Therefore, it is of extremely urgency to fabricate functionalized materials with stable superhydrophilicity and underwater superoleophobicity for the separation of oil and harsh corrosive aqueous solutions mixture in a simple, economical and effective approach.

Chitosan (CS), whose structure is presented in Fig. 1, is an abundant and low-cost polymer, and extracted from chitin that is a primary ingredient in crustacean seashells. CS has many characteristics that make it a promising candidate for oil/water separation membrane coatings such as biocompatibility, good film forming ability, high mechanical strength and hydrophilicity [4,5]. SiO_2-based coatings have also performed superhydrophilicity property [6,7]. Various research groups have confirmed that the silanol groups of SiO_2 from the hydrolysis of tetraethoxysilane (TEOS) can react with the hydroxyl groups of CS [5-8]. It is well-known that CS can be cross-linked with glutaraldehyde (GA) through reaction of the aldehyde groups of GA with the amino groups of CS [9,10]. The process of synthesis of CS–SiO_2–GA composite is also presented in Fig. 1. As shown in Table 1, many studies have developed a new route to enhance separation efficiency in the field of oil/water separation by coating the advanced materials to the support membrane. In this study, new coating materials with desirable coating properties, prepared by three highly hydrophilic materials including CS, SiO_2 and GA, are used to form thin coatings on stainless steel mesh to improve their oil/water separation efficiency. To the best of our knowledge, this study is the first example of GA-cross-linked CS/SiO_2 being used for oil/water separation.

Herein, a superhydrophilic and underwater superoleophobic mesh was fabricated by coating CS–SiO_2–GA hybrid materials on a stainless steel mesh. The modified mesh was used for oil/water separation experiments only under driven gravity, which showed a separation efficiency >99.0% for different oil–water mixtures. In addition, the modified mesh also show stable superhydrophilicity and underwater superoleophobicity towards many corrosive solutions (0.5 mol/L HCl, 0.5 mol/L NaOH and 0.5 mol/L NaCl solutions), which shows the high stability of the modified mesh in harsh environments.

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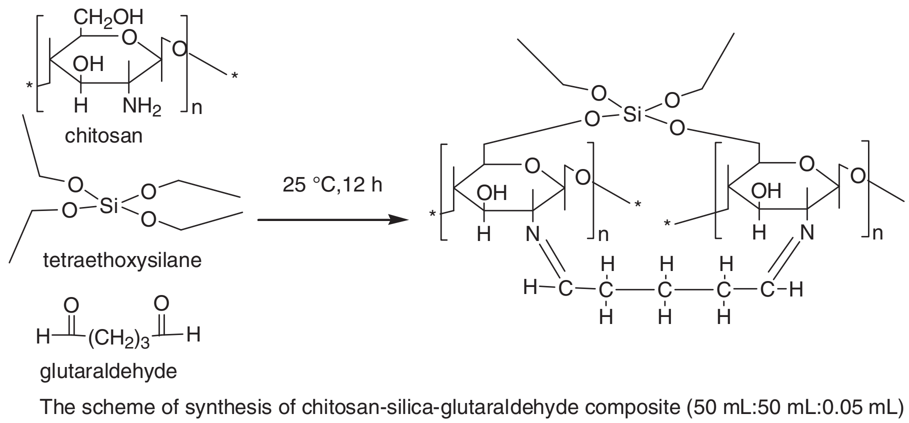

Fig. 1. The synthesis process of CS–SiO_2–GA composite.

2. Materials and methods

2.1. Materials

TEOS as the SiO_2 precursor and GA were purchased from Sigma-Aldrich. CS (degree of deacetylation is 80.0–95.0, viscosity is 50–800 mPa·s), sulfuric acid (95–98%) (H_2SO_4), hydrogen peroxide (30%) (H_2O_2), ammonia, ethanol and acetic acid were obtained from Sinopharm Chemical Reagent Co., Ltd.

Table 1
Selected studies on superhydrophilic and underwater superoleophobic material for oil/water separation.

Coating material	Support membrane	Reference
Poly(methacrylic acid)	Cotton fabric	[11]
ZnO nail	Stainless steel mesh	[12]
Cellulose	Electrospun PVDF–HFP	[13]
Silicalite-1	Stainless steel mesh	[14]
Polyelectrolyte-fluorosurfactant complexes/SiO_2	Stainless steel mesh	[15]
Graphene oxide	Stainless steel mesh	[16]
Nanostructured TiO_2	Stainless steel mesh	[17]
Poly(sulfobetaine methacrylate)	Glass fiber filters	[18]
Stearic acid ethanol solution/tetrahydrofuran	Copper mesh	[19]
TiO_2	Single-walled carbon nanotube network film	[20]
Poly(ethylene glycol) diacrylate	PVDF membrane	[21]
ZnO nanoparticles/polyurethane	Stainless steel mesh	[22]
Silica gel	Quartz fiber mesh	[23]
N-alkanoic acids	Copper films	[24]
Magnetic pickering emulsions	Carbon nanotube	[25]
Poly(2-methacryloyloxylethyl phosphorylcholine)	Stainless steel mesh	[26]
Polyethyleneimine	Graphene oxide membrane	[27]
NiOOH	Metal meshes	[28]
Palygorskite	Copper mesh	[29]
Hierarchical TiO_2 nanotubes	Porous titanium	[30]
$Fe(NO_3)_3$	Carbon fiber aerogel	[31]
$CaCO_3$	Polypropylene non-woven meshes	[32]
Polyaniline and polypyrrole	Stainless steel mesh	[33]
$Cu(OH)_2$	Copper mesh	[34]
Poly(sulfobetaine methacrylate)/polydopamine	Stainless steel mesh	[35]
Polypyrrole	Stainless steel mesh	[36]
Sodium silicate/TiO_2 nanoparticles	Stainless steel mesh	[37]
Chitosan	Stainless steel mesh	[38]
Poly(acrylic acid)	PVDF filtration membrane	[39]
Poly(3-(N-2-methacryloxyethyl-*N*,*N*-dimethyl)) ammonium propanesultone	PVDF membrane	[40]
TiO_2 and polyurethane	Stainless steel mesh	[41]
CS–SiO_2–GA composite	Stainless steel mesh	This study

2.2. Preparation of CS–SiO_2–GA hybrid solution

First, 2 g of CS was dissolved in 80 mL of acetic acid solution (2 wt%) while stirring on a magnetic stirrer for over 4 h. Then, SiO_2 was prepared by using Stober's method [42,43]. Briefly, 50 mL of deionized water and 8 mL of ammonia (28 wt%) was successively added to 250 mL of ethanol. After that, 0.3 mL of TEOS was added to the solution followed by stirring at 25 °C for 12 h. The CS–SiO_2 solution (3: 1, 2: 1, 1: 1, v/v) was produced by mixing the above solutions and stirring for 2 h. Finally, 0.05 mL of GA solution was added to the CS–SiO_2 solution followed by stirring at 25 °C for 12 h.

2.3. Fabrication of CS–SiO_2–GA hybrid-coated mesh and glass sheet

The stainless steel mesh (100, 300, 350 and 400 mesh size) and glass sheet were washed with distilled water and ethanol solution using ultrasonic wave at room temperature, respectively. Then, the pre-cleared mesh was immersed into piranha solution (H_2SO_4: H_2O_2 = 3:1, v/v) at 60 °C for 3 h followed by rinsing with deionized water and drying at 60 °C for 12 h. The CS–SiO_2–GA solution was coated onto the pre-cleared mesh with 0.4 MPa nitrogen gas using a spray gun. In order to ensure uniform coating, the above process was repeated three times. After dried in air, the modified mesh was immersed into NaOH (0.1 mol/L) solution for 15 min and washed with deionized water followed by drying in air.

2.4. Characterization

Scanning electron microscopy (SEM) images of the substrates were obtained using a field-emission SEM (Hitachi S-4800, Japan). Attenuated total reflectance Fourier transform infrared spectroscopy (FTIR-ATR) were measured by NEXUS (Thermo Nicolet, America). Contact angles (CAs) were measured on a KSV CM20 machine (KSV, Finland) at ambient temperature.

2.5. Oil/water separation experiments

The modified mesh was fixed between two glass tubes. Six types of oils and organic solvents, including gasoline, chloroform, bean oil, rapeseed oil, petroleum ether and toluene, were used for separation experiments. They were dyed with Oil red O and mixed with water followed by stirring. The different oil/water mixtures (20%, v/v) were slowly poured onto the modified mesh, which was pre-wetted by water. The