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Smart modification of the single conical nanochannel to fabricate dual-responsive ion gate by self-initiated photografting and photopolymerization



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ABSTRACT

A simple, rapid and general method of self-initiated photografting and photopolymerization (SIPGP) was first introduced to fabricate dual-responsive nanochannel with a solid-state conical nanopore for the first time. The high density of carboxyl and hydroxyl groups on the internal surface of the etched poly(ethylene terephthalate) (PET) nanochannel acted as photo-active sites to provide further growth and amplification of polymer brushes via SIPGP. Poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) was chosen as a prototypical polymer which can be grafted on the surface of the nanochannel with high efficiency. SIPGP provided a smart and simple strategy to graft polymer brush on the surface of the nanochannel without the need of a surface bonded initiator. Series of characterizations including current–voltage curves, scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) indicated the successful construction of the polymer. The functionalized nanochannel was finally used for the construction of smart gate with perfect responsibility, reversibility and stability towards CO₂ and temperature. This modification strategy combined with unique character of the polymer may hold a great potential in building various smart responsive systems.

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1. Introduction

Biological nanochannels embedded in cell membranes play an important role in physiological functions of life processes and other proper performance of cellular and biological processes, such as the exchange of basic cellular molecules, signal transduction, energy conversion [1–4]. These nanochannels can open and close in response to the diverse environmental stimuli [5–7]. Inspired by this favorable character, many researchers have attempted to explore various abiotic nanochannels to mimic the gating functions of the biological nanopores, such as the use of synthetic solid-state nanopore that modified DNA aptamer or other molecular compound with special response to construct biosensors [8–10]. For this purpose, a variety of functional groups need to be introduced into the synthetic nanochannels through coupling chemistry or electrostatic interaction, which can tune the transport properties according to ambient stimuli, such as pH [5,11], ions [12], temperature [11], light [13,14], gas [15,16], electric fields [17], etc.

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The structure of the polymeric micelles can shift quickly under the influence of the environmental stimuli and thus can be coupled with nanochannels as the popular stimuli-responsive functional materials for a variety of biological and biomedical applications [18–20]. And atom transfer radical polymerization (ATRP) has been used as a general technique to synthesize well-defined polymers or (co) polymer on various substrates in recent years [21,22]. For example, Zhao and co-workers [23] utilized ATRP approach to graft poly(N, N-diethylaminoethyl methacrylate) (PDEAEMA) onto a silicon surface, which can allow for reversible adsorption and release of a protein through conformational change triggered by CO₂. Li and co-workers [11] further introduced the ATRP strategy to the surface of the single glass conical nanochannel using PDMAEMA as stimuli-responsive functional materials. And a smart nanochannel ion gate with high conversion efficiency between on and off state was constructed based on the conformational change of the polymer brush tuned by CO₂ and temperature.

Although ATRP provides a versatile synthetic tool that enables the modification of new polymers, the process and condition for these reactions is complex [24,25]. Firstly, initiator is needed to induce ATRP reaction.[26,27] Secondly, since ATRP is a catalytic process, redox-active transition metal complex (Cu in Cu^I/L and

X-Cu^{II}/L) is involved in the reaction system [28,29]. In 1996, Rånby and co-workers [30] developed the bulk surface photografting polymerization process without the need of initiators pre-immobilized on the substrates. Subsequently, self-initiated photografting and photopolymerization (SIPGP) was widely used to fabricate polymer brushes with an effective control on their structural parameters in a simple and fast mode [31,32]. SIPGP can be realized on the surface of various substrates, such as silicon oxide, glassy carbon, polyethylene, poly(ethylene terephthalate) (PET), and polyvinylchloride [31,33,34]. And amounts of the hydroxyl or carboxyl functional groups were introduced based on the SIPGP, which can be acted as photo-active sites to graft polymer with one-step reaction at room temperature under UV-irradiation.

Herein, SIPGP was first introduced to modify the solid-state conical nanopore for fabricating dual-responsive nanochannel. After the wet etching of a single track in the PET membrane, the internal surface of the membrane possesses a high density of carboxyl and hydroxyl groups. According to the literatures reported by Jordan [35,36] and Chen [37,38], HO-groups of the carboxyl and hydroxyl groups can be acted as photo-active sites for further growth and amplification of polymer brushes via SIPGP. PDMAEMA with good biocompatibility was chosen as a prototypical polymer to graft on the surface of the nanochannel due to the good response to the temperature and CO₂ [39]. The smart nanodevice can be reversibly switched due to the conformational changes of the PDMAEMA brush tuned by temperature and CO₂.

2. Experimental section

2.1. Nanochannel fabrication and diameter calculation

According to the reported literatures [40–42] and our previous works [43–45], wet-etching method was used for the preparation of asymmetrical single nanochannel and cylindrical multi-nanochannel. More details including channel diameter calculation were described in the Supporting Information.

2.2. SIPGP on the surface of the nanochannel

The freshly etched nanochannel was immersed into 2 mL of 2-(dimethylamino)ethyl methacrylate (DMAEMA) in a beaker and ultrasound for 2 min. The mixture in the beaker was placed under a UV lamp (A 300 W xenon lamp, PLS-SXE300, Beijing Trusttech Co. Ltd., China) under stirring and irradiated for 3 h under dry nitrogen at room temperature. Here, the wavelength of the UV lamp used in this reaction ranged from 200 to 400 nm. The distance between the reaction mixture and the light source was 10 cm and the current was set at 20 A. After the SIPGP, the nanochannel was washed with ethanol and acetone in order to remove the ungrafted polymer. Finally, the nanochannel was dried in vacuum at 40 °C for subsequent use.

2.3. Current–voltage measurements

The ion transport characteristics of the single conical single nanopore before and after modification of PDMAEMA polymer were measured through a Keithley 6487 picoammeter/voltage source. The single conical nanopore embedded in polymer membrane was mounted between two halves of the conductivity cell, and 10 mM phosphate buffer solution (PBS: 100 mM KCl, pH = 7.0) was chosen as electrolyte. Sensitive and stable Ag/AgCl electrodes were used to apply a transmembrane potential and the scanning voltage varied from -1 V to +1 V with a period of 40 s. Each test was repeated three times to obtain the average current value at different voltages. The supporting solution which was filled in the

cells was bubbled with CO₂ and N₂ for 10 min, respectively. And the temperature was controlled using an intelligent heating plate.

2.4. Characterization of the nanochannel

Similar SIPGP process was used for the grafting PDMAEMA brush in the freshly etched multi-nano.channel membrane. X-ray photoelectron spectrum (XPS) data were obtained with an ESCA-Lab220i-XL electron spectrometer from VG Scientific using 300 W Al K α radiations. Contact angles (CA) were measured using a DSA10-Mk2 contact angle system (KRÜSS GmbH, Germany) at 25 °C. In each measurement, an about 2 μ L droplet of water was dispensed onto the surface of the PET membrane. The average CA value was obtained at five different positions of the same membrane. A Multi-mode 8 Atomic Force Microscope (Veeco) was used for atomic force microscopy (AFM) imaging and surface roughness analysis. The membrane samples were adhered to the metal plate with smooth surface and all the images were analyzed using Nanoscope Analysis 1.20.

3. Results and discussion

3.1. Design principle of the dual-responsive channel

The single conical nanopore used in this study was fabricated through asymmetric wet etching of the PET membrane and the large opening (base) of the conical nanopore was about 560 nm in diameter (Fig. 1) and the small opening (tip) was about 13 nm calculated according to well-established electrochemical measurement [8]. After etching, one carboxyl or hydroxyl group per nm² can form on the nanochannel surface (Scheme 1) [46,47]. Most of previous works have demonstrated that the generated -OH or -COOH group on the solid surface could be initiated as a photoactive site for the further growth of polymer brushes by SIPGP without a surface bonded initiator [32,35]. To realize the two functions towards temperature and CO₂ within one single nanopore, PDMAEMA polymer was chosen and grafted on the surface of the nanochannel using SIPGP with high efficiency. As seen from Scheme 1 B, CO₂ stimulation mainly affects the charging state of the nanochannel surface. Tertiary amine groups of PDMAEMA can be protonated by CO₂ bubbled into the water to form charged ammonium bicarbonate, which can be transferred to the uncharged state upon CO₂ removal [38,48]. In addition, PDMAEMA with the low critical solution temperature (LCST) of

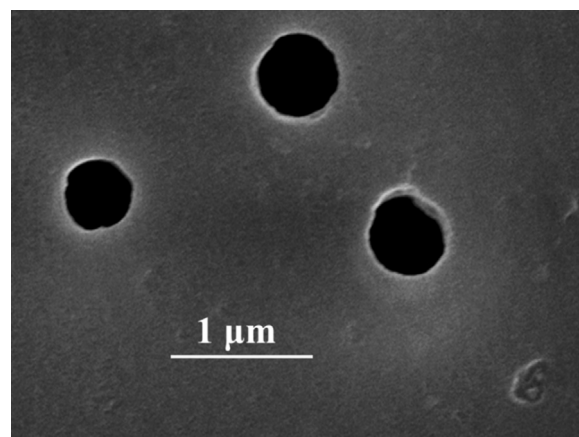


Fig. 1. SEM of the base side of the membrane multipore in PET polymer (1×10^6 tracks cm^{-2}) under the same etching conditions as that for single track-etched nanochannel. The diameter of the base side is about 560 nm, and the tip diameter of the single nanopore was calculated to be 13 nm.

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