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Nanotechnology

Ionic Transport Through Single Solid-State Nanopores Controlled with Thermally Nanoactuated Macromolecular Gates**

*Basit Yameen, Mubarak Ali, Reinhard Neumann, Wolfgang Ensinger, Wolfgang Knoll, and Omar Azzaroni**

Biological nanopores acting as membrane channels play a determinant role in all living systems. They operate as very sensitive devices in charge of regulating key functions as electric potential, ionic flow, and molecular transport through membranes.[1] Ion channels of biological membranes are formed by pore-like single proteins that span cell membranes and open and close in response to stimuli like changes in the transmembrane potential, binding of a ligand, or mechanical stress.[2] These stimuli-sensitive biological building blocks embedded into the membrane enable the modulation of ion transport through the protein channel due to passage of single molecules or proteins.[2] They are responsible for providing the conducting pathways for the ions species. When they are in a open conformation, ions pass through the pore, and when they are resting in a closed, non-conducting conformation, ion transport is precluded.[3,4] This indicates that nanopore channels change their conformations between different states in order to enable or prohibit the transport of species through the biological membrane, thus acting as a gate. In addition, the conformational transition between the states is usually referred to as gating. Hence, these biological channels work as nanodevices that control the molecular transport through a physical interface.[5] Biological nanopores, such as α-hemolysin, provide unique features in regard to single molecule sensitivity;[6] however, they are labile and difficult to handle in environments different from the lipid membrane and not fully compatible with nanodevice systems.[2a] This explains the growing interest in developing chemical devices that mimic the function of biological ion channels.[7–9] The possibility of creating fully artificial (''man-made'') nanogating devices is one of the remaining challenges in nanotechnology,[10–13] in which the generation of bioinspired switchable and easily controllable molecular gates would provide new tools for the creation of complex nanomachineries. In this context, solid-state nanopores have been demonstrated to be a robust alternative to biological nanopores.[14–21] Besides, they also offer better control over channel geometry and compatibility with the integration into functional systems.[20] They show huge potential in biomolecular recognition and also on creating gating functions, like rectification, in which the gating behavior can be modulated by ionic strength or high-valent ions.[20] However, controlling the internal architecture and the chemical features of synthetic nanopores, as precisely as α-hemolysin or other biological ion channels, is a non-trivial task.

This introduces a new nanotechnological demand focused on the quest for novel alternative switchable nanopore machineries capable of being ''nanoactuated'' by external stimuli in a controllable manner. In this regard, one stimulus of particular interest in biological and non-biological systems is temperature.[22] Biological ionic channels activated by temperature changes transduce this information into conformational changes that open the channel pore. A typical example is thermosensation that is carried out by the direct activation of thermally gated ion channels in the surface membranes of sensory neurones.[23] This complex task is accomplished by temperature-sensitive ion channels, which are members of the extensive TRP family (transient receptor potential channels).[24] Another good example concerns *N*-methyl-D-aspartate (NMDA) receptors which are glutamate-gated Ca^{2+} permeable

[*] Dr. O. Azzaroni
Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA)
CONICET – Universidad Nacional de La Plata
CC 16 Suc.4 (1900) La Plata (Argentina)
E-mail: azzaroni@inifta.unlp.edu.ar

B. Yameen, Prof. W. Knoll
Max-Planck-Institut für Polymerforschung
Ackermannweg 10, 55128 Mainz (Germany)

M. Ali, Prof. W. Ensinger
Technische Universität Darmstadt, Fachbereich Material- u. Geowissenschaften, Fachgebiet Chemische Analytik
Petersenstraße 23, D-64287 Darmstadt (Germany)

Prof. R. Neumann
Gesellschaft für Schwerionenforschung (GSI)
Planckstraße 1, D-64291 Darmstadt (Germany)

Prof. Dr. W. Knoll
Austrian Research Centers GmbH
Donau-City-Straße 1, 1220 Vienna (Austria)

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ion channels constituted of heteromultimers involving NR1 and NR2 subunits activated by glutamate and glycine. Recently, Cais et al. demonstrated that these subunits undergo significant conformational transitions at 21.9–46.5 °C, which could have strong implications on the neuronal excitability at physiological temperatures.[25] With the inspiration of examples from nature, the scientific community started to build-up biomimetic thermosensitive pores, as is the case of Movileanu and co-workers, who created temperature-responsive protein pores containing elastin-like polypeptide (ELP) loops.[26] These ELP loops were placed within the cavity of the lumen of the α-hemolysin pore. Below the transition temperature the ELP loop is fully expanded and blocks the pore, above its transition temperature the ELP is dehydrated and the structure collapses, enabling a substantial flow of ions through the pore. In a similar vein, Reber et al. explored the use of poly-*N*-isopropylacrylamine hydrogels in order to control the transport of methylene blue and bovine albumin through multi-pore ion track membranes.[27]

In this context, here we describe for the first time the application of solid-state nanopores modified with thermo-responsive brushes as molecular gates nanoactuated by temperature-driven conformational transitions. We demonstrate the creation of ''fully artificial'' smart nanopores with tunable nanoscale diameters controlled by temperature changes in the physiological range. These results demonstrate the huge potential of ''soft nanotechnology''[28,29] to emulate and replicate complex biological functions using soft matter-based man-made systems.

Solid-state single conical nanopores used in this study were fabricated in polyimide (PI) membranes by asymmetric chemical etching of the latent track of an energetic heavy ion.[19] The chemical etching process led to the formation of carboxyl groups on the nanopores surface, which were then converted into amino groups by covalent linkage of diamine using conventional EDC/PFP coupling chemistry.[30] Next, we modified the single pore-containing membrane with the thermo-responsive polymer brushes. This was easily accomplished by using aqueous surface-initiated atom transfer radical polymerization (SI-ATRP)[31] leading to the formation of a dense polymer layer (brush) covalently tethered at one end to the nanopore sidewall (Figure 1). Even though it is well known that polymer brushes can be grown by a number of different polymerization techniques,[32] ATRP resulted in a very attractive alternative due to its simplicity to synthesize different polymer architectures in aqueous environments.[33] The solvents used in the aqueous ATRP are fully compatible with the membrane material, thus avoiding any detrimental effect on the single pore characteristics, that is, closure, due to the swelling of the PI. Firstly, we modified the membrane having a single aminated channel with the initiator groups. Secondly, we proceeded to the polymer brush growth (Figure 1) by immersing the initiator-modified membrane into the corresponding polymerization solution under conditions described elsewhere (see also Experimental Section).[34] The choice of a *N*-isopropylacrylamide-based thermoresponsive system was motivated by the fact that it requires a simple and widely available monomer and that its temperature-driven conformational changes are well documented in the literature.[35] After polymerization, the brushes were extensively rinsed with water and methanol for removing the polymerization solution and kept under water prior to performing the thermoactuated gating experiments.

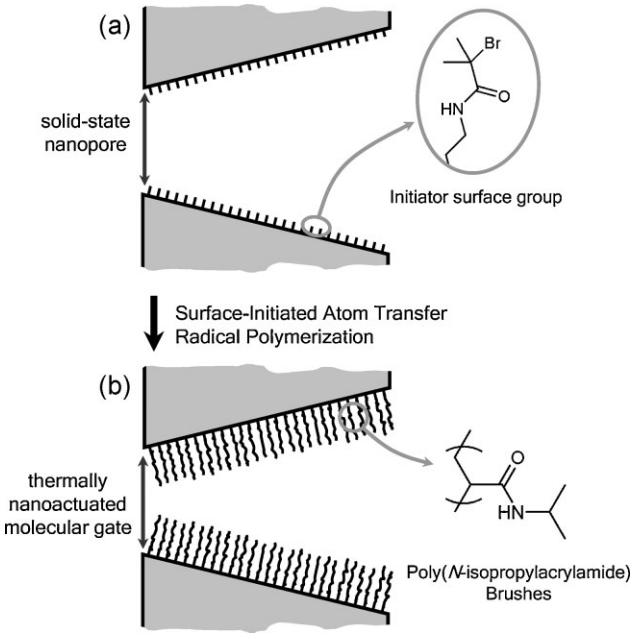

Figure 1. Scheme illustrating the surface modification of the nanopore by a polymerization step resulting in polyNIPAM brushes. Firstly, the aminated pore wall is modified with the initiator groups (a). Then, the aqueous ATRP is carried out (b). The figure also describes the chemical structures of the ATRP initiator and the polyNIPAM brushes.

The track-etching technique allows control over the shape of the nanopores, and in our experiments the etched single nanopore was conelike. Its large opening (base) was usually $\approx$1.0–1.5 μm, and the narrow opening a few tens of nanometers. Diameter measurements of single conical nanopore were conducted with a commonly used electrochemical measurement.[20]

An electrochemical method described by Siwy and co-workers[36] was used to calculate the tip diameter, d, of the single conical nanopores. Briefly, this method involves mounting the membrane containing the conical nanopore in a cell setup. The membrane divides the cell in two halves in which each side of the half-cell is filled with 1 M KCl and a Ag/AgCl electrode is immersed into each half-cell solution. A current–voltage (I–V) curve for the electrolyte-filled nanopore is then obtained. The slope of this I–V curve is equal to the ionic conductance, G (in Siemens, S) of the nanopore. The diameter of the small opening (d) was estimated from its conductivity by the following equation:

$$d = \frac{4L}{\pi\kappa D}\frac{I}{V} \quad (1)$$

Here L is the length of the pore, D the diameter of the large opening of the pore, κ the specific conductivity of the electrolyte, V the voltage applied across the membrane, and I is the measured current.

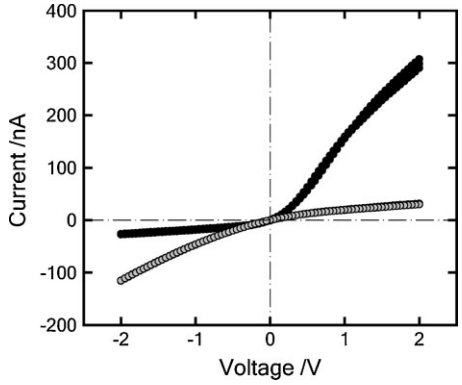

Figure 2. Current–voltage characteristics of a PI conical nanopore in 1 M KCl having $d \sim 48$ nm and $D \sim 1.45$ μm, prior to (●) and after (●) after modification with ethylenediamine. The terms d and D refer to the diameters of the small and large opening of the pore, respectively.

At neutral pH, the carboxylate-modified conical nanopores rectify the ion current due to the presence of negative charges on the pore surface. After modification with ethylenediamine, the pore walls were positively charged (due to the protonated amino groups), which resulted in the inversion of rectification as shown in Figure 2.

The gating performance of our PNIPAM brush-modified nanopore ($d \approx 8$ nm) was studied using the same experimental setup by measuring the ionic current across the channel at different temperatures.

Figure 3 shows the *I–V* curves of single PI nanopore modified with PNIPAM brushes obtained at different temperatures. PNIPAM brushes neutralize the surface charge of the pores resulting in the loss of the rectifying behavior and, consequently, the pore exhibits a linear *I–V* characteristic (Figure 3). At room temperature (23 °C) PNIPAM brushes remain swollen, thus decreasing the effective cross section of the nanopore. This is described by the low slope of the *I–V* curve, which is associated with a low conductance of the nanopore, 17 nS. Raising the temperature above the lower critical solubility temperature promotes drastic changes on the conformational state of the NIPAM brushes. In this case, the brushes suffer a transition into a collapsed state,[35] which also

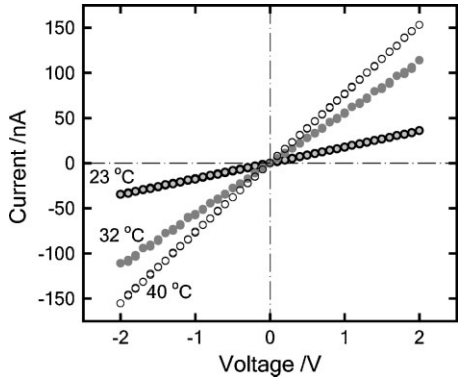

Figure 3. *I–V* curves in 1 M KCl for a PI conical nanopore after modification with polyNIPAM brushes at different temperatures ($d = 8$ nm, $D = 1.45$ μm).

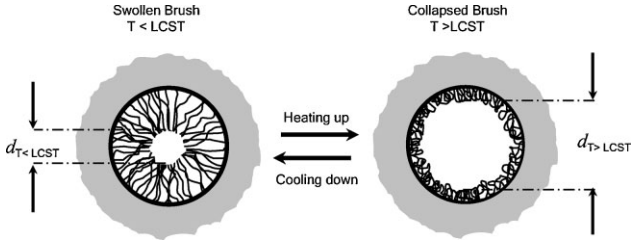

Figure 4. Cartoon describing the thermally driven nanoactuation of the polyNIPAM brushes in the nanopore.

has an impact on the effective diameter of the nanopore (Figure 4).

The conformational transition into a more compact state promotes the widening of the nanopores, which is evidenced as an increase in conductance, as derived from the slope of the *I–V* plots at 40 °C. Regarding the latter, it is worth mentioning that the increased slope of the *I–V* plots could also be attributed to changes in the specific conductivity of the electrolyte.[36] In order to estimate the contributions to the conductance coming from the specific conductivity changes due to temperature variations[37] we proceeded to estimate the nanopore conductance considering the corrected values of the specific conductivity (Table 1)

$$G^T = \frac{\kappa^T \pi D d^T}{4L} \tag{2}$$

The superscript T indicates the parameters estimated at temperature T. In Equation 2 we are assuming that the effective diameter of the large opening (base) and the thickness of the membrane film are not sensitively affected by the conformational changes of the PNIPAM brushes. In this context, a more realistic estimation of the variation on the effective cross section of the nanopore is given by:

$$\frac{G^{23°C}}{G^{40°C}} = \frac{\kappa^{23°C} d^{23°C}}{\kappa^{40°C} d^{40°C}} = \frac{17\,\text{nS}}{76\,\text{nS}} \tag{3}$$

Considering that the specific conductivity of 1 M KCl at 23 and 40 °C is 0.1073 and 0.1417 $S \cdot cm^{-1}$, respectively, we estimated from the electrochemical measurements that the effective diameter of the nanopore changed in accordance with

$$\frac{d^{40°C}}{d^{23°C}} \sim 3.4 \tag{4}$$

Table 1. Changes in conductance (G), specific conductivity (κ), pore opening and pore diameter (d) upon variations in temperature.

T [°C]	G [nS]	κ [$S \cdot cm^{-1}$]	$\frac{d^T}{d^{23°C}}$	d [nm]
23	17	0.1073	1	~8
32	56	0.1252	2.8	~22
40	76	0.1417	3.4	~27

These results clearly evidence the nanoactuating behavior of the PNIPAM brush that above the LCST undergoes a sharp change in its conformational state leading to a three-fold increase of the effective cross-section of the nanopore. The thermoresponsive brush is acting as a thermally driven macromolecular gate controlling the ionic flow through the nanopore. The very sensitive nature of the thermoactuated nanopore is also evidenced when studied at temperatures near the LCST. Figure 3 depicts the *I–V* plots for the PNIPAM-modified pore measured at 32 °C. In that case we recorded a very stable *I–V* curve with a slope corresponding to a nanopore conductance of 56 nS, which is in between 17 nS (23 °C) and 76 nS (40 °C). This fact further evidences the molecular-level control of the gating process in the nanoconfined environment driven by the fine tuning of the temperature. In other words, temperature variations in the physiological range (23–40 °C) can lead to an accurate control of the macromolecular nanogate through temperature-driven intermediate conformational states (Table 1).

Another important aspect of these thermoresponsive nanoarchitectures relies on the reversibility of the conformational changes, which are evidenced as reversible changes in the ionic current through the nanopore. Figure 5 displays the temperature cycling between 23 and 40 °C of a PNIPAM brush-modified single nanopore with $d < 5$ nm. It can be clearly seen that the variations in the ionic flux originated from the thermally trigged conformational changes of the PNIPAM brush are completely reversible. This fact further illustrates the versatility of polymer brushes to achieve an accurate and reversible control of the topological characteristics of nanoconfined environments with dimensions comparable to biological pores.

In summary, in this work we have described, for the first time, the combined use of thermoresponsive polymer brushes together with single solid-state nanopores in order to create fully artificial stimuli-responsive nanochannels that resemble those commonly encountered in nature. We demonstrated that the PNIPAM-modified nanopores act as thermally driven molecular gates with closure stages that can be remotely controlled by simply tuning the working temperature in the 23–40 °C range. Achieving a delicate control of the nanoactuating characteristics of this molecular device in the physiological temperature range is an interesting feature that could be of much interest for the implementation of artificial nanosystems propelled and/or controlled by temperature variations in living systems, such as human beings. In this context, one interesting application could be in the area of biomedical science and nanomedicine through the implementation of these fully ''abiotic'' nanogating devices as ''intelligent'' pores enabling the temperature-tuned release of drugs.

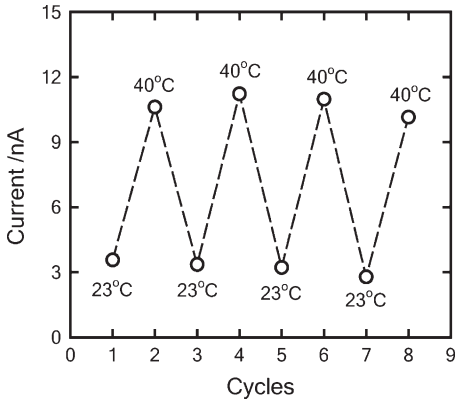

Figure 5. Temperature cycling between 23 and 40 °C corresponding to a single conical nanopore modified with PNIPAM brushes. $D = 1.26$ μm, $d_{23\,^\circ C} = 1.2$ nm, $d_{40\,^\circ C} = 4.8$ nm. Electrolyte: 1 M KCl.

Experimental Section

Materials: PI (Kapton 50 HN, DuPont) membranes of 12-μm thickness were irradiated at the linear accelerator UNILAC (GSI, Darmstadt) with single swift heavy ions (Pb, U) of energy 11.4 MeV u^{-1}. *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (98%, Fluka), *N*-hydroxysuccinimide (98%, Aldrich), ethylenediamine (99+%, Merck, Germany) succinic anhydride (99%, Fluka), 2-bromopropionyl bromide (97%, Aldrich), copper (I) bromide (99.999%, Aldrich), and *N*,*N*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) were used as received for the chemical modification. *N*-Isopropylacrylamide (99%, Acros Organics, Belgium) was purified by recrystallization from a mixture of toluene/hexane (1:4) and dried in vacuum. Triethylamine was refluxed overnight with calcium hydride before distilling and stored under argon.

Conical nanopore fabrication: In order to obtain conical pores, the heavy ion-irradiated PI membrane was etched from one side only in a conductivity cell in which it served as a dividing wall between the two compartments.[20,38] An etching solution sodium hypochlorite (13% active chlorine content) was filled on one side at 50 °C, while a stopping solution potassium iodide (1 M KI) was placed on the other side of the membrane, so that as soon as the track etched through completely, the etchant in the pore tip was neutralized, thus keeping the diameter small. This was helped further by applying a potential of −1 V on the side containing the etchant with the other grounded, so that once the pore opened, the active ClO^- ions were swept back from the pore tip. Shortly after breakthrough the pores were washed with stopping solution, followed by deionized water. The etched membrane was immersed in deionized water in order to remove residual salts. After etching, the diameter of the large opening (*D*) of the pore was determined by scanning electron microscopy (SEM) using a PI sample containing 10^7 pores cm^{-2}, which was etched simultaneously with the single pore under the same conditions. The diameter of the small opening (*d*) was estimated from its conductivity as described in the text (Equation (1)).

Functionalization with ethylenediamine: For the activation of the carboxyl groups into pentafluorophenyl esters, an ethanol solution containing (0.1 M EDC and 0.2 M PFP) was placed on both sides of the track-etched polymer membrane. The reaction was carried out for 60 min at room temperature. After washing with ethanol several times, the solution was replaced with 0.1 M ethylendiamine (EDA) on both sides of the membrane overnight. Finally, chemically modified membranes were washed three times with ethanol followed by distilled water.

Immobilization of ATRP initiator on the membrane: A solution of 2-bromoisobutyryl bromide (BIBr) (0.185 mL, 3 mmol) and

triethylamine (0.205 mL, 3 mmol) in dry dichloromethane (30 mL) was injected over the membranes with surface $-NH_2$ groups under N_2 at room temperature and left for 2 h. The membranes were washed with dichloromethane followed by absolute ethanol, and dried under a stream of N_2.

PolyNIPAAm brush growth: The polymerization was carried out using aqueous ATRP as reported in the literature with slight modifications. Briefly, NIPAAM (2.5 g, 22.1 mmole) was dissolved by stirring in methanol (5 mL) and water (5 mL) at room temperature. To this solution PMDETA (0.138 g, 0.8 mmole) was added. The mixture was stirred and degassed by N_2(g) bubbling for an hour before Cu(I)Br (0.032 g, 0.22 mmole) was added. The mixture was degassed with N_2(g) bubbling for another 15 min. The membrane was sealed in a Schlenk tube and degassed by four high-vacuum pump/N_2(g) refill cycles. The reaction mixture was syringed into this Schlenk tube, adding enough to cover the membrane completely, and the mixture was left overnight under N_2(g). The samples were removed and thoroughly rinsed with methanol and deionized water.

Keywords:
ion channels · membranes · molecular devices · nanotechnology · polymers

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