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Rapid and reversible switching between superoleophobicity and superoleophilicity in response to counterion exchange

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ABSTRACT

We use a simple layer-by-layer (LbL) assembly and counterion exchange technology to rapidly and reversibly manipulate the oleophobicity of the textured aluminum surfaces. Such textured surfaces can be produced by the HCl etching and boiling water treatment of the flat aluminum plates. The LbL deposition of polyelectrolytes is performed on these surfaces to generate the polyelectrolyte multilayer films. The films are able to coordinate with perfluorooctanoate anions, leading to the surfaces with different oleophobicity. The resulting surface produced by 1.5 cycles of polyelectrolyte deposition exhibits superoleophobicity by displaying contact angles greater than 150° with low surface tension liquids. Counterion exchange in this polyelectrolyte multilayer emerged easily to control the surface composition, which leads to tunable wettability that can be rapidly and reversibly switched between superoleophobicity and superoleophilicity.

1. Introduction

The functional surfaces with responsive wettability have recently generated extensive interest because of their potential applications in various fields [1–5]. Various research groups have developed surfaces that can switch their wettability between superhydrophobicity and superhydrophilicity in response to changes in temperature [6,7], solvent [8–10], light irradiation [11–13], and mechanical strain [14,15]. These external stimuli can effectively trigger chemical or topographic changes at the surface, leading to control the contact angle (θ) of water droplets from $\theta > 150°$ to $\theta \sim 0°$. However, for oily liquids having lower surface tensions than that of water, the accessible range of contact angle values via changes in surrounding environment is rather limited. This largely comes from the difficulty in producing superoleophobic surfaces ($\theta > 150°$ with low surface tension liquids [16]) by using general stimuli-responsive materials, which always do not have the high concentration of fluorinated carbons to provide adequately low surface energy [17–19]. Until recently, switchable wettability for low surface tension liquids using mechanical strain or thermal annealing as stimuli was realized on fabrics [20,21], while the limitation of substrates and approaches makes it difficult to extensively apply the property of switchable oleophobicity. Therefore, it would be desirable to explore a simple route using the textured surfaces as substrates for the construction of stimuli-responsive surfaces with switchable oleophobicity.

Recently, the exchange of counterions of charged organic films was found to be a novel and valuable strategy to achieve reversible wettability conversion [22–25]. Upon direct exchange of the anions coordinated to the quaternary ammonium (QA^+) groups, surface wettability can be precisely determined depending on the property of the anion. Switchable wettability between superhydrophobicity and superhydrophilicity via counterion exchange has been achieved on structured gold surfaces [26,27]. In our recent work, we used counterion exchange to simultaneously tune hydrophobicity and oleophobicity of cotton fabrics [28]. However, switchable superoleophobicity has not previously been realized. In this study, we fabricate a textured aluminum surface with wettability that can be rapidly switched between superoleophobicity and superoleophilicity by counterion exchange. Such textured surfaces were produced by the HCl etching and boiling water treatment of the flat aluminum plates. The layer-by-layer (LbL) assembly technique was used to deposit polyelectrolytes and immobilize charges onto the rough surfaces. By the alternate adsorption of oppositely charged polyelectrolytes, the polyelectrolyte multilayer was assembled on the textured surfaces. Counterion exchange in the polyelectrolyte multilayer emerged rapidly to control the surface composition, which leads to a fast response of wettability switching for low surface tension liquids, such as hexadecane (surface tension $\gamma_{lv} = 27.5$ mN/m).

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2. Materials and methods

2.1. Materials

Poly(diallydimethylammonium chloride) (PDDA, Mw = 200,000–350,000), poly(sodium 4-styrene sulfonate) (PSS, Mw = 70,000), and perfluorooctanoic acid ($CF_3(CF_2)_6COOH$) were all purchased from Sigma–Aldrich. Sodium chloride (NaCl), sodium hydroxide (NaOH), and sodium dodecyl sulfate (DYS) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. Sodium perfluorooctanoate (PFO) (0.10 M) was prepared by the reaction of perfluorooctanoic acid with NaOH in water.

2.2. Preparation of textured aluminum

An aluminum plate ($20 \times 20 \times 0.25$ mm^3, 99.5%) was cleaned ultrasonically with acetone and ethanol to get rid of grease. The cleaned aluminum plate was etched in a 2.5 M HCl solution for 8 min at room temperature. After being rinsed with deionized water, the sample was immersed in boiling deionized water for 20 min and subsequently dried with a nitrogen stream.

2.3. LbL deposition and counterion exchange

The polyelectrolyte deposition was performed following a literature procedure [27]. The textured aluminum was immersed in PDDA (1.0 mg/mL, with 1.0 M NaCl present) aqueous solutions for 30 min to obtain a positively charged surface. Then, the PDDA-modified substrate was immersed in PSS (1.0 mg/mL, with 1.0 M NaCl present) aqueous solutions for 30 min, followed by rinsing with water. This cycle of PDDA treatment followed by PSS treatment was repeated to obtain the multilayer film of $(PDDA/PSS)_n$, where n represents the number of deposition cycles. Counterion exchange was carried out by immersing the polyelectrolyte-deposited substrates in an aqueous solution (0.10 M) of the required anion for 1 min, followed by rinsing with deionized water and drying with a nitrogen stream.

2.4. Characterization

Contact angle measurements were performed using a Krüss DSA 100 (Krüss Company, Ltd., Germany) apparatus at ambient temperature. The volumes of various liquids in all measurements were approximately 5 μL. Scanning electron microscopy measurements were carried out using a JSM-6701F field-emission scanning electron microscopy (FESEM, JEOL, Japan). X-ray photoelectron spectroscopy (XPS) analysis of the sample was performed on a PHI-5702 electron spectrometer using an Al Kα line excitation source with the reference of C 1s at 285.0 eV.

3. Results and discussion

To simply construct needed rough structures, a flat aluminum plate was etched in HCl solution for 8 min, subsequently treated with the boiling water for 20 min. Surface morphologies of the flat and textured aluminum surfaces characterized with FESEM are shown in Fig. 1. The flat aluminum plate shows the smooth surface (Fig. 1a). After the etching in HCl solution, the aluminum surface can be textured to form the needed microstructures with large numbers of protrusions and pores (Fig. 1b). Detailed FESEM analysis of surface morphology reveals that these microstructures were covered with a number of nanoflakes with the thickness of 20–40 nm (Fig. 1c and d), which is attributed to the boiling water treatment [29]. During this treatment, the initial native oxide layer on the aluminum surface reacts with water to form crystalline boehmite that dissolves in the boiling water [30]. In addition to

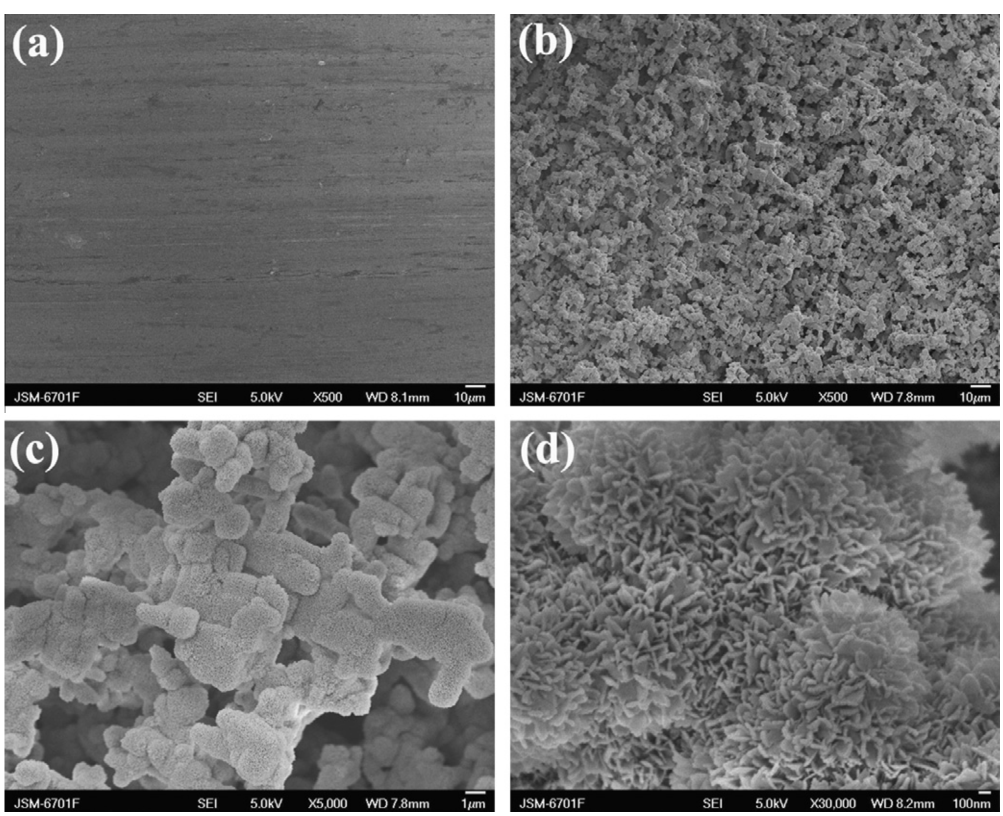

Fig. 1. FESEM images of the flat aluminum surface (a) and the textured aluminum surface (b). (c and d) Magnified images of (b).