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Preparation and characterization of underwater superoleophobic chitosan/poly(vinyl alcohol) coatings for self-cleaning and oil/water separation

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ABSTRACT

In this paper, chitosan (CS)/poly(vinyl alcohol) (PVA) coatings cross-linked with glutaraldehyde (GA) were prepared. Effects of the coating composition and NaOH solution treatment on surface morphology and topography were investigated by scanning electron microscope and atomic force microscope. It was found that the process of immersing the CS/PVA coatings into NaOH solution was crucial to enhance rough structure on the coating surface. The rough surface structure and the hydrophilic groups of CS and PVA made the CS/PVA coatings possess underwater superoleophobicity and low adhesion to oil. Oil contact angle of the prepared CS/PVA coatings was up to 161° and slide angle was only 3°. Moreover, the CS/PVA coatings showed stable superoleophobicity in high salt, strong acidic, and alkaline environments as well as underwater self-cleaning property and excellent transparency. The CS/PVA coatings could be used for gravity driven oil/water separation with high efficiency.

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1. Introduction

Underwater superoleophobic surfaces have been attracted considerable attention in recent years owing to their important practical applications [1], such as oil/water separation [2–6], anti-fouling or self-cleaning [2,7], fluidic devices [8], bio-adhesion control [9], liquid manipulation [10], etc. Inspired by the special wettability of the fish scales, a number of functional materials with underwater superoleophobicity have been fabricated using different approaches [6,11,12]. Generally, a combination of hierarchical micro/nano structured surfaces with high surface energy was considered as one of the most efficient strategies to achieve subaqueous superoleophobic surfaces [13,14]. As illustrated in Scheme 1, in an oil/water/solid system, water can be trapped in the hierarchically rough structures, leading to a water–solid interface. The trapped water serves as a support to prevent the penetration of oil droplets, yielding superoleophobic and low-adhesive surfaces in water [12].

There are several polymer materials which have been successfully used to fabricate underwater superoleophobic coatings or surfaces. The poly(ethyleneimine)/poly(vinyl-4,4-dimethylazlactone) coatings mimicking the scales of fish and other natural anti-oil-fouling surfaces exhibited underwater superoleophobicity [14]. The polyvinylidene fluoride membrane fabricated by an interfacial polymerization showed superior oil/water emulsion separation performance [15]. The filter paper coated with poly(vinyl alcohol) hydrogel (cross-linked using glutaraldehyde) could separate oil-water mixtures with high efficiency (>99%) [16]. The poly(sulfobetaine)/polydopamine coated meshes indicated underwater superoleophobic behavior and ultra-low adhesive properties towards oil [17]. The oil-repellent coatings fabricated by calcium alginate were effectively used in solutions of high salinity [18].

Chitosan (CS), one of natural biodegradable, nontoxic, and biocompatible polysaccharides, is yielded from deacetylation of chitin and has potential use in multiple fields, such as in biotechnological, functional membranes/fibers, food/nutrition, and agricultural/environmental applications [19–23]. CS was used to fabricate superoleophobic surface for oil/water separation recently [22,24,25]. The hydrophilicity of CS, partly due to the presence of the amine groups, is very important for preparing underwater superoleophobic surfaces. CS is sensitive to acidic solution, swells in an aqueous solution and has poor mechanical performance [26,27]. Poly(vinyl alcohol) (PVA) is one of the commonly used polymers to blend with CS for improving the stability, biocompatibility, and mechanical properties of CS [28–30]. Glutaraldehyde (GA) is a widely used agent for cross-linking CS and PVA [24,31]. The cross-linking between CS and GA is via covalent bond formation, preferably through the amine groups (CS) reacting with the

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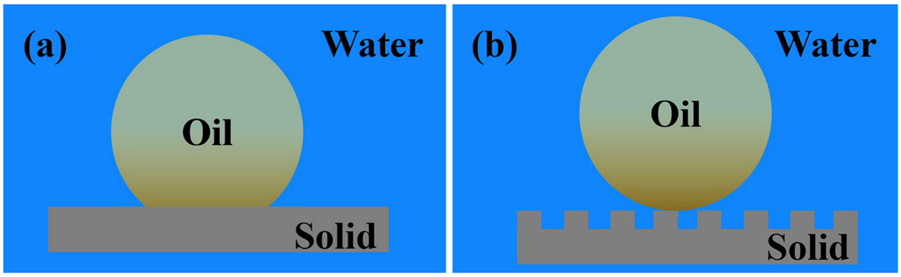

Scheme 1. Cassie-Baxter state at the water/oil/solid interface.

bi-functional aldehyde groups (GA) [28]. The reaction between PVA and GA occurs between the hydroxyl groups of PVA and the aldehyde groups of GA to form an acetal bridge [32]. In addition, NaOH solution treatment could prevent CS films from excessive swelling in an aqueous solution [27].

Generally speaking, hierarchical rough structure and hydrophilic chemical compositions are the key factors to design underwater superoleophobic surfaces [33]. In this paper, a facile and low cost method to prepare GA cross-linked CS/PVA coatings with underwater superoleophobicity was presented. The key point of the method is a NaOH solution solidification treatment combining with controlling the cross-linking and the coating composition, which gives the coating a suitable roughness and surface energy. Scanning electron microscope (SEM) and atomic force microscope (AFM) were used to observe morphology and topography of the CS/PVA coatings. Fourier transform infrared (FTIR) was used to investigate interactions among CS, PVA and GA. Water contact angle in air and oil contact angle underwater of the CS/PVA coatings with different compositions were examined to reveal the effect of surface roughness and composition on surface wettability. Swelling degree and transmittance of the CS/PVA coatings were also investigated. Finally, performances of self-cleaning and oil–water separation of the CS/PVA coatings were evaluated.

2. Materials and method

2.1. Materials

CS with 88.0% degree of deacetylation and viscosity of 51 mPa s, PVA with average polymerization degree of 1750, acetic acid and 1,2-dichloroethane were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). GA was obtained from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). NaOH was purchased from Beijing Chemical Works (Beijing, China). All reagents were used as received.

2.2. Preparation of coatings

CS solution was prepared by dissolving 2.0 g CS in 98.0 g acetic acid aqueous solution (1%, v/v) at 50 °C with stirring of 200 rpm for 30 min. PVA solution was prepared by dissolving 2.0 g PVA in 98.0 g distilled water by stirring at 95 °C for 2 h. The CS solution and PVA solution were mixed together with stirring for 1 h to form homogeneous CS/PVA solutions with mass ratios of 100/0, 75/25, 50/50, 25/75 and 0/100. In order to cross-link the CS/PVA coatings, certain amount of 1 wt % GA aqueous solution was added to the CS/PVA solutions. The amount of added GA was calculated based on the mole ratio of GA to the $-NH_2$ in CS (ranged from 0% to 8%), which was corresponding to about 0–80 μL GA aqueous solution (1 wt %) in one gram of CS/PVA solution. After that, 0.5 mL CS/PVA solution was dripped on a cover glass which was placed on a spin coater (KW-4A, Institute of Microelectronics, Chinese Academy of Science, China), the cover glass was spun at 500 r/min for 9 s first and then at 1000 r/min for 30 s. This coating procedure was repeated 3 times to achieve adequate thickness of the coatings. Afterwards, the cover glass coated with the CS/PVA coatings was immersed in NaOH aqueous solution (4 wt %) for 1 min and washed with deionized water. The obtained coatings were kept in a chamber at room temperature (21 ± 2 °C) and 37% relative humidity for 24 h before measurements.

2.3. Characterizations

Measurements of static contact angle and dynamic sliding angle were conducted by using a contact angle meter equipped with a tilting table (JC2000APowereach, China). The tilting angle of the table was adjustable from 0° to 80°. The measurements of water contact angles were carried out with sessile drop method at ambient temperature using 3 μL droplets. For the underwater measurements, oil (1,2-dichloroethane) droplets were carefully dropped onto the coatings which were immersed in water. After the static contact angle was measured, the table was tilted and the subsequent measurement of sliding angle at the same position was performed. All contact angles and dynamic sliding angles were measured at five different positions and averaged. Zeiss EVO 18 SEM (Zeiss, MERLIN Compact, Germany) was used to observe morphology of the coatings. The specimens were sputter-coated with gold before the observation. Topographies of the coating surfaces were investigated using AFM (Dimension Icon Microscope, Bruker, Germany) equipped with a Nanoscope V controller images. The Root-Mean-Square roughness, Rq, was obtained by the standard deviation of the height values within the analyzed region as described by Gao et al. [34]. FTIR spectra of the CA/PVA coatings were recorded from 4000 to 400 cm^{-1} at resolution of 4 cm^{-1} and 32 scans using Nexus 670 FTIR Spectrometer (Walthman, USA). Transmittance spectra of the coatings were obtained using a miniature fiber optic spectrometer (Ocean Optics USB4000, Ocean Optics, USA). The spot size of the incident beam was 5 mm in diameter and the spectrometer was calibrated with a standard white board STD-WS that was certified by the National Institute of Metrology of China and a standard glass under T model.

3. Results and discussions

3.1. Interactions in the CS/PVA coatings

During the preparation of the coating solutions, CS, PVA and GA were mixed together. As described in Fig. 1, interactions among these components may occur. As a result of cross-linking reaction between the amino groups of CS and the aldehyde groups of GA, C=N could form (Fig. 1a). In addition, acetal group could form due to the reaction of GA with the hydroxyl groups of PVA as predicted in Fig. 1b. There are many hydroxyl groups in PVA, and CS also has abundant hydroxyl groups and amine groups. Strong hydrogen bonds between the hydroxyl or amino groups of CS and the

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