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Continuously tunable ion rectification and conductance in submicro-channel stemming from thermoresponsive polymer self-assembly

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Abstract: Here, for the first time, we reported a biomimetic conical submicro-channel (tip side: ~400 nm) with functions of continuously tunable ion rectification and conductance based on thermoresponsive polymer layer-by-layer (LbL) self-assembly. These self-assembled polymers with different layers exhibited a capability to regulate the effective channel diameter, different ion rectifications/conductance were achieved. By controlling temperature, the conformation and wettability of the assembled polymers were reversibly transformed, thus the ion rectification/conductance could be further adjusted subtly. Due to the synergistic effect, the ion conductance could be tuned over a wide range spanning three orders of magnitude. Moreover, the proposed system can be applied for on-demand on-off molecule delivery, which was important for disease therapy. This study opened a new door for regulating channel size according to actual demand and sensing big targets with different size with one channel.

Bioinspired channels possess interesting ion/molecule transport properties and are similar to biological channels with respect to their gating and rectification abilities.^[1] Up to date, various stimuli-responsive molecules were modified onto the inner surface of channel with only small tip size (~10-30 nm) to achieve smart gating and rectification functions,^[2] because it was difficult to achieve ion rectification when the pore diameter was 10 times larger than the Debye length.^[3] Due to the small dimension, low ion flux was generated and the adjustable range of ion rectification was limited, which strictly restricted the practical application. Recently, some new avenues were reported to extend ion rectification to the micrometer scale,^[4] although obvious ion rectification was observed, the ion rectification and conductance of these modified channels cannot be further regulated once they were prepared, because employed polymers were grafted on the channel in monolayer configuration and without stimuli-response. To promote the function of bioinspired large-scale channels, such as nuclear pore, it is nec-

essary to achieve adjustable ion conduction and rectification of large-scale channels.

Layer-by-layer self-assembly is a powerful method to construct multilayer films on the surface with controlled architectures and properties.^[5] Benefiting from different building units (nanoparticles, enzymes, polymers), driving forces (electrostatic interaction, covalent interaction, host-guest interaction) and assembly technologies (immersion, spin, spray) of LbL self-assembly, various LbL assembly systems have been developed for different purposes.^[6] LbL films assembled using covalent interaction have attracted increasing attention owing to their long-term stability and good biocompatibilities.^[7] PBOB-PNIPAM is a synthesized thermoresponsive copolymer via free-radical polymerization, where PBOB block containing sugar-binding benzoboroxole groups. PMan is a kind of glycopolymer with cis-diols.^[8] PBOB-PNIPAM and PMan can build LbL multilayers through the covalent interaction between phenylboronic acid in PBOB-PNIPAM and cis-diols in PMan.^[9]

Herein, we firstly reported a conical submicro-channel (tip side: ~400 nm) based on thermoresponsive polymer LbL self-assembly method with smart ion transport properties: continuously tuned ion rectification and conductance over a wide range (Figure 1). To accomplish polymer self-assembly inside the channel, self-assembly precursor, Man-C₈-NH₂, was firstly modified onto the inner surface of the channel. Then, through LbL method, polymers (PBOB-PNIPAM and PMan) were self-assembled in the conical channel driven by dynamic covalent interaction. Effective diameter of the channel can be adjusted by well controlling the number of the self-assembled polymer layers in the channel, which resulted in multiple ion rectification and conductance. After polymers self-assembly, under each state, the ion rectification and conductance could be further adjusted stemming from temperature-triggered reversible conformation and wettability transition of the polymers. The ion conductance can be tuned over a wide range spanning three orders of magnitude. By adding competing molecules, Adenosine triphosphate (ATP), the self-assembled polymers in the channel were eliminated and the channel almost completely recovered. The prepared channel also exhibited excellent stability. More importantly, the system could be further utilized for on-demand on-off molecule delivery. This study provided a basic platform for enhancing the functionalities of large-scale channels and promoted the application of artificial fluidic devices in energy conversion, drug delivery and clinic treatment.

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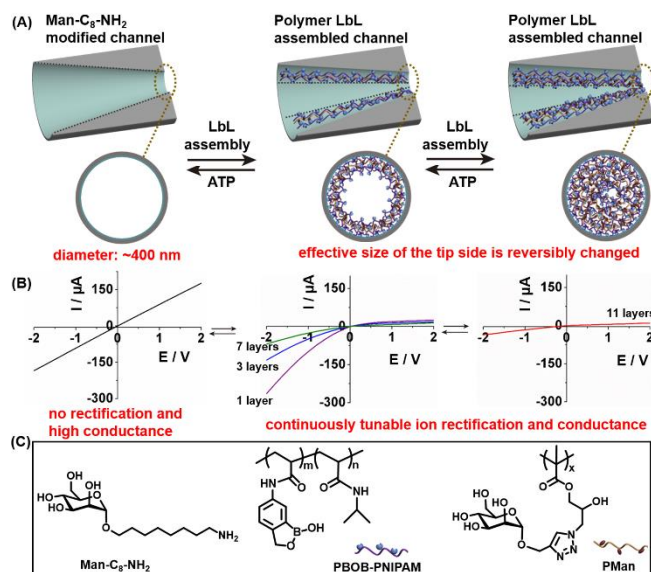


Figure 1. Continuously tunable and reversible ion rectification/conductance in a submicro-channel (~400 nm) based on thermoresponsive polymer LbL self-assembly method. (A) Schematic illustration of the preparation process of the channel, Man-C₈-NH₂ was firstly modified onto the channel, then PBOB-PNIPAM and PMan were sequentially assembled in the channel. (B) The ion transport properties of the prepared channel. For Man-C₈-NH₂-bound channel, there was no rectification and high conductance, after polymers LbL assembly, effective diameter of the channel was gradually decreased, ion rectification generated and changed at different assembled layers, ion conductance was also corresponding decreased. The process was reversible, because ATP has higher binding affinity with phenylboronic acid, thus after the addition of appropriate concentration of ATP, removing PBOB-PNIPAM and PMan from the prepared channel and getting the primary Man-C₈-NH₂-bound channel. (C) The molecular structures of Man-C₈-NH₂, PBOB-PNIPAM and PMan.

Scheme S1 described the preparation procedures of the biomimetic large-scale channel through thermoresponsive polymer LbL self-assembly. We designed and synthesized Man-C₈-NH₂, PBOB-PNIPAM and PMan in advance (Note 1 in Supporting Information, Scheme S2 and Fig. S1-6). The conical channel in poly(ethylene terephthalate) (PET) membrane with a pore density of 10⁷ pores/cm² was prepared by the well-developed asymmetric track-etching technique (Note 2 in Supporting Information, Scheme S3).^[10] As observed with scanning electron microscopy (SEM), the initial base and tip diameters were around 1.5 μm and 400 nm, respectively (Fig. S7). During chemical etching process, negatively charged carboxyl groups were created on the channel surface, Man-C₈-NH₂ molecules were firstly immobilized in the inner wall of the nanopore via a conventional 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide/N-hydroxysulfosuccinimide sodium salt (EDC/NHSS) coupling reaction.^[11] PBOB-PNIPAM polymers were introduced in the channel surface through the formation of stable boronate ester between phenylboronic acid of PBOB-PNIPAM and cis-diols of Man-C₈-NH₂ (Scheme S4).^[12] Then PMan and PBOB-PNIPAM polymers were LbL self-assembled in the channel surface driven by the dynamic

covalent interaction of phenylboronic acid and cis-diols (Scheme S5). The initial tip diameter of Man-C₈-NH₂ modified channel was ~400 nm (Fig. S8A), after modification with one-layer PBOB-PNIPAM (PBOB-PNIPAM₁PMan₀), named as [1] state, the effective tip diameter had no obvious change (Fig. S8B), while six-layer PBOB-PNIPAM and five-layer PMan (PBOB-PNIPAM₆PMan₅) were assembled, named as [11] state, the tip side was obviously blocked (Fig. S8C), these results demonstrated that the tip diameter could be adjusted through polymer LbL self-assembly method. The membranes before and after modification could be further confirmed by X-ray photoelectron spectroscopy (XPS). Before modification, the membrane only showed C 1s and O 1s peaks (Fig. S8D), while after modification with Man-C₈-NH₂, a clear N 1s peak was observed (Fig. S8E), and a typical B 1s peak was observed for PBOB-PNIPAM modified membranes (Fig. S8F), providing direct evidence for the successful modification of Man-C₈-NH₂ and PBOB-PNIPAM.

The ion transport property of the proposed channel was investigated by recording transmembrane currents under 0.1 M KCl electrolyte solutions (pH ~9). As shown in Figure 2A, a linear current-voltage curve was obtained at bare channel of ~400 nm in tip diameter in 0.1 M KCl solution, because the diameter was much larger than the thickness of the electrical double layer (ca. 3 nm).^[13] After modification with Man-C₈-NH₂, the ionic current was almost no change (Fig. S9). It is reasonable because the size of the Man-C₈-NH₂ is too small compared with the diameter of the channel (ca. 400 nm). When PBOB-PNIPAM was introduced, named as [1] state, an asymmetric ion transport behavior, and diode-like current-voltage curve was observed, the rectification ratio enhanced ~10 folds, from 1.04 to 10.66 (Figure 2B). This phenomenon was considered to originate from the negative charges of PBOB-PNIPAM while the tip size was kept the same (Fig. S8B), which was consistent with the report by Mao's group.^[4a] Then as the assembled layers of PMan and PBOB-PNIPAM grew, the ion rectification and conductance of the channel were gradually decreased (Figure 2B and 2C), because the self-assembled polymers blocked the nanochannel, inducing the reduction of effective tip diameter (Fig. S8C). Thus the ion rectification and conductance of the channel could be optionally regulated by controlling the self-assembled polymer layers. The prepared channel exhibited good stability and reversibility. I-t curves of Man-C₈-NH₂-bound state, [3], [5], [7], and [11] states were measured at -0.2 V. As shown in Fig. S10, each state could remain stable for at least 30 min. The reversibility between the polymer assembled state and Man-C₈-NH₂-bound state can be achieved by the addition of ATP. Because ATP has higher binding affinity with phenylboronic acid, the binding of ATP to PBOB-PNIPAM lead to the disassembly of the polymer structures (Scheme S6), which free the path for ion conduction. The ion current (Figure 2D and 2E) gradually increased with ATP concentration from 1 nM to 11 nM. Figure 2F pointed out that the channel could be cyclically and reversibly switched for at least 4 cycles.

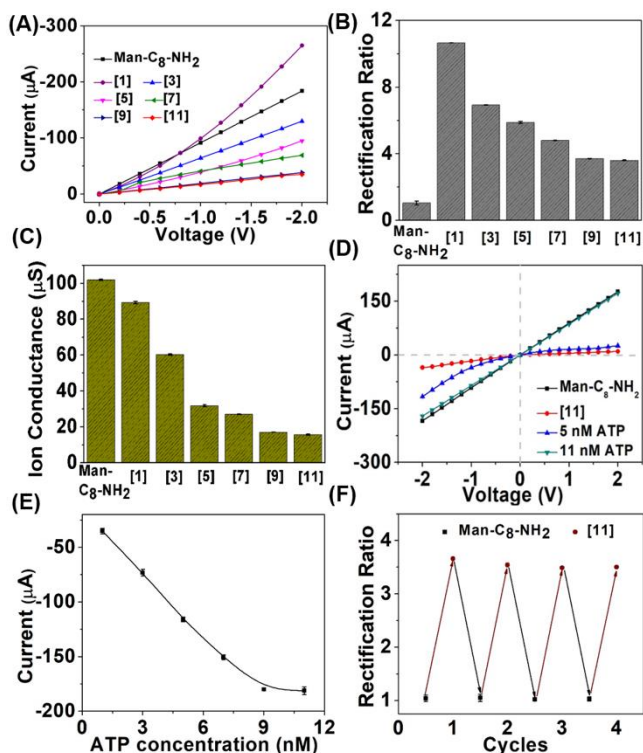


Figure 2. I-V curves (A), ion rectification ratios (B) and ion conductance (C) of the channel under different states: Man-C₈-NH₂-bound state, [1] state: PBOB-PNIPAM₁PMan₀, [3] state: PBOB-PNIPAM₂PMan₁, [5] state: PBOB-PNIPAM₃PMan₂, [7] state: PBOB-PNIPAM₄PMan₃, [9] state: PBOB-PNIPAM₅PMan₄, [11] state: PBOB-PNIPAM₆PMan₅. After assembled one layer, the ion current at -2 V and rectification ratio increased, then as the assembled layers grew, the ion current at -2 V and rectification ratio gradually decreased. I-V curves (D) and the ion current at -2 V (E) of the channel after the treatment of different concentration of ATP. As the ATP concentration increased, ion current at -2 V gradually increased, when the concentration was up to 11 nM, the channel was almost recovered to Man-C₈-NH₂-bound state. (F) Reversible changing of the rectification ratios of the channel between Man-C₈-NH₂ state and [11] state.

Under each state, the ion rectification and conductance of the channel can be further tuned due to the temperature responsive feature of used polymers. PNIPAM is one of the most popular temperature sensitive materials, and exhibits a lower critical solubility temperature (LCST) in water of 32 °C.^[14] At room temperature (25 °C), PBOB-PNIPAM remained swollen, raising the temperature (45 °C), the polymer suffered a transition into a collapsed state, when the temperature cooled to 25 °C, the polymer returned back to its original state (Figure 3A). The polymers assembled channel exhibited a temperature-stimuli switching between high and low ion conducting states (Figure 3B). On the other hand, the wettability change of the prepared channel at different temperature was also investigated. As shown in Figure 3C, at 25 °C, the channel was hydrophilic with the water contact angle of $53 \pm 2.7^\circ$ due to the intermolecular hydrogen bonds between the PNIPAM chains and the water molecules. At 45 °C, the contact angle increased to $91 \pm 2.3^\circ$, the channel became hydrophobic, because the hydrogen bonds between the C=O and N-H groups in the PNIPAM chains made

it difficult to interact with water molecules.^[15] When the temperature cooled to 25 °C, the contact angle nearly recovered. The reversible geometry and wettability change of the polymer resulted in the ion rectification and conductance of the channel could be further tuned under each state. As shown in Figure 3D-F, at 25 °C, the prepared channel worked on the high ion conducting state (ON state). When the temperature was raised to 45 °C, the ionic conductance remarkably decreased (OFF state). Interestingly, this observation was opposite with previous reported PNIPAM brushes modified nanochannels.^[16] In those cases, polymers were in situ grown from the nanopore wall through surface initiated radical polymerization process, the growth directions were mainly perpendicular with the channel. When the temperature raised from 25 °C to 45 °C, the nanochannel changed from a low ion conductance state to a high ion conductance state, this was resulted from the conformational collapse of the PNIPAM brushes, which increased the effective tip side of the nanochannel. While for our system, polymers were attached in the channel via dynamic covalent interaction, there were many binding sites on the channel for coupling with polymers, so their assembled direction were largely parallel with the channel, at 45 °C, PBOB-PNIPAM polymers collapsed, leading to the blockage of the tip side that inhibited ions flow. As discussed above, it was reasonable to assume that the ion transport properties of the prepared polymers assembled channel were the incorporation result of wettability and geometry. When the temperature gradually increased from 25 °C to 45 °C, the effective tip size and wettability were both decreased, the ion conductance at -0.2 V exhibited a dramatic decrease, indicating the gating state was gradually changed from ON to OFF (Fig. S11). The thermal-gating ratio was gradually increased with the increasing self-assembled polymer layers and reached a maximum value of ~28.56 at [11] state (Figure 3G), which is much higher than that of the existing temperature gated nanochannels, where polymers were introduced through conventional surface-initiated radical polymerization process. Figure 3H showed the reversible switch between ON and OFF state of the channel under [11] state for 4 cycles, and no obvious ionic fatigue was observed.

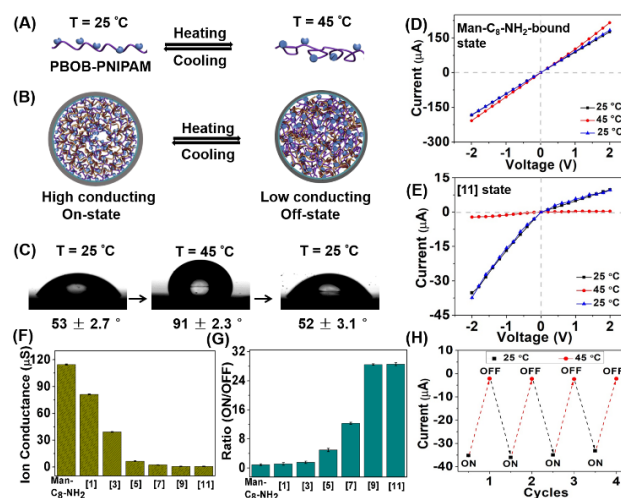


Figure 3. Temperature responsive property of the channel under different self-assembled states. (A) The conformation change of PBOB-PNIPAM under 25 °C and 45 °C, it remained swollen at 25 °C, raising the temperature to 45 °C, the polymer suffered a transition into a collapsed state. (B) The ion conductance state of polymer self-assembled channel, switched between high ion conducting state (On-state) and low ion conducting state (Off-state). (C) Reversible change of the contact angle of polymer self-assembled channel between 25 °C and 45 °C. When the temperature increased to 45 °C, the channel changed from hydrophilicity to hydrophobicity. The temperature sensitive ion gating function of polymer self-assembled channel under different states (D-E). (D) Man-C₈-NH₂-bound state, (E) [11] state: PBOB-PNIPAM₆PMan₅, at 25 °C, the channel was “ON” state, at 45 °C, the channel was “OFF” state, when the temperature cooled to 25 °C, the ion current was almost completely recovered to “ON” state. The ion conductance (F) and thermal gating ratio (G) of the channel under different states, the ratio increased with the increasing assembled layers of polymers. (H) Reversible switching of the channel under [11] state between “ON” and “OFF” states.

In comparison, homo-PNIPAM polymer was used instead of PBOB-PNIPAM, there was no change for the transmembrane ion current (Fig. S12), this was ascribed to the failure of polymer self-assembly and neutral charge of homo-PNIPAM.

The polymers self-assembled channel showed a unique application is that it can realize on-demand molecule delivery, which was important for disease therapy. To accomplish this aim, left reservoir contained 0.5 mg/mL sulfonated rhodamine dye (SRD) molecules in aqueous solution (donor side) while right reservoir contained water alone (receptor side; Figure 4A). The dye molecules could diffuse through the channel along the concentration gradient into a bath of water, the process was assessed by measuring the rate of fluorescein flux between two reservoirs. For the initial channel (Figure 4B), at different temperatures: 25, 30, 35, 40, 45 °C, the fluorescence intensity all exhibited the same increase trend over time, from 2 h to 8 h. While for polymers assembled channel, [11] state was used as an example (Figure 4C), the fluorescence intensity increased sharply over time at 25 °C, then gradually slowed down with the temperature increased, because of the blockage and hydrophobic resulting from the conformational change of polymers. When SRD dye molecules with negative charges were replaced by rhodamine 6G with positive charges, the on-demand molecule delivery could also be observed from the change of the fluorescence intensity (Fig. S13). These results indicated that the polymers assembled channel could be utilized as a gatekeeper to realize controlled delivery of various molecules. Fig. S14 showed the relationship of the cumulative fluorescence intensity of SRD with time when the temperature was 25 °C and 45 °C alternately. When the temperature was 25 °C, the gate is ON, the fluorescence intensity increased with time, while the fluorescence intensity kept almost constant over time at 45 °C, which indicated that no dye molecules were delivered through the channel due to the OFF state of the gate. The on-demand molecule delivery was successfully achieved through the alternate ON and OFF states of the channel.

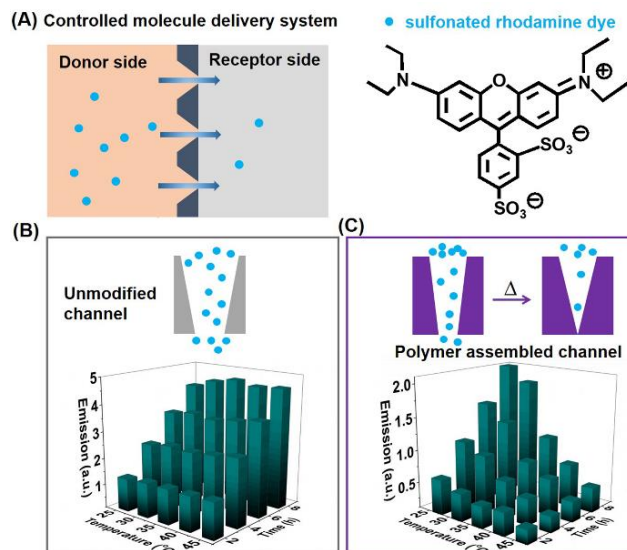


Figure 4. (A) Schematic illustration of controlled sulfonated rhodamine dye (SRD) molecule delivery (left), the structure of SRD molecule (right). (B) The molecule delivery of the unmodified channel along with time under different temperatures. (C) The molecule delivery of the polymer self-assembled channel ([11] state) along with time under different temperatures.

In summary, a versatile biomimetic submicro-channel has been successfully fabricated based on thermoresponsive polymer layer-by-layer self-assembly, the characteristics of continuously tunable ion rectification and conductance were exhibited. The polymer self-assembly was accomplished through the formation of stable boronate ester between phenylboronic acid of PBOB-PNIPAM and cis-diols of Man-C₈-NH₂/PMan. By controlling polymer self-assembly layers, the tip side diameter of channel can be adjusted, thus multiple ion rectification and conductance were achieved. Through controlling temperature, the ion rectification and conductance could be further tuned, the principle was attributed to the conformation and wettability change of the polymer brushes. Due to the synergistic effect of polymer self-assembly and temperature stimuli, the ion rectification/conductance could be continuously adjusted and the ion conductance tuned over a wide range spanning three orders of magnitude. The prepared channel exhibited good reversibility and stability, it could be also used for controllable molecule delivery.

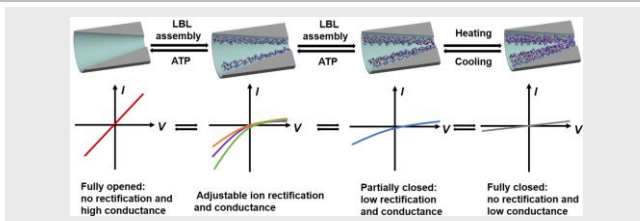
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Keywords: submicro-channel • thermoresponsive polymer • self-assembly • tunable ion rectification • tunable ion conductance

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COMMUNICATION



A biomimetic submicro-channel (~400 nm) with functions of continuously tunable ion rectification and conductance based on thermoresponsive polymer layer-by-layer (LbL) self-assembly was presented. The ion rectification/conductance could be continuously adjusted and the ion conductance tuned over a wide range spanning three orders of magnitude. The proposed system can also be applied for on-demand on-off molecule delivery, which was important for disease therapy.

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Page No. – Page No.

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