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Journal of Membrane Science

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

Durable superhydrophilic coatings formed for anti-biofouling and oil–water separation

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ARTICLE INFO

Article history:

Received 14 October 2015

Received in revised form

16 December 2015

Accepted 19 January 2016

Available online 28 January 2016

Keywords:

Layer-by-layer assembly

High stability

Anti-biofouling property

Oil–water separation

ABSTRACT

Building up unique interfaces by means of layer-by-layer (LbL) assembly is of interest for a variety of practical applications, particularly those that require the advantages of special wettability. Herein, a UV-cured superhydrophilic coating with high stability was constructed in the form of a hydrogen-bonding-based LbL multilayer incorporating silica nanoparticles (SNPs). In our present work, hydrophilic branched poly(ethylenimine) (BPEI) and SNPs were assembled into LbL multilayers in the presence of UV-curable poly(urethane acrylate) (PUA), which is described herein as (PUA–SNPs/BPEI)_n. The as-prepared architectures showed good acid, thermal, and mechanical stability following crosslinking by UV exposure. Crosslinking is of great importance for LbL film, considering the weak interactions among polyelectrolytes. Owing to the superhydrophilicity of the coating, the anti-biofouling properties were enhanced to some extent for gram-positive *Staphylococcus aureus* and gram-negative *Pseudomonas aeruginosa* contamination. Furthermore, the superhydrophilic polycarbonate track-etched (PCTE) membrane coated with (PUA–SNPs/BPEI)_n coatings with different numbers of LbL deposition cycles were also investigated for oil–water separation. To the best of our knowledge, this is the first demonstration of rough structures created on a straight pore PCTE membrane. Commercial PCTE membranes with robust coatings, which allow water to penetrate the membrane while oily substance are intercepted, have been developed for regular oil–water separation with more than 99% efficiency.

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1. Introduction

Numerous challenging issues involving the marine ecosystem are increasingly serious, thanks in large part to seawater pollution from human activities [1,2]. In response to this, much progress has been made on research into preventing pollutants in the oceans from further spreading. Typically, contaminants in water, which mainly include oily substances and water-miscible organic molecules resulting from oil spill accidents, need to be removed urgently and in an effective way. Oil–water separation undoubtedly serves as a unique strategy that has been of considerable interest. However, to some extent, problems of traditional separation technologies using flotation, gravity, centrifugation, and pressure-driven membrane filtration are still challenging, considering inefficient, incomplete, time-consuming, and low-profit processes [3–6]. For instance, the centrifugation process strongly depends on the centrifuge, which is limited to high-speed machines requirement. In addition, traditional filtration systems heavily rely on

vacuum devices, which will result in extra energy and incomplete oil or water separation [4]. Recently, novel superwettable materials, such as poly(vinylidene fluoride) (PVDF) [7], polyethersulfone (PES) [8], polypropylene microfiltration membrane (PPMM) [9], polysulfone (PSF) [10], and filter paper [11] membranes, have been used for greatly improved oil–water separation [12,13]. However, traditional filter membranes were readily blocked by impurities and bacteria because of their disordered inside channels, and thus cannot be reused over long periods of time. Additionally, straight channels in thin membrane always show high permeability. Thus, the commercial polycarbonate track-etched (PCTE) filter with unique structure served as a model microfiltration membrane in our present research. Then, hydrogen-bonding-based (PUA–SNPs/BPEI)_n LbL multilayers assembled by hydrophilic BPEI and SNPs in the presence of UV-curable PUA were coated onto straight PCTE channels for unique non-vacuum oil–water separation.

In terms of working conditions in seawater, fouling of filter membranes is also a long-standing problem, leading to a short service life in recycling [14–16]. Not limited to the field of oil–water separation, the development of an environmentally friendly fouling-resistant coating to reduce powering penalties is also of

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major interest in the marine industry [17]. It is well known that biofouling activities, such as cell adhesion [18], protein adsorption [19], and other biofilm formation [20], are highly associated with the wettability and chemical nature of the substrate surface [17,21]. Therefore, superhydrophilic coatings of (PUA–SNPs/BPEI)₃₀ with near-zero contact angles were prepared and tested under *Staphylococcus aureus* and *Pseudomonas aeruginosa* contamination.

The layer-by-layer (LbL) technique, which is an optional multilayer build-up strategy, can assemble multilayers with specific functionalities using a wide range of functional materials, such as DNA, proteins, graphene, and nanoparticles [22–24]. Researchers have been attracted to the creation of superhydrophilic LbL thin films for a variety of applications. Specifically, different forms of superhydrophilic coatings based on SiO₂/TiO₂ Bragg stacks [25], all-nanoparticle assemblies [26], silica hollow spheres [27] and raspberry- or strawberry-like composites [28] have been extensively investigated in diverse fields. Even though superhydrophilic coatings that are mainly driven by electrostatic interactions or hydrogen bonding could be easily fabricated, the low stability owing to the non-covalent nature of the thin films has to be taken fully into account [29–32]. In fact, all superwettable coatings should show robust performance in aqueous environments, particularly for self-cleaning, anti-fouling, anti-fogging, and oil–water separation [33–35]. Therefore, we recently focused on making a unique LbL multilayer film with elevated acid, thermal, and mechanical stability to better deal with different environments. We introduced UV-curable poly(urethane acrylate) (PUA) into multilayers via hydrogen-bonding interactions with branched poly(ethylenimine) (BPEI) and silica nanoparticles (SNPs). Once the as-prepared LbL film is exposed to UV radiation, covalent bonds can be formed to enhance the stability to some extent.

Therefore, UV-curable and durable superhydrophilic (PUA–SNPs/BPEI)_n coatings with anti-biofouling property was focused on and applied to commercial PCTE membrane for oil–water separation, which has not been previously reported. Herein, the high efficiency of the as-prepared modified PCTE membranes for regular oil–water separation was also demonstrated. In the present work, our unique coatings based on layer-by-layer assembly can serve as a beneficial platform for functionalization of other membranes.

2. Materials and methods

2.1. Materials

Polyurethane acrylate (PUA-301) was purchased from Minuta Technology, Korea. Polycarbonate track-etched membrane (PCTE, Nuclepore, 47 mm diameter, Whatman) branched poly(ethylenimine) (BPEI, average Mw ~25,000, Aldrich), tetraethoxysilane (TEOS, 99%, Aldrich), and ammonium hydroxide (28%, Sigma-Aldrich) are available commercially. All other reagents were of analytical grade and used without further purification.

2.2. Synthesis of SiO₂–OH nanoparticles

SNPs with hydroxyl groups on the outside surface were synthesized by the modified Stober method, as reported previously [36,37]. Briefly, to a well-dispersed mixture of 4 mL ammonium hydroxide and 100 mL ethanol, 4 mL TEOS was added quickly to trigger SNPs synthesis. All processes were carried out at room temperature and using 40 kHz sonication. The reaction was kept for 2 h and then aged at least overnight. As a result, the as-prepared SNPs dispersion was uniform without aggregation.

2.3. Fabrication of crosslinked (PUA–SNPs/BPEI)_n LbL films

LbL multilayer films were fabricated on silicon wafers and PCTE membranes by the normal hand-dipping method at room temperature. First, a mixture of as-prepared SNPs and 2 mg/mL PUA (1:1 v/v, PUA–SNPs) in ethanol was obtained, and substrates were pre-treated for 2 min with oxygen plasma to create modified surfaces for hydrogen-bonding interactions. Then, the substrates were immersed into the dispersed PUA–SNPs solution for 10 min. The substrates were rinsed with ethanol for 3 times to remove extra polyelectrolyte molecules, which is 2 min, 1 min, and 1 min, respectively. And there are no other procedures during rinsing step. Next, the substrates were dipped into 1 mg/mL solution of BPEI in ethanol for 10 min. Subsequently, an identical ethanol rinsing process was immediately conducted. Thus, Si/(PUA–SNPs/BPEI)₁ and PCTE/(PUA–SNPs/BPEI)₁, corresponding to 1 bilayer deposition on the substrates, were fabricated. The layer-by-layer assembly process was continued until the desired number of bilayers on the substrate was acquired, with multilayers denoted as (PUA–SNPs/BPEI)_n ($n=0, 4, 8, 12, 16, 20, \text{ and } 30$). To crosslink the PUA prepolymer in the LbL-assembled films, a UV-curing process of at least 3 h was used since oxygen molecules in air can serve as a radical scavenger [38]. After UV radiation, the cured (PUA–SNPs/BPEI)_n multilayer films were obtained and used for the following tests.

2.4. Characterization of crosslinked (PUA–SNPs/BPEI)_n LbL films

The morphologies of the cured Si/(PUA–SNPs/BPEI)_n ($n=10, 20, \text{ and } 30$) multilayers were examined via field emission scanning electron microscopy (FE-SEM). The film thickness growth was monitored using a profilometer (Dektak 150, Veeco) at three different positions on the film surface. The UV–vis absorption spectra were measured on a spectrophotometer to examine the assembly growth of the multilayer film after the deposition of every four bilayers. Furthermore, the morphologies of the cured (PUA–SNPs/BPEI)_n ($n=20 \text{ and } 30$) coatings were verified using atomic force microscopy (AFM, Park Systems X-10) with a scan area of 2 μm × 2 μm in typical tapping-mode. Fourier transform infrared (FTIR) spectra were investigated to characterize the as-synthesized pristine PUA and (PUA–SNPs/BPEI)₃₀ films. UV/vis/near-infrared reflectance (UV/vis/NIR) spectroscopy was employed to calculate the separation efficiency by measuring the residual oil content.

2.5. Stability tests on cured LbL films

The acidic, thermal, and mechanical stability of the films were respectively tested using a series of treatments, such as pH 2 solution (adjusted by HCl) corrosion, 200 °C heating, and 500 rpm washing. More specifically, a resultant cured Si/(PUA–SNPs/BPEI)₃₀ LbL film with 1 × 2 cm area was directly dipped into 10 mL of pH 2 deionized water at room temperature to determine the acidic stability. In a similar way, cured Si/(PUA–SNPs/BPEI)₃₀ LbL films were put into oven for a 200 °C heating process to test the thermal stability. The mechanical stability was checked by washing the Si/(PUA–SNPs/BPEI)₃₀ LbL film in deionized water under 500 rpm stirring. Designated periods of handling time ranging from 0 to 6 h were all applied to verify the change in thickness, roughness, and hydrophilicity of the treated films compared with that of the pristine LbL films.

2.6. Anti-biofouling examination of LbL films

The anti-biofouling properties of the cured Si/(PUA–SNPs/BPEI)₃₀ films were tested using gram-positive *S. aureus* (KTCT1621, ATCC25923) and gram-negative *P. aeruginosa*

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