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Nanofluidic Bipolar Transistors**

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There are well-known devices for controlling the transport of electrons but very few control ions in a solution. Ionic rectifiers prepared on the basis of single conically shaped glass nanopipettes[1,2] and nanopores[3–5] were the first examples of a system that could control ionic flows electrically without the necessity of introducing moving (mechanical) parts. The next step forward was made by preparing ionic diodes that function according to a similar mechanism as that of semiconductor diodes[6–8]. These rectifying devices were capable of rectifying ion currents with degrees of rectification reaching several hundreds. Efforts were also made towards achieving even more precise control of the transport of ions and charged molecules by constructing ionic transistors. A field-effect ionic transistor (FET) applied to the regulation of DNA and protein transport was the first experimental realization of an ionic transistor[9–11]. This system was based on a single channel, with a height of several tens of nanometers, having a gate electrode lithographically placed on the outer part of the channel. Voltage applied to the gate would change the electric potential inside the nanochannel that influenced the ionic transport through the whole device. The native surface charge in a nanofluidic FET is considered a rather undesired feature resulting in the requirement of high gate voltages[10,11]. In this Communication, we report the first bipolar ionic transistor that functions in a similar way to its semiconductor bipolar junction (BJT) counterpart. The device consists of a single nanopore in a polymer film with the pore opening between 2 and 6 nm in diameter. We show we can chemically influence the electric potential in a sufficient manner to gate the ion current.

The key element for these ionic nanoporous devices is the possibility of influencing the type of ions and the concentration of ions inside a nanopore by means of the surface charge of the pore walls. If the opening of the pore is comparable to the thickness of the electrical-double layer, the nanopore will be predominantly filled with ions of opposite charge to the charges on the surface[12]. This implies that a positively charged nanopore will be filled mainly with anions (for example chloride ions), and a negatively charged pore will be filled mainly with cations (for example potassium ions). Creating a junction between the two parts of the pore with positive and negative surface charges resulted in the formation of an ionic diode, as shown in ref.[6]. It follows directly from these results that arranging two such ionic diodes in series (Fig. 1) will lead to an ionic bipolar transistor[13]. The three regions of the pore create the emitter, gate and collector, if we compare the pore to a semiconductor device. In a semiconductor transistor, we have a direct way to apply voltage to the gate, changing the electric potential in the device. The same principle could be employed for nanofluidics[14]. In our ionic device, we influence the electric potential chemically by changing the surface charge of the pore walls. This was accomplished by changing the pH and concentration of the bulk electrolyte.

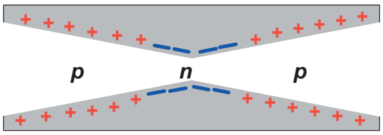

Figure 1. Scheme of a nanofluidic bipolar transistor.

A single hour-glass shaped nanopore provides the template for the transistor. The nanopore was prepared in a 12 μm thick poly(ethylene terephthalate) (PET) foil by the track-etching technique. Briefly, this technique is based on the irradiation of a polymer film with heavy ions and subsequent chemical etching of the damage tracks left by the heavy ions[15]. The double-conical shape was achieved by etching both sides of the membrane in 9 M NaOH. As described in ref.[3], etching of irradiated PET foils in a highly concentrated base causes the pore to be conical, therefore etching from both sides assures a double-conical (hour-glass) shape. The diameter of the small opening can be calculated by the electrochemical method[3] in a similar way as shown for a single conical nanopore. As a result of the fabrication process, the walls of the pores are covered with carboxyl groups at density of ca. 1 per nm^{2}[16]. The presence of these surface charges determines the behavior of the pores in electrolytes of various concentrations and pH. Figures 2a and b show current-voltage curves recorded through a single double-conical nanopore at KCl concentrations in the range from 0.1–1 M, and with a pH range from 3.7 to 9. Double-conical nanopores, in contrast to single conical nanopores, do not rectify ionic current due to the lack of broken symmetry in their electrochemical potential[4]. The nanometer-scale opening of our pores is also con-

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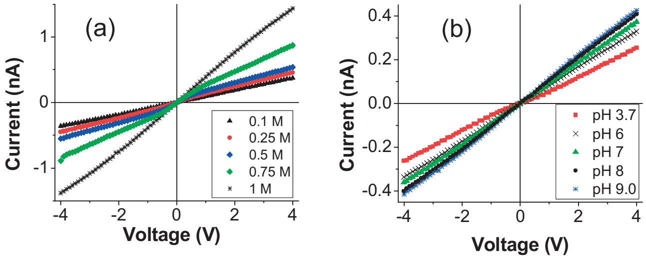

Figure 2. Current-voltage curves of a single, double-conical nanopore with openings of 2 nm (tip) and 180 nm (base) as a function of (a) KCl concentration at pH 7, and (b) pH, studied at 0.1 M KCl.

firmed by the saturation of ion currents at low KCl concentrations when measured at pH values at which the pore walls are negatively charged (pH 7 in Fig. 2a). This effect occurs when the size of the pore opening becomes comparable to the thickness of the electrical double layer in the system. In this case, the number of ions in the pore, and therefore the ion current, is controlled by the surface charge and becomes independent of the bulk concentrations[17]. Change of the pH of 0.1 M KCl between 3.7 and 9 changed the current value by ≅40%.

Preparation of a bipolar transistor from a single double conical nanopore requires patterning the surface of the pore walls such that there is a series of regions with positive, negative and then positive charges, or vice versa, (Fig. 1). Such surface patterning is much easier to achieve if we work with a nanopore whose cross-section changes along the pore axis, rather than a cylindrical pore. The main advantage of such a pore, such as the hour-glass shaped pores we used in this experiment, is the non-homogeneity of the distribution of a chemical introduced from only one side of the pore along the pore's centerline, once the system has achieved steady-state. If the chemical is a modifying agent that reacts with the surface, the modification will occur only where the concentration of modifying agent is sufficiently high[6]. Figure 3 shows the steady-state distribution of a chemical placed only on one side of a double conical pore, while the other side is in contact with a buffer. The curve is a graphical visualization of the following formula derived from the diffusion equation considered just along the pore axis x, with a valid approximation $a << A$.

$$c(x)=\begin{cases} c_0\left(\frac{1}{2}\cdot\frac{a\cdot L}{x\cdot A-a\cdot L}+1\right), & -L<x<0\\ c_0\frac{1}{2}\cdot\frac{a\cdot L}{x\cdot A+a\cdot L}), & 0<x<L\end{cases} \qquad (1)$$

There is a very steep decrease of the concentration in the middle of the pore where the narrowest opening is located. This assures a high concentration at the opening on the side where the chemical of interest is, and basically zero concentration at the other opening. Due to the symmetry of the nanopore, the concentration in the middle (x=0, Fig. 3a) is still high, half of the boundary condition c_0. Depending on the value of c_0, this can lead to at least partial modification in the center of the pore. To prevent this, we introduced a stopping medium opposite the modifying agent. In this way, the action of the modifying agent is weakened in the middle, and remains unaffected on the side where the modifying agent was added. In order to modify the surface of PET nanopores, we couple the surface carboxyl groups with amines using 1-Ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride (EDC)[18]. The reaction between the carboxyl groups and diamines changes the surface charge from negative to positive. This reaction has the highest rate at slightly acidic pH values between 5 and 6. The stopping medium used is 0.1 M phosphate buffer of pH 8 with added NaOH, giving the solution final pH in the range between 10 and 10.5. The stopping solution raises the pH in the center section of the pore out the optimal range for EDC modification, greatly reducing the rate at which the center section of the pore is modified.

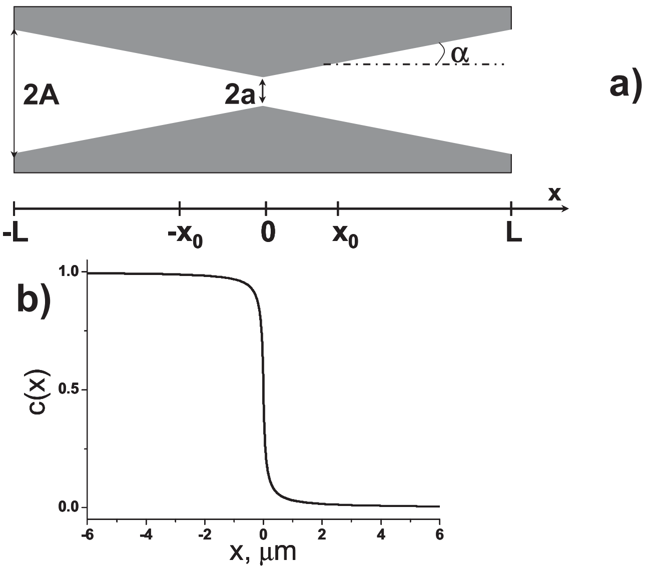

Figure 3. (a) Scheme of a double-conical nanopore (b) graphic representation of Equation (1), which is a solution of the steady-state one-dimensional diffusion problem for the following boundary conditions: $c(-L)=c_0=1$; $c(L)=0$. The pore diameters were 2 and 180 nm.

The modification was performed in two steps, each lasting 50 min, leading to the formation of positive charges near both openings of the pore and leaving the center of the pore intact. Figure 4 shows the subsequent modification steps together with the recorded current-voltage (I–V) curves in each step. The data are compared to the I–V curve for the unmodified pore (Fig. 4a). As expected, the first modification leads to the formation of an ionic diode (Fig. 4b)[6]. The second modification step, which brings a positive charge near the other opening, reduced the currents for voltages of both polarities (Fig. 4c). This current-voltage curve has the characteristics typical for a transistor in its off-state; an increase of current for low voltages up to some maximum value, and then the current becoming independent of the applied voltage past this point. This behavior is due to the formation of a charge depletion zone at one of the two junctions between the positive and

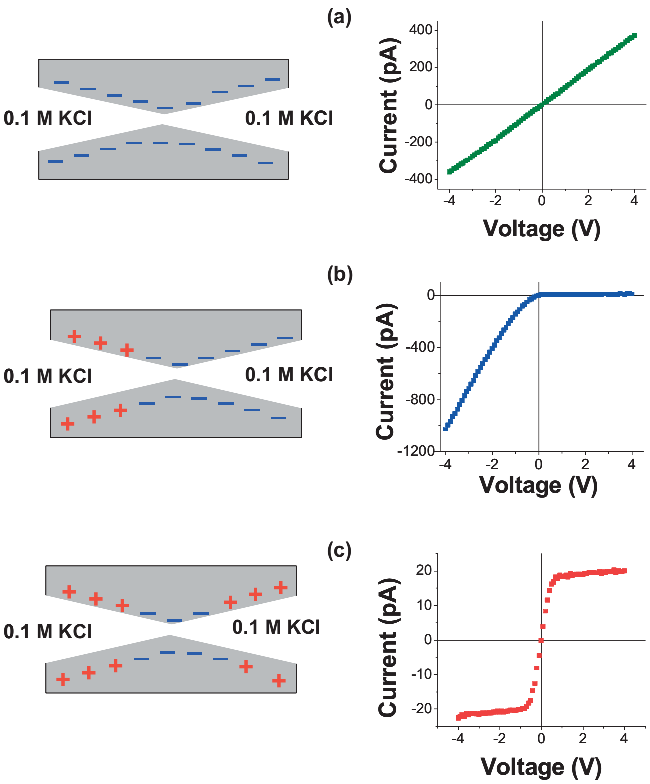

Figure 4. Formation of an ionic bipolar transistor. (a) Scheme of a double-conical nanopore with inside diameter 2 nm and outside diameters of 180 nm, together with its current-voltage curve recorded in 0.1 M KCl, pH 7. (b) and (c) show the same pore as in (a) after subsequent chemical modifications.

negatively charged portions of the pore walls[13]. This limiting current is 20 times smaller than the current before the surface patterning. The transistor shown in Figure 4c can be treated as an equivalent of a semiconductor pnp device.

Unlike other nanofluidic transistors reported[9,10], the BJT-like transistor created by the surface modification described here is not gated by any external electrical method by which the electrical potential of the walls may be changed. The gate in our devices is controlled chemically by changing the surface charge on the pore walls. This can be accomplished by changing the concentration and pH of the electrolyte[19]. An increase of the KCl concentration leads to a thinner electrical double-layer and a smaller electric potential at the emitter, base and collector parts of the device. As a consequence, at higher electrolyte concentrations, the three charged sections of the pore are less ion selective, and larger off currents are recorded (Fig. 5a and b). Our recordings also show even for very high KCl concentrations of 1 M, the device has distinct transistor characteristics, i.e. current plateaus, which again points to the truly nanometer scale of the pore opening.

The surface charge of nanopores can also be directly influenced by the electrolyte pH. At pH 6–8, both carboxyl and amine covered parts of the pore walls are charged, forming "+ - +" state and the transistor characteristics are very distinct (Fig. 5c). By lowering the pH, the carboxyl groups in the center of the pore are protonated, thus creating a pore with positively charged walls near the large exterior openings and neutral surface at the center of the pore: "+0+". Raising the pH to 9 has the opposite effect; the walls near the outside of the pore become charge neutral, while the center section remains negatively charged: "0–0". Our experiments show that the devices with reduced charge in the center of the pore operate predominantly in the open state (*I–V* curve for pH 5.4 in Fig. 5d). The transistor with just a negatively charged center of the pore shows the formation of the depletion zone at higher voltages of ≅3V. The plateau currents in this case are still significantly lower than the currents observed with the unmodified pore (Fig. 4a).

One of the determinative factors for nanofluidic transistor behavior is the size of the unmodified region ($2x_0$, Fig. 3). In order to understand which values of x_0 assure the formation of an ionic transistor we solved the Poisson-Nernst-Planck (PNP) equations (Eq. 2) for a single hour-glass pore with the surface charge pattern as shown in Figure 1.

$$\begin{cases} -\varepsilon_0\varepsilon\Delta\varphi = (C_{k+} - C_{Cl-})\cdot \mathrm{F} \\ \nabla\cdot D_i(-\nabla C_i - \frac{z_i}{RT}\cdot F\cdot C_i\cdot\nabla\varphi) = 0) \end{cases} \qquad (2)$$

In Equation (2), φ stands for electric potential, F is the Faraday constant, D_i is a diffusion coefficient equal to $2\cdot10^{-9}$ m^2 s^{-1} for K$^+$ and Cl$^-$, C_i stands for ionic concentration, z_i is charge, ε - dielectric constant, and i indicates K$^+$ or Cl$^-$.

Obviously, the value of the saturation (plateau) current and voltage at which the saturation occurs change with x_0, nanopore shape, KCl bulk concentration and surface charge.

When x_0 is too small, the formation of the depletion zone (at $x = x_0$) is hindered due to a low ionic selectivity of the $2x_0$ segment, as well as the proximity of the enhanced concentration region (at $x = x_0$)[13] and the depletion zone. Too lengthy segment $2x_0$ is also unfavorable because the pore radius increases, and thus ionic selectivity decreases, with the coordinate x. As follows from this intuitive picture, for a given voltage there must be a minimum of the plateau current where the depletion zone is fully formed. This is exactly what we obtained in the simulations. Figure 6a shows calculations of ionic currents for a single double-conical nanopore of pore openings a=4 nm and A=100 nm, in 0.1 M KCl and 1 V. The surface charge density was assumed as: 0.5**e** nm^{-2} at the regions $x\in\{-L,-x_0\}\&\{x_0,L\}$, and –0.5**e** nm^{-2} for $x\in\{-x_0,x_0\}$. These parameters are always used in the calculations unless stated otherwise. The transistor-like behavior, i.e. existence of the plateau current, was indeed observed only for $x_0\cong\{30$ nm, 2 µm$\}$.

Experimental surface charge density (σ) distribution inside the nanopore is not readily available, because it involves many parameters such as pH distribution inside the pore during chemical modification. In our previous publication [6] we estimated the x_0 to be ca. 100 nm for a conical geometry. We

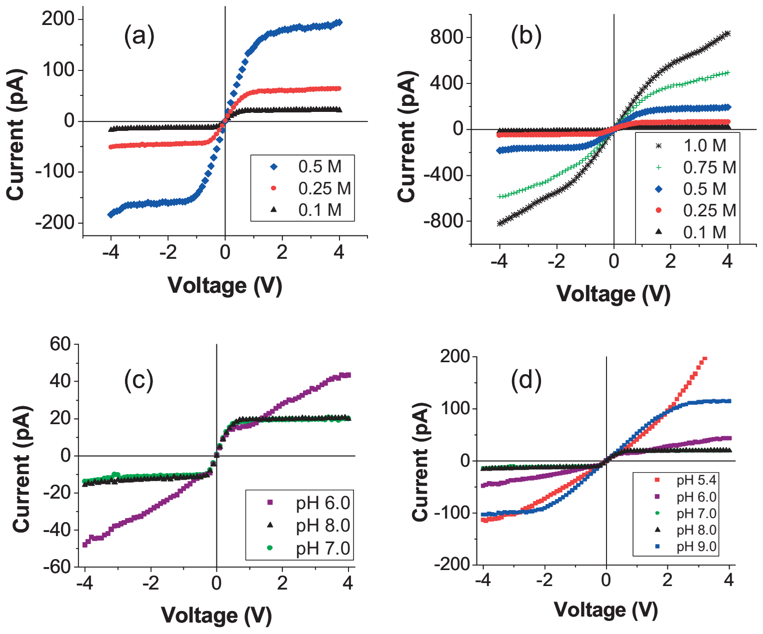

Figure 5. Functioning of an ionic transistor. (a,b) dependence of *I–V* curves of the transistor on KCl concentrations at pH 7; (a) is a magnified part of (b); (c,d) dependence of *I–V* curves of the transistor on pH of 0.1 M KCl solution; (c) is a magnification of (d) showing details for pH values between 6 and 8. This pore had openings of 200 and 3 nm.

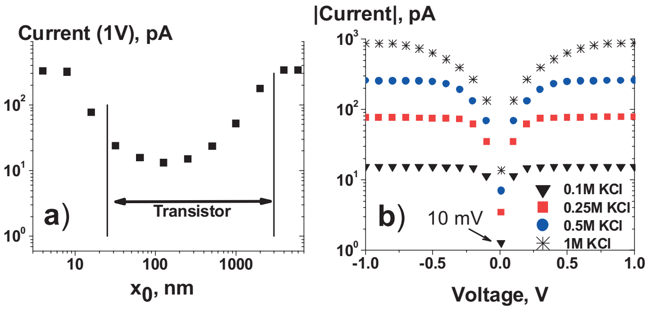

Figure 6. a) Dependence of the calculated currents on the x_0 position (Fig. 3) for an ionic transistor shown in Figure 1 at 1 V. b) Calculated I–Vs for x_0=±64nm, and different KCl bulk concentrations, as indicated in the Figure. 10 mV was the lowest voltage for which the current was calculated.

believe this value can serve as a rough estimate for a double conical pore as well. Figure 6b shows simulated *I–V* curves for an ionic transistor in different KCl concentrations, with x_0 placed at ± 64 nm. Indeed, the calculated currents and the experimental data agree semi-quantitatively. The calculated values of the ion current plateau represent the measurements shown in Figures 5a and b: the current value increases with an increase of KCl concentration, and the saturation of ion currents occurs at higher voltages.

Calculated *I–Vs* as a function of pH (Fig. 7) also show the same behavior as our experimental data (Figs. 5c and d). Depending on pH, the nanopore segments could be positive (“+“), negative (“–“) or neutral (“0“). At neutral pH, our modified nanopore acts as “+ - +“ transistor, showing the lowest currents. Basic pH makes the outer parts of the nanopore uncharged, forming a junction of a type “0-0“, which shows larger currents than the “+ - +“ device. The carboxylated tip becomes uncharged at acidic pHs leading to the formation of “+0+“ junction. This last configuration has the weakest capability to gate ion currents, and it allows the largest currents to flow. This device did not show existence of the plateau current at 1 V.

In conclusion, we fabricated BJT-like transistors from single double-conical (hour-glass) shaped nanopores using controlled modification of the nanopore walls. Ion currents recorded at various stages of the modification ensure that we have a true pnp-like structure. Both experimental measurement and theoretical modeling of the ion current showed that the device can be switched from its off-state behavior, where the ion flux through the nanopore is independent of the applied voltage and limited to some small leakage value, to on-state behavior. This on/off switching was accomplished by changing pH and concentration of the bulk electrolyte. Future applications of this material platform are the control of flux of ions and charged molecules in nanofluidic systems.

Experimental

A single-pore membrane was placed between two chambers of a conductivity cell, as described in [3]. The chambers were filled with 0.1 M KCl solutions buffered to various pH with a phosphate buffer and adjusted with 0.1 M HCl and 0.1 M NaOH. Current recordings were taken using lab-made Ag/AgCl electrodes and measured with a 6487 Keithley picoammeter/voltage source.

Calculations of ion currents were performed using 2-D axial symmetry of a double-conical geometry, with L = 6 µm, a = 4 nm, A = 100 nm (Fig. 3). Pore entrances were connected to the 2 µm square reservoirs. Meshing was 1 nm; further mesh decrease did not

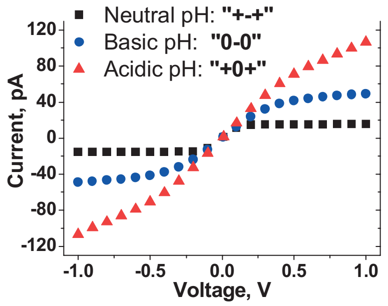

Figure 7. Calculated current-voltage curves for an ionic transistor as a function of pH. At neutral pH both amines and carboxyls are charged, forming “+ - +“ junction. At acidic and basic pH values, we obtain “+0+“ and “0-0“ junctions, respectively.

substantially change the total current. All calculations were performed using COMSOL 3.3.a software.

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