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Full Length Article

Salt- and thermo-responsive polyzwitterionic brush prepared via surface-initiated photoiniferter-mediated polymerization

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ABSTRACT

Zwitterionic polymer brushes with strong anti-polyeletrolyte effect have shown great potential in applications of tunable friction, protein absorption/desorption, and "killing and release" antibacterial surfaces. However, such polymer brushes are presently prepared by surface-initiated atom transfer polymerization (SI-ATRP) which is a sophisticated and time-consuming process. In this paper, a simple method, i.e. surface-initiated photoiniferter-mediated polymerization (SI-PIMP) was used to prepare poly (3-(dimethyl (4-vinylbenzyl) ammonio) propyl sulfonate) (polyDVBAPS) brush on silicon wafer. It was shown that the reaction solution had a significant effect on the growth rate and surface roughness of the resulting brushes. In suitable solution (e.g. 0.53 M NaCl solution) brushes with controllable thickness and smooth surface could be obtained. Contact angle and surface friction measurement indicated that the brush prepared by SI-PIMP showed identical salt-responsive properties compared to the brushes from SI-ATRP. In addition, the thermo-responsive properties of polyDVBAPS brush was also investigated, which was further used for tuning surface friction of the brush. Due to the thermo-responsive properties, polyDVBAPS brush showed super lubrication ($u \sim 10^{-3}$) in water and NaCl solutions with low concentrations (0.1 M and 0.53 M) when the temperature was increased to 70 °C, 65 °C and 55 °C respectively. Although ultralow friction could be achieved under the conditions of different temperature and salt concentration, the stability against long-term friction highly depended on the environmental condition. At 40 °C and in 1.0 M NaCl solution, ultralow friction was well retained up to 1500 s, while under other conditions (saturated NaCl solution of 25 °C and 0.53 M NaCl solution of 55 °C), aqueous lubrication was rapidly deteriorated. This work not only demonstrated the practicability of the SI-PIMP for the preparation of polyDVBAPS brush, but also realized the tunable surface friction of such polyzwitterionic brush under different environmental conditions, extending its applications in both academic and industrial communities.

1. Introduction

Zwitterionic polymers are one kind of the most important functional coatings to resist biofouling and have shown great potential in many biomedical and engineering applications due to their intrinsically high surface hydration [1–3]. Apart from high surface hydration, these polymers also show another unique property, i.e. "anti-polyelectrolyte effect" [4,5], which means that the polymer chains adapt collapsed structure in water while stretch in salt solution. More importantly, such salt-responsive behavior strongly depends on both salt concentration and ion type, namely ion specificity [6–9]. These unique characteristics open up many new applications for zwitterionic polymers, such as protein absorption/desorption control [10,11], responsive separation membranes [12,13], and switchable friction/lubrication surface [14,15].

PolyCBMA and polySBMA are typical and most commonly used zwitterionic polymers. Due to the strong water association abilities, thin films of these polymers as brushes grafted on different substrates have shown excellent antifouling capability and biocompatibility by largely reducing nonspecific adsorption of proteins, cells, and/or bacteria [16–20]. However, their anti-polyelectrolyte effect is slight. In other words, the changes in surface properties induced by environmental switching from water to salt solution are small. Recently, we developed some new polyzwitterionic-grafted surfaces which exhibited pronounced change in many properties, such as wettability, antifouling, and surface friction. These surfaces were further developed as smart surfaces with tunable friction, protein/bacteria absorption and desorption, and bacteria killing-release functions [6,21,22]. In these studies, surface initiated atom transfer radical polymerization

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(SI-ATRP) was used to get densely packed brushes. As we all know, ATRP process needs copper salt as catalyst and special handling procedure under inert atmosphere. And more important, when ATRP was used to fabricate the above-mentioned polyzwitterionic brushes with strong anti-polyeletrolyte effect, a longer reaction time was needed to obtain suitable film thickness [23]. Therefore, developing an efficient method for fabricating such polyzwitterionic brushes are highly desirable.

Among the various surface-initiated "grafting from" methods, photoiniferter-mediated polymerization (SI-PIMP), first proposed by Tovar and coworkers, possesses certain advantages against atom transfer radical polymerization or reversible addition fragmentation transfer (RAFT) [24–26]. First, it performed little requirement to temperature and could take place in the room temperature in most instances. Second, as UV-light is used to trigger the reaction, therefore, it could circumvent the toxic and hardly-removed metal catalyst and alleviate the problem of the surface biocompatibility. Noticeably, it has been proved that the neutral, anionic, cationic and zwitterionic monomersare all possible with the SI-PIMP for homo-polymer and block-polymer fabrication [23,27–30].

In this study, we demonstrated the practicability of using SI-PIMP to fabricate polyzwitterionic brushes with strong anti-polyelectrolyte effect. Growth rate and surface morphology of the brush under different conditions, in particular in different reaction solutions were investigated. Under optimal condition, densely packed polyDVBAPS with controllable thickness and smooth surface could be prepared. Both contact angle and aqueous surface friction measurements indicated that polyDVBAPS brush prepared by SI-PIMP exhibited comparable salt-responsive anti-polyelectrolyte effect with that from SI-ATRP. In addition, thermo-responsive behavior of polyDVBAPS brush was investigated by testing the surface friction in water and NaCl solutions at different temperatures. Finally, long-term stable surface with ultralow friction was realized by optimizing the synergistic effect of thermo and salt solution.

2. Materials and methods

2.1. Materials

Sodium N,N-diethyldithiocarbamate and [p-(Chloromethyl)phenyl]trimethoxysilane were purchased from J&K (Beijing). 4-Vinlybenzyl chloride (90%), dimethylamine solution (40 wt.% in H_2O), 1,3-propanesultone (98%) and copper(I) bromide (CuBr) (98%), were purchased from Sigma-Aldrich(Shanghai). The chloroform and acetonitrile were obtained from Linfeng Chemical Reagent Co., Ltd. (Shang hai, China). Water used in these experiments was purified by a Millipore water purification system with a maximum resistivity of 18.0 MΩ cm. All other reagents and solvents were commercially obtained at extra-pure grade and were used as received without any purification. The DVBAPS monomer was synthesized and purified using the previously published method [31].

2.2. Synthesis of (4-trimethoxysilylphenyl) methyl N, N-diethylcarbamodithioate(SBDC)

The photoinitiator (4-trimethoxysilylphenyl) methyl N, N-diethylcarbamodithioate (SBDC) was synthesized and purified using the previously published method [32]. [p-(Chloromethyl) phenyl] trimethoxysilane (0.74 g, 3.0 mmol) and Sodium diethyldithiocarbamate (STC) (0.51 g, 3.0 mmol) were dissolved in 5.0 mL anhydrous THF, respectively. After 30 min agitation, the STC solution was slowly injected into [p-(Chloromethyl) phenyl] trimethoxysilane solution with N_2 flow, the mixed solution was stirred for 3 h at room temperature. After the removal of the white precipitate using a spherical filter, the yellow viscous liquid, which named SBDC was obtained.

2.3. Fabrication of polyDVBAPS brush via SI-PIMP

Silicon wafers (20 mm * 15 mm) were ultrasonically cleaned in ethanol and deionized water, then placed into a fresh piranha solution (H_2SO_4: H_2O_2 = 3:1) at 120 °C for ~0.5 h. After being washed with deionized water and dried with N_2 flow, the substrates were subsequently treated with plasma (CORONA Lab. CTP-2000, Nanjing, China) for 1.5 min. The cleaned wafers were placed into dehydrate chloroform solution containing the photoinitiator SBDC for 12 h at room temperature to obtained the initiator-grafted surfaces.

DVBAPS monomer (0.35 g, 1.96 mol) was dissolved in 2.5 mL NaBr (0.05, 0.53, 1, 6.1 mol/L) solution, the mixture and the initiator immobilized silicon wafers were then put into the quartz tube to deoxygenize by N_2 flow for 30 min. The quartz tube was then put into photo-reactor system for the SI-PIMP reaction. After different controlled time, polyDVBAPS brushes were obtained.

2.4. Thickness by ellipsometry

The thickness of polymer brushes were measured by Ellipsometric measurements performed on a an α-SE ellipsometer (J.A. Woollam Co., Lincoln, NE) with a He-Ne laser (λ) 632.8 nm) and a fixed angle of incidence of 70°.

2.5. Surface composition by X-ray photoelectron spectroscopy (XPS)

The surface composition of modified silicon wafers was characterized by X-ray photoelectron spectroscopy (XPS) (Kratos Analytical). The instrument is equipped with a monochromatized aluminum X-ray source powered at 15 kV and 3 mA that delivers an X-ray beam of 300 × 700 μm^2. The takeoff angle was 45° with respect to the surface normal, making the X-ray-to-electron angle be 90°.

2.6. Atomic force microscopy (AFM) imaging

AFM (Bruker Daltonics Inc., USA) in the tapping mode was used to investigate the surface morphology of polyDVBAPS brushes. All images were acquired at a typical scan rate of 0.6 Hz with a Scan Range of 4.0 μm. The root-mean-square (RMS) that indicates the roughness of the surface was determined by AFM analysis.

2.7. Contact angle measurement

Drop shape analysis (Eastern-Dataphy Instruments Co., Ltd., Beijing) was applied to explore the contact angle (CA) of the brushes by sessile dropping method. A 4 μL droplet of water or 1 M NaCl solution was dropped on the surface, and a built-in software was used to calculate the contact angle. The data presented were the average value of five independent measurements on different positions.

2.8. Macroscopic friction test

The surface friction properties of polyDVBAPS brush were measured in different solutions and at a series of pre-specified temperature on a Universal Micro-Tribometer (UMT-2, CETR) by sliding an elastomeric poly-(dimethylsiloxane) (PDMS) hemisphere (~6.0 mm in diameter) against polyDVBAPS brushes. The sliding velocity and distance were set at 2 × 10^{-3} m/s and 10 mm, respectively. For