



Dual-responsive polymer brushes as an electrochemical logic gate



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ABSTRACT

Stimuli-responsive polymer brushes modified surfaces and binary polymer surfaces can be created on an initiator terminated substrate *via* surface initiated atom-transfer radical polymerization (SI-ATRP), in which the growth kinetics can be modulated by Cu(II) ratio. As stimuli-responsive brushes, many environmental triggers can drive their conformation change such as pH and salt concentration. The external-stimuli modulated reversible conformational changes of polymer brushes can influence the charge transport behavior investigated by electrochemistry method, which have potential applications in *in situ* switching ion permeability and charge transport. The charge transport of binary polymer brush can be switched on or off by different ion flexibly which is an electrochemical logic switch.

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1. Introduction

Polymer brushes are covalently tethered on a substrate with ultrathin soft polymer layers, which is densely arranged polymer chains stretching away the substrate [1–6]. Polyelectrolyte (PE) brushes are a promising class of materials for the development of responsive surfaces, and the excluded volume interactions combined with the osmotic pressure of the counterions lead to swelling and collapse transitions under the influence of a variety of environmental triggers, such as pH, electrolyte, temperature, and electric fields [1–4]. The ionic strength of the solution, as well as the nature of the electrolyte in solution, strongly affects the degree of stretching in polyelectrolyte brushes [5–8], which has been exploited in the formation of surfaces with tuneable wettability, ion permeability, and film stiffness [7–11]. Generally, the equilibrium of association-dissociation of charged polyelectrolyte brushes and the charge distribution on polymer highly depends on solution pH, salt concentration, and temperature [11,12]. The ionic strength of the solution, as well as the nature of the electrolyte in solution, strongly affects the degree of stretching in polyelectrolyte brushes, which has made it useful for diverse applications, especially in smart surface, chromatographic separations, anti-biofouling materials and lubrication [13–20]. Stimuli-responsive polymer interfaces [21–23], which switch their physical and chemical properties in response to external stimuli [24–27], have great potential in many technologically important areas such as drug delivery, controlled permeation membrane, surface patterning,

temperature-induced switching and actuate microdevices constitution, separation [28–32]. As typical examples, poly (N-isopropylacrylamide) (PNIPAm) and poly(acrylic acid) (PAA), which are easily synthesized, as well as chemically and mechanically robust, attract extensive research interest for application in the engineering of smart surfaces because of their excellent responding ability to environmental changes.

Cationic and anionic polyelectrolytes are responsive anion and cation of the electrolytes, respectively. The electrochemical behavior of cationic polyelectrolyte in different electrolyte solution has been studied in the previous work. In this report, binary oppositely polyelectrolyte was synthesized by combination of microcontact printing and surface initiated ATRP. The binary polymer brush as electrochemical logic gate displays novel electrochemical responsive behavior switched on or off by different electrolyte solution with different anions and cations flexibly. We believe these polymer brush assembles, especially binary polymer brushes can be used to construct complex electrochemical interfaces in response to diverse environmental stimuli for smart surface with switchable gating applications.

2. Experimental

2.1. Materials

Copper (I) bromide (CuBr) (99.99%) was purified by reflux in acetic acid before usage. 2,2'-Bipyridyl (Bipy, 99%) was obtained from Aldrich. Phosphoric acid (99.99%), sodium hydroxide (99.99%), sodium hydrogen phosphate and sodium dihydrogen

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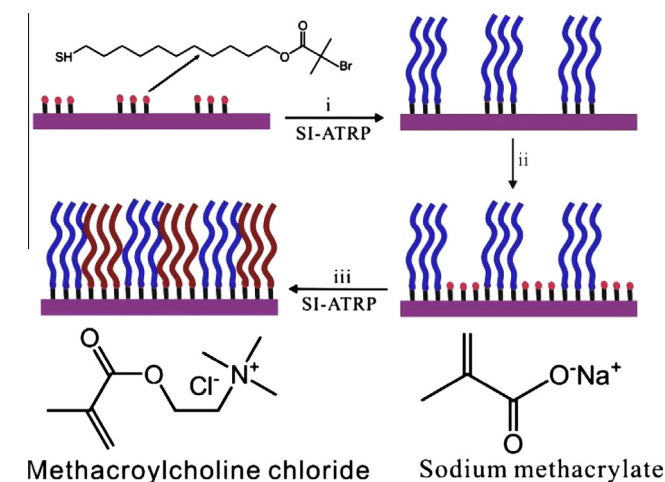
phosphate solution is for adjusting pH. Dimethylamino ethyl methacrylate (DMAEMA) was obtained from Aldrich and re-distilled in the presence of CuCl before use. Ultrapure water used in all the experiments was obtained from a NANO pure infinity system from Barnstead/Thermolyne Corporation. Other reagents were used as received. $\text{BrC}(\text{CH}_3)_2\text{-COO}(\text{CH}_2)_6\text{SH}$ and $\text{BrC}(\text{CH}_3)_2\text{-COO}(\text{CH}_2)_{11}\text{SH}$ were synthesized according our previous work [25].

2.2. Preparation of the polymer-modified electrodes

Gold substrates were prepared by evaporating 200 nm gold on silicon wafer with 2 nm chromium as the adhesive layer. Gold substrates were modified with thiol initiator ($\text{BrC}(\text{CH}_3)_2\text{-COO}(\text{CH}_2)_6\text{SH}$) (ethanol solution) for 12 h. Polymer brushes were prepared according to a recipe of [DMAEMA]: [CuBr]:[Bipy]: [CuBr₂] = 100:2:5:0.2 in a MeOH:H₂O (1:1) solution at room temperature. A typical polymerization: DMAEMA, 15.7 g; CuBr, 0.288 g; CuBr₂, 0.0448 g; Bipy, 0.78 g; solvent 30 mL. The solution was de-oxygenated with N₂ for 30 min and transferred to Schlenk tube. After polymerization, samples were thoroughly rinsed with distilled water. The temperature test is carried out in a thermostat with an increasing rate of 10 °C/h, and afterward the electrochemical test was performed. Binary polymer brushes were prepared according to previous report, which used (microcontact printing)μCP to get well-defined surface attached polymers.

2.3. Preparation of binary oppositely polyelectrolyte brushes

Patterned samples on gold coated silicon wafers were prepared by combination of microcontact printing of initiator $\text{BrC}(\text{CH}_3)_2\text{-COO}(\text{CH}_2)_{11}\text{SH}$ and surface initiated atom transfer radical polymerization (ATRP). ATRP was carried out as follows (Scheme 1): 9 g METAC was dissolved in 27 mL water and degassed by passing a continuous stream of dry N₂ through the solution while being stirred (15 min), then bipy (0.62 mg) and CuBr (0.288 g) were added. The mixture was then further stirred and degassed with a stream of dry N₂ (15 min). Initiator patterned gold substrates which is obtained by microcontact printing were sealed in Schlenk tubes, degassed (three times high-vacuum pump/N₂ refill cycles). Polymerization solution was injected into Schlenk tubes to allow to polymerize for 1 h. Afterward the patterned PMETAC brush was immersed in 10 mM solution of NaN₃ in anhydrous DMF under N₂ atmosphere for 24 h at room temperature for passivation the



Scheme 1. Depiction of constructing binary polymer brushes by combination of microcontact printing and surface initiated ATRP. (i) SIP from contact printed initiator to generate 1st brush; (ii) passivation and second assembling initiator; (iii) second ATRP resulting in 2nd brush, and the structures of two monomers.

activity of terminated Br atom. Then the patterned brush was immersed in initiator solution to self-assemble initiator on bare gold. For the second brush growth, the polymerization solution contained 20 mL of 3 mol/L MAA aqueous solution (60 mmol monomer), CuBr (0.144 g, 1 mmol), bipyridine (0.33 g, 2 mmol). Polymerization was carried out for 2 h at room temperature [33]. All the reaction solutions must be kept in an inert atmosphere, especially to ensure complete dissolution of all components in ATRP solution.

2.4. Electrochemical measurements

Impedance measurements were carried out on a CHI 660B Electrochemical workstation. EIS data were simulated using the software CHI 660B. A conventional three-electrode cell was used. All experiments were conducted at constant temperature. Polyelectrolyte brush modified Au is as a work electrode (0.196 cm²), and a platinum wire with a diameter of 0.80 mm is as a counter electrode, saturated calomel electrode (SCE) is as a reference electrode. Impedance spectra were measured using the attached frequency response analyzer. In impedance measurement, The frequency range of EIS was between 10,000 and 0.1 Hz using amplitude of 5 mV at an open circuit potential. Electrochemical measurement were performed in the presence of 1 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1) mixture as a redox probe in 0.1 M NaNO₃ solution for cyclic voltammetry (CV) at the scan rate of 50 mV s⁻¹.

2.5. Characterization

Ellipsometry measurements were performed on a DRE ELX-02C ellipsometer with a $\lambda = 632.8$ nm laser at an angle of incidence of 70° from the normal. Optical constants were measured prior to monolayer formation. A refractive index of 1.45 was used in the calculation of monolayer thickness and a refractive index value of 1.50 was used for brush. A minimum of five spots were measured on each sample. AFM measurements were performed using a Molecular Imaging (Phoenix, Arizona) PicoSPM, version 2.4 in MAC mode with a 1 Hz scan rate under variable applied loads. Sessile water droplet contact angle values were acquired at a DSA-100 optical contact angle meter (Kruss Co., Ltd., Germany) at ambient temperature (room temperature). 5 μL of deionized water was dropped on the samples using an automatically dispense controller, and the contact angles were determined automatically by using the Laplace–Young fitting algorithm.

3. Results and discussion

3.1. Cu(II) mediated polymerization kinetics

In a standard atom-transfer radical polymerization, Cu(I) complex is the catalyst to enable the macromolecular chain propagation owing to high alkyl radical concentration generated, which enables less control of the polymerization as well. As considering all aspects to realize ideal polymerization with improved controllability, adding deactivation rate can be easily observed. When adding 10% Cu(II) to exert the polymerization, a deferred brushes growth can be observed that only 100 nm thick brushes formed after 20 h. Further increasing Cu(II) ratio even slowed polymerization rate and thus a thin brushes of 30 nm. Therefore, polymer brushes growth can be well controlled by adjusting Cu(II) content or polymerization time. Cu(II)/Cu(I) ratio is a simple approach to adjust polymerization kinetics, where the presence of Cu(II) deactivators benefit to keeping polymerization living for even longer time and a slower polymerization rate. Fig. 1 displays the brush growth kinetics in different Cu(II) content, wherein the Cu(II) ratio

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