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The rectification of mono- and bivalent ions in single conical nanopores

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ABSTRACT

The polyethylene terephthalate (PET) films were irradiated with single 6.9 MeV/u $^{58}Ni^{19+}$ ions at the Lanzhou Interdisciplinary Heavy Ion Microbeam (LIHIM), and single conical nanopores were produced by asymmetric chemical etching of the latent ion tracks. Then, the current-voltage (I–V) characteristic was measured in LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$ solution at different concentrations to study the transport properties of different cations in the single conical nanopores respectively. The measured I–V data showed that the conical nanopores have rectified transportation of these cations at the applied voltage of between +2 V and −2 V. The rectification coefficient γ of the mono- and bivalent ions was determined in their solution of 0.0001–1 M measured at 1 V, the result showed that the rectification coefficient is dependent on the valence of the ions and the electrolyte solution.

1. Introduction

In the last two decades, there is an rapid development in nanotechnology which have induced important applications of single nanopores and nanochannels in the fields of molecular sensors, nanofluidic power source, nanofluidic devices, mass transport, DNA sequencing and so on [1–6]. Due to the symmetry breaking, single conical nanopores show characteristics of ion-current rectification, which has a great potential in the application to ion separation, power supplier and chemical valve [7]. Recently, many studies have reported on the influence of electrolyte concentration and PH, surface charge density, orifice diameter, cone angle, pressure, scan-rate on the rectification of single conical nanopores [8–17]. However, most of the electrolyte solutions used in these studies were potassium chloride [8–17], there are very few reports on the behavior of other electrolyte solutions in single conical nanopores [6]. Ions with different valence states have different hydrated ionic radius, Debye screening length and shielding effect, which may result in different effects and impacts in the nanoscale devices. Therefore, in this work we focused on the rectification of several species of mono- and bivalent ions in the single conical nanopores.

In order to understand the transport of ions in the conical nanopores, we used polyethylene terephthalate (PET) film bombarded by single high energy heavy ions in the Lanzhou Interdisciplinary Heavy Ion Microbeam (LIHIM), and the single latent ion track was chemical etched to prepare the single conical nanopores (Fig. 1(a)). Then the conduction of different cations (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) in the single conical nanopores was measured, and the rectification coefficients of these ions and results were discussed.

2. Experimental

2.1. Sample irradiation

The single ion hit system at LIHIM has been described previously [18,19]. In short, the beam is adjusted to several ions per second and the pre-sample ion detector (PSID) or behind-sample ion detector (BSID) can produce a signal when one ion hits the sample. Then, this ion-hit signal is coupled to a 6 kV high voltage beam switch, which turns off the ion beam within 1 microsecond. The pre-sample ion detector is a channel electron multiplier (CEM, #KBL1010, Sjuts Optotechnik) mounted in the vacuum chamber towards the vacuum window. The vacuum window is coated with gold to enhance the production of secondary electrons. The behind-sample ion detector is an Au-Si surface barrier detector. Because the thickness of the PET film is only 12 μm (far less than the ion range, the range of 6.9 MeV/u $^{58}Ni^{19+}$ in PET is 84.51 μm), both the PSID and the BSID can be used. Fig. 2 shows the SEM

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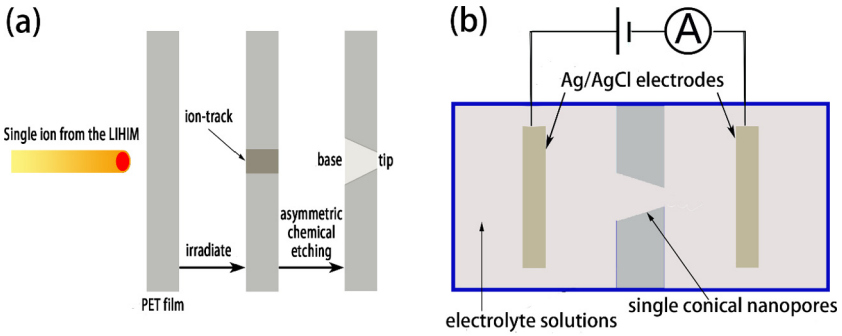

Fig. 1. (a) Schematic of the preparation process of single conical nanopores. (b) The setup for the I–V measurement of nanopores.

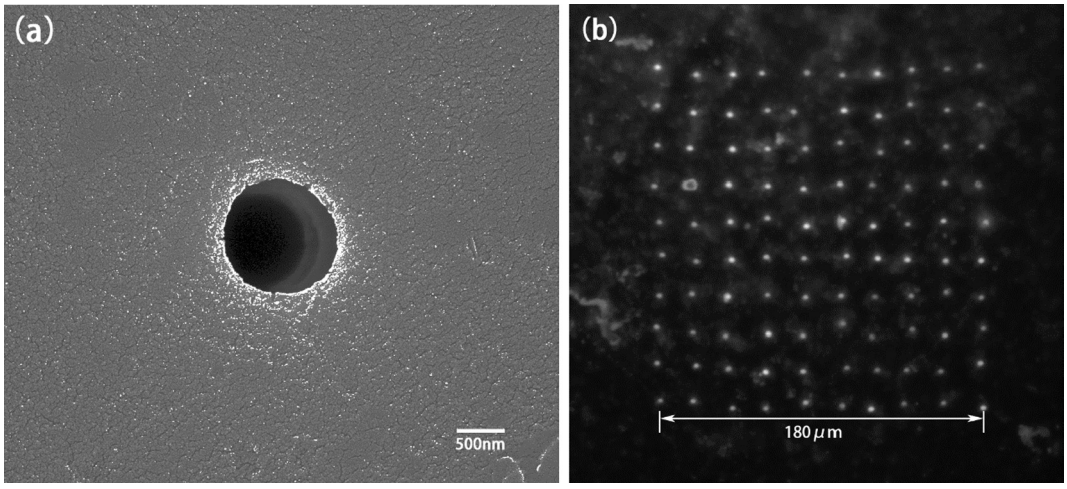

Fig. 2. (a) SEM image of the single pore PET sample (b) 10 × 10 single-ion pattern on PET film [19].

image of a single pore in PET irradiated by single 6.9 MeV/u $^{58}Ni^{19+}$ ion and 10×10 single-ion pattern on PET film irradiated by 25 MeV/u $^{86}Kr^{26+}$ ions [19].

2.2. Chemical etching

The latent ion tracks were chemical etched from one side in 5 M sodium hydroxide solution at 50 °C, and stopping solution (1 M HCOOH and 1 M KCl) was used in the other side to neutralize the etchant and slow down the pore-opening etching when the pore penetrated the PET film. During the etching process, the transmembrane ionic current was recorded by a Keithley 6482 picoammeter/voltage source. Its value was less than a few picoampere before the nanopores opening and increased to more than 100 pA quickly within several seconds when the conical nanopores opened. The chemical etching was stopped when the current reached 1 nA. The larger end of the conical pore is called "base" and the smaller one is called "tip". The base size was measured by scanning electron microscope, and the tip size was calculated using Eq. (1) [20]:

$$d_{tip} = \frac{4\rho l}{\pi R_{pore} d_{base}} \quad (1)$$

where ρ is the resistivity of the electrolyte (we used the 1 M KCl solution), l is the length of the pore, R_{pore} is the resistance of the conical pore filled with electrolyte, and d_{base} is the base diameter. In this experiment, the d_{base} of the nanopore sample (#7) is 1200 nm (obtained by SEM measurement), and the d_{tip} is 9 nm as calculated using formula (1).

2.3. Ion current measurement

In the study of the transport properties of cations in the conical nanopore (#7), the current-voltage (I–V) characteristic curves were measured by a Keithley 6482 picoammeter/voltage source in the LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$ solutions at concentrations from 0.0001 M to 1 M (the setup shown in Fig. 1(b)). The scanning voltages applied to the Ag/AgCl electrodes were from −2 to +2 V. The '−' means that the negative electrode was placed in the 'base' end and the positive electrode was placed in the 'tip' end, while the '+' was just opposite. The measurements were performed at room temperature. In order to describe the intensity of ion-current rectification, the current rectification coefficient $\gamma = |I(U_-)/I(U_+)|$ was defined and calculated at given voltages.

3. Results and discussion

Fig. 3 shows the I–V curve of the same conical nanopore measured in the LiCl, NaCl, KCl, solutions at concentrations from 0.001 to 0.316 M. All the current-voltage characteristic curves show significant asymmetry and nonlinearity. The ionic current measured at positive potentials is much lower than that at the same negative potentials, which demonstrates the ion-current rectification in single conical nanopores. In addition, the current values, i.e. the conductance of the nanopore in these solutions, demonstrate that $I_{KCl} > I_{NaCl} > I_{LiCl}$ at the same concentration and voltage (shown in Fig. 3(d)). This conductance sequence in the solutions is opposite to the size of hydrated ionic radius of those cations ($K^+ < Na^+ < Li^+$) [21], and the smaller hydrated ionic radius

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