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A pH-Gating Ionic Transport Nanodevice: Asymmetric Chemical Modification of Single Nanochannels

By *Xu Hou, Yujie Liu, Hua Dong, Fu Yang, Lin Li,** and *Lei Jiang**

Ion channels that regulate ion permeation through cell membranes are very important for the implementation of various significant physiological functions in life processes.[1] The components of these channels are asymmetrically distributed between membrane surfaces.[2] Inspired by these asymmetrical nanochannels – including both the various components of ion channels that are not uniform in distribution and the structural asymmetry – the generation of artificial nanochannels has strong implications for the simulation of the different ionic transport processes as well as the enhancement of the functionality of biological ion channels.[3] Recently, we and others have successfully developed simple and functional pH-controllable nanochannels.[4] Here, we further develop the concept of a smart nanochannel system, which is not subject to the solution environment restriction of the chemical modification,[5] by using a plasma asymmetric chemical modification approach. Compared to other systems,[4] this responsive nanochannel system has the advantage that it provides *simultaneous* control over the pH-tunable asymmetric[4a–4c] and pH gating[4d] ionic transport properties.

This highly effective method can be used in the near future to build smarter, biologically inspired nanochannel machines with more precisely controlled functions by designing more complicated functional molecules.

There has been rapid progress in developing chemical properties and chemical modification of the interior surface of the nanochannels with functional molecules, such as specific ions,[6] light,[7] pH,[4] and temperature.[8] In order to achieve different functionalities of artificial nanochannels, various methods have been invented, such as electroless deposition,[9] solution chemical modification,[4a] electrostatic self-assembly[10] and to only cover the whole inner surface of the nanochannels.

Plasma technology, which mainly includes plasma etching and plasma modification, offers an effective method for nanoscale surface engineering of materials. Plasma etching has often been used in template synthesis of nanomaterials.[11] Plasma modification can functionalize a specific local area precisely, whether via symmetric or asymmetric chemical modification. This advantage can provide the potential variety of nanoscale features and new properties for developing advanced nanomaterials. Even though multiple nanochannel membranes using plasma modification have been studied[12] for the control of the water permeability of polymeric membranes, we still need an optimal system, such as a single nanochannel system, for studying transport properties of different ionic or molecules in a confined space, without having to average the effects of multiple channels. Therefore, in this work, we developed a perfect pH gating ionic transport nanodevice using plasma asymmetric chemical modification, and this approach can be considered as a platform for developing more ways of the precise asymmetric chemical modification of the interior surface of nanochannels, which have strong implications for the simulation of different ionic transport processes as well as the enhancement of ion channel functionality.

As shown in Figure 1, we prepared a single nanochannel membrane with the well-developed ion track etching technology.[5,13] In this work the etched single nanochannel is symmetric and hour-glass shaped (see Supporting Information, Fig. S1). Diameter measurements of hour-glass shaped nanochannels were conducted with a commonly used electrochemical method.[13] The opening at the base was usually ∼250–300 nm wide and the narrow center (tip) was ∼10–30 nm wide. Only one side of the nanochannel was treated by plasma-induced grafting in the vapor phase of the distilled acrylic acid (AAc), which became a pH-responsive polymer,[14] poly acrylic acid (PAA), after plasma-induced graft polymerization. To explore the surface properties of the PET films before and after plasma treatment, the films have been studied by contact angle (CA) measurements. The CA of the PET film (Hostaphan RN12 Hoechst, 12 μm thick) surfaces after plasma treatment (Fig. 2b) was smaller than the one before treatment (Fig. 2a). The results of the CA measurements showed that the plasma treatment could lead to a visible change of the surface wettability (from $66.6^\circ \pm 1.3^\circ$ to $36.7^\circ \pm 6.9^\circ$), which indicated a change of the chemical composition. This result may spark further experimental approaches to study the relationship between the wettability and ionic transport properties within a confined space at the nanoscale.[15]

PAA is a weak polyelectrolyte that adopts a coiled conformation dependant upon the degree of dissociation or protonation, which is controlled by the pH and ionic strength of the surrounding solution,[16] due to ionic repulsion between anionic groups. PAA contains carboxylic groups that become ionized at pH values above its pK_a of 4.7 (Fig. 1).[14a] The conformation of this weak polyelectrolyte changes from coiled at low pH to stretched at high pH.[17] The effect of pH on chain conformation on the surface is schematically outlined in Figure 1 (right insert). At low pH values the formation of intramolecular hydrogen bonds in PAA prevails,

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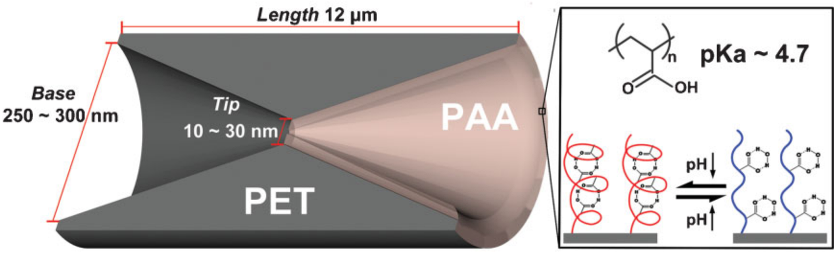

Figure 1. Scheme of the single hour-glass shaped nanochannel after plasma-induced graft polymerization (left), and hypothetical conformations of hydrogen bonding between the copolymers and water which reveal two kinds (right): the intramolecular hydrogen bond among the carboxylic acid groups in the polymer chains when the pH is below pK_a, and the intermolecular hydrogen bonds between PAA chains and water molecules when the pH is above pK_a.

which leads to a hydrophobic surface. However, in the case of a high pH value, intermolecular hydrogen bonds between water molecules and PAA were formed, and a hydrophilic surface was obtained.

Ionic transport properties of the nanochannel (Sample 1) before and after plasma treatment have been examined by current measurements. Figure 3a shows current-voltage (*I–V*) properties of the nanochannel before treatment, and the nanochannel exhibits linear *I–V* curves at different pH values. No change could be observed both when the pH changed from 5.8 to 2.8 and from 2.8 to 10, which meant that the original nanochannel (sample 2) does not rectify at different pH values and without gating property (Fig. 4). After plasma treatment, there was a remarkable difference in that significant rectifications were observed as *I–V* curves (Fig. 3b). By changing the pH from 5.8 to 2.8, a significant decrease in the transmembrane ionic current was observed for the same ion concentration as that of the test solution (KCl 0.1 M). Then, a significant increase in the transmembrane ionic current could be observed when the pH changed from 2.8 to 10. It was thought that this asymmetric ionic transport property was caused by asymmetric chemical modification, which results in structural asymmetry and the non-uniform chemical composition of the nanochannel.

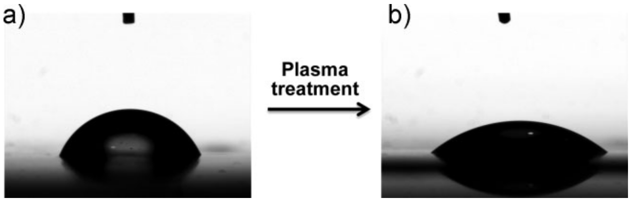

Figure 2. The CA of the PET film surfaces before and after plasma treatment. a) Before plasma treatment. b) After plasma treatment.

The open/close switching ability of the smart nanochannel system upon alternating the pH of the test solution between 2.8 and 10 (start and end at pH 5.8) is shown in Figure 5a (Sample 2), which reflects the reproducible and reversible character of the pH gating ionic transport nanodevice. The ionic transport properties of this system changed immediately after the change in pH value of the test solution. The degree to which the ionic transport can be controlled depends on the size of the original nanochannel and the degree of plasma treatment. Some previous studies[4,6,16,18] related to responsive nanochannels and nanopores have shown that there were three major influencing factors bringing the change of ionic current at the same ion concentration and a certain voltage: surface charge,[4,18c] the effective pore size,[4a,6,18a,18b] and the wettability[4d,15] of the nanochannel.

In our strategies, the asymmetric ionic transport property was caused by the non-homogeneity of the distribution of surface charge and the structural asymmetry of the channel after plasma treatment (see Supporting Information, Fig. S2). It is generally believed that the conformation of the PAA chains changes from coiled to stretch, which would plug the pores and result in the decrease in the effective pore size, and therefore the transmembrane ionic current is correspondingly reduced.[18a] However, in

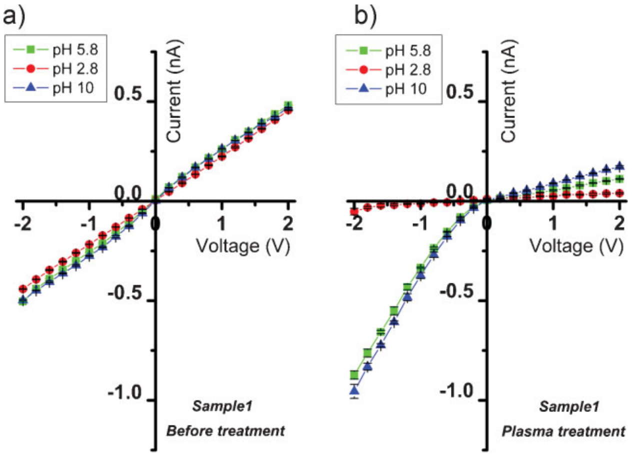

Figure 3. a,b) Current–voltage (*I–V*) properties of the single nanochannel under different pH conditions (pH 5.8,■,green; pH 2.8,●,red; pH 10,▲,blue). (Sample 1, base ~250 nm, tip ~11 nm, before plasma treatment)

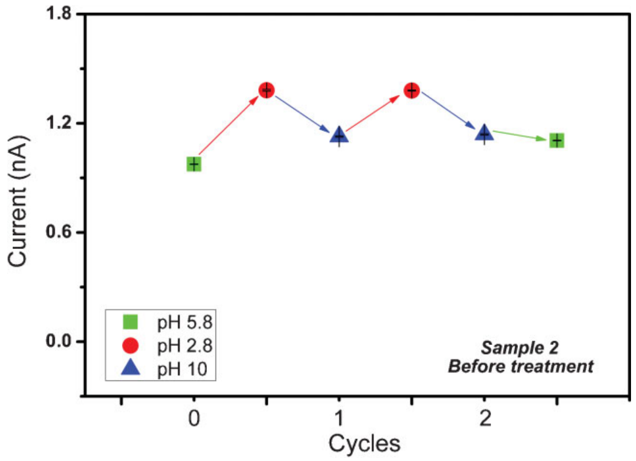

Figure 4. Reversible variation of the ionic current transport of the single nanochannel before plasma treatment at 2 V (anode facing the plasma treatment side of the nanochannel, pH 5.8,■,green; pH 2.8,●,red; pH 10,▲,blue). (Sample 2, base ~270 nm, tip ~30 nm, before plasma treatment).

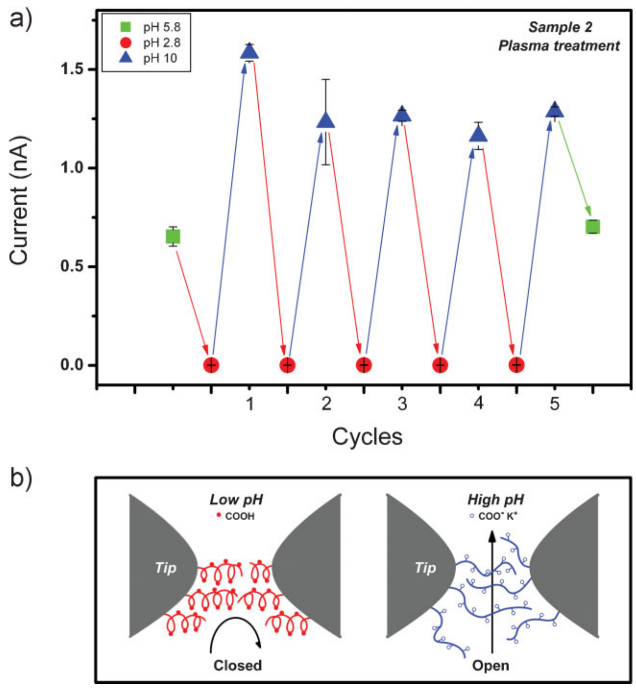

Figure 5. a) Reversible variation of the ionic current transport of the single nanochannel system at 2 V (anode facing the plasma treatment side of the nanochannel, pH 5.8,■,green; pH 2.8,●,red; pH 10,▲,blue). (Sample 2, base ~270 nm, tip ~30 nm, before plasma treatment). b) Explanation of pH-dependant water permeation through the single hour-glass shaped nanochannel.

our case, the transmembrane ionic current change is totally opposite, which indicates variations in the effective pore size are not the major influence during the pH change. These results coincided with the hypothesis of Azzaroni et al.,[4d] who concluded that an increase in hydrophobicity of the nanochannel could lead to mediation of ionic transport in the boundaries of the nanochannel wall, due to hindering of the formation of the mobile electrolyte layer. It is thought that the wettability of the nanochannel is the key factor in our system. Considering the dependence of water permeation on pH, the tip of the nanochannel carrying carboxylic groups permeated water at higher rates under high pH conditions, in terms of hydrophilic state. This behavior can be simply explained by the mechanism shown in Figure 5b. To be clearer, when the pH changes from low to high, the wettability of the nanochannel plays a prominent role in the ionic transport properties of the smart nanochannel because of the PAA transition from a hydrophobic state to a hydrophilic state.

In summary, we experimentally demonstrate a smart nanochannel material, which displays the advanced feature of providing simultaneous control over the pH-tunable asymmetric[4a–4c] and pH gating[4d] ion transport properties. Moreover, our simple plasma approach could promote an alternative to asymmetric chemical modification with various complicated functional molecules on the wall of the single nanochannels in order to simulate different ionic transport processes as well as to enhance the functionality of ion channels.

Experimental

Nanochannels Preparation: The single hour-glass shaped nanochannel was produced in a PET polymer film using the well-known ion track etching technique (see Supporting Information). In this work, the base of the single channel was usually controlled from ~250 to ~300 nm, and its tip ranged from ~10 to ~30 nm.

Plasma-Induced Graft Polymerization: The PET film was first soaked in water for 5 h after the etching experiment. Then, distilled AAc was injected into a plasma-induced grafting reactor (Suzhou Omega Machinery Electronic Technology Co., Ltd., DJ-01). Vacuum before switching on the glow discharge was 21 Pa and the working temperature was 20 °C. In our experiment setup, the argon atmosphere was kept at about ~50–70 Pa and these conditions would be kept for 15 min. Then, a Start R-F power supply source (Suzhou Omega Machinery Electronic Technology Co., Ltd., DT-01) was applied at 20 W to obtain glow discharge, which was maintained for 30 min. After the glow extinguished, grafting of the AAc monomers would take place in the grafting reactor, where a vacuum of ~300–600 Pa was maintained for about 20 min. Finally, the chamber was connected with air and the plasma treatment had finished. The ionic transport properties of the nanochannel were studied by measuring the ionic current through the nanochannels before and after

Current Measurement: The ionic transport properties of the nanochannel were studied by measuring the ionic current through the nanochannels before and after plasma treatment. Ionic current was measured by a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH). A single hour-glass shaped PET membrane was mounted between two chambers of the etching cell mentioned above. Ag/AgCl electrodes were used to apply a transmembrane potential across the film. The forward voltage was the potential applied on one of the base sides, which was the opposite side of the plasma treatment. The main transmembrane potential used in this work was evaluated and the scanning voltage varied from −2 to +2 V with a 40 s period. The electrolyte concentration was also evaluated (see Supporting Information, Fig. S2). Finally, 0.1 M potassium chloride solution was chosen as electrolyte. The pH of the electrolyte was adjusted with 1 M HCl and KOH solutions, and the influence of addition substance quality can be ignored. Each test was repeated 5 times to obtain an average current value at different voltages. The testing temperature was 20 °C.

CA Measurement: Contact angles were measured using an OCA20 (DataPhysics, Germany) contact-angle system at ambient temperature and saturated humidity. The original sample was treated with 9 M NaOH for 15 min. The sample was then taken out from the etching solution and treated with the stopping solution (1 M KCl + 1 M HCOOH) for half an hour. After that, the sample was treated with the deionized water, and had been stored for 5 h in the deionized water before further experiments. Before the CA test, the sample was blown dry by N_2. Deionized water droplets (about 2 μL) were then dropped carefully onto the surfaces. The average contact angel value was obtained at five different positions of the same sample. Finally, the results were summarized.

The Supporting Information includes more experimental details: environmental scanning electronic microscopy images of the hour-glass shaped nanochannels (base sides) before plasma treatment and the different concentrations of KCl solutions for the current measurements of the single nanochannel before and after plasma treatment.

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Supporting Information

A pH Gating Ionic Transport Nanodevice: Asymmetric Chemical Modification of Single Nanochannels

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The single hour-glass shaped nanochannel investigated here was produced in polymer films using the ion track-etching technique.[S1-S4] Before the chemical etching process, the samples of the polyethylene terephthalate membrane (PET, Hostaphan RN12 Hoechst, 12 μm thick, with single ion track in the center) were exposed to the UV light for 1 h from each side. To produce an hour-glass shaped nanochannel, etching was performed from both sides. For the observation etching process, the voltage (1 V) used to monitor the etching process was applied in such a way that the transmembrane ionic current can be observed as soon as the nanochannel open. Both sides of the cell were added a solution that is able to neutralize the etchant as soon as the nanochannel open, thus slowing down the further etching process. The following are the etching and stopping solutions for the etching of PET: 9 M NaOH for etching, 1 M KCl + 1 M HCOOH for stopping. The opening of the hour-glass shaped nanochannel was called base, while the small center was called tip. The diameter of the base was estimated from the multitrack membranes etch rate measured in the parallel etching experiments by environmental scanning electronic microscope (ESEM, Fig. S1), due to the difficulty[S5] of locating the base of the single nanochannel in ESEM. In this work, its base is usually controlled from ~250 to ~300 nm, and its tip is from ~10 to ~30 nm.

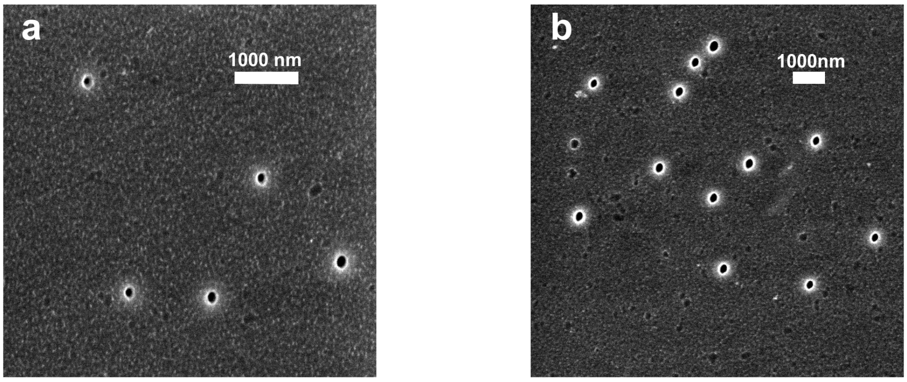

Figure S1. The ESEM of pore sizes of multi-nanochannels on the different chemical etching times. a, 10 min. b, 15 min. Scale bars, 1000 nm.

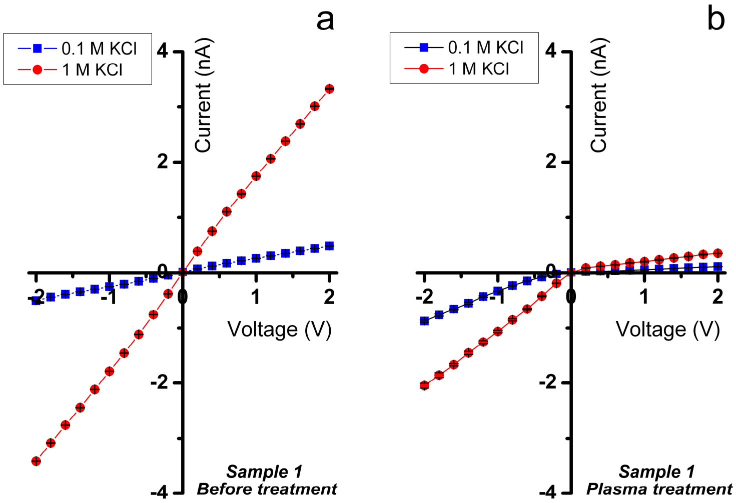

Figure S2. The different concentrations of KCl solutions for the current measurements of the single nanochannel before and after plasma treatment. (a) and (b) show the current-voltage (*I*-*V*) properties of the nanochannels with the different concentrations (0.1 M,■,blue; 1 M,●,red;). (Sample1, base ~250 nm, tip ~11nm, before plasma treatment)

Current Measurement: The ionic transport properties of the nanochannel were studied by measuring ionic current through the nanochannels before and after plasma treatment. Ionic current was measured by a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH). A single hour-glass shaped PET membrane was mounted between two chambers of the etching cell mentioned above. Ag/AgCl electrodes were used to apply a transmembrane potential across the film. Forward voltage was the potential applied on one of base sides, which is the opposite side of plasma treatment. The main transmembrane potential used in this work was evaluated and a scanning voltage varied from -2 to +2 V with a 40 s period was selected. The concentration of the electrolyte in this work was also evaluated (Fig. S2), and we finally chose 0.1 M potassium chloride solution as electrolyte. The pH of the electrolyte was adjusted by 1M HCl and KOH solutions, and the influence of addition substance quality can be ignored. In this work, each test was repeated 5 times to obtain the average current value at different voltages. The testing temperature was 20 ^{o}C.

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