Fabrication of nanofluidic diodes with polymer nanopores modified by atomic layer deposition

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Surface charge distribution is a crucial factor for the ionic transport properties inside nanopores. Modifying the surface charge inside a single conical nanopore can greatly affect the rectification behavior of the ionic current through the nanopore and afford nanofluidic diodes. In this work, we describe a new method to fabricate nanofluidic diodes by atomic layer deposition (ALD) on conical track-etched nanopores. Thorough investigation of the ionic transport behavior through ALD-modified polyethylene terephthalate (PET) nanopores is carried out. Our results demonstrate that ALD is a simple and effective method to modify the inner surface of the polymer nanopores for fabricating nanofluidic devices. In addition, we also investigate the stability of the ALD-modified nanopores, and the results suggest that the long-time stability could be compromised by high voltage applied along the nanopore. © 2014 AIP Publishing LLC.

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I. INTRODUCTION

Track-etched polymer nanopores have attracted wide attentions, as they exhibit interesting ionic selectivity and ionic current rectification.^{1–7} Previously, researchers have demonstrated that the rectification effect is due to the asymmetric geometric nanopore shape and/or an inhomogeneous charge distribution on the pore wall.^{5,8–11} The current rectification behavior is correlated with the ionic transport properties inside nanopores, and thus much work has been devoted to study this behavior, in order for designing sophisticated functional nanofluidic devices.

Track-etching is an effective method to fabricate nanopores with a variety of the pore shapes (e.g., cylindrical or conical).⁷ The inner surface of the track-etched nanopores can be further modified to anchor various functional groups. For example, amino-terminated molecules or pH/thermo-responsive polymer molecules can be immobilized on the pore surface by certain types of chemical reactions;^{12–17} metals, such as gold, can be deposited on polymer nanopores by an electroless deposition method;^{18,19} and physical adsorption of surfactants is another effective approach to modify the nanopore surface.^{20–22} Provided great progresses in the development of the surface modification methods, difficulties still exist in precisely controlling the modification process and the stability of the modified nanopores.

Atomic layer deposition (ALD) has exhibited many merits in modifying nanoscale systems (e.g., flexible choices of precursors and materials, flexible processing conditions, large area uniformity, excellent conformality, and reducing the noise level of nano-devices).^{23–26} Among

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these merits, the most attractive advantage for ALD to be used in modifying track-etched nanopores is its accurate and straightforward control of the thickness of the deposited films. In this work, we demonstrate a new type of devices with ALD modified polymer nanopores. The polymer nanopores were fabricated on polyethylene terephthalate (PET) foils by the track-etching method to generate a single conical nanopore on each foil. Then, the nanopore was deposited with Al_2O_3 by ALD. By controlling the modified region, the rectification effect could be enhanced and the preferential current direction could be reversed, which could lead to new types of nanofluidic devices.

II. MATERIALS AND METHODS

A. Fabrication of single conical nanopores

The foil of PET with $12\text{ }\mu\text{m}$ thick was irradiated with single swift heavy ions (Au) of energy 11.4 MeV/nucleon at the linear accelerator UNILAC (GSI, Darmstadt, Germany). 1 h UV irradiation ($4.2 \times 10^3\text{ }\mu\text{W/cm}^2$) was performed on both sides of the foil prior to the following chemical etching process. During the asymmetric etching process, the foil was mounted between two chambers of a custom-designed cell. One of the chamber was filled with the etchant (9M NaOH), and the other chamber was filled with the stop medium (1M HCOOH + 1M KCl). Two platinum electrodes were used and 1 V voltage was applied. A Keithley 6487 picoammeter was used to monitor the break-through current. Once the etchant penetrates the foil, the current increases steeply and the acidic stop medium immediately neutralizes the basic etchant and reduces further etching. With this asymmetric etching method, single conical nanopores were obtained. The diameter of the larger opening (i.e., base side) of the nanopore (D_{base}) was calculated based on bulk etching rate, and the diameter of the smaller opening (i.e., tip side) of the nanopore (D_{tip}) was calculated from the conductance by the following equation:

$$D_{\text{tip}} = \frac{4LI}{\pi\kappa UD_{\text{base}}}, \quad (1)$$

where L is the length of the nanopore, I is the ionic current, U is the applied voltage, and κ is the conductivity of 1M KCl aqueous solution, respectively.

B. ALD method

ALD of Al_2O_3 was performed in a home-made flow reactor at 120°C with trimethylaluminum (TMA) and H_2O as the precursors. Since our nanopore structure has a fairly high aspect ratio, prolonged purging times were used to completely remove the excess precursors. The growth rate per cycle of the Al_2O_3 film could be estimated by measuring the total film thickness divided by the total cycle number. Therefore, we can use the ALD method to precisely tune the nanopore size in a subnanometer level through controlling the number of deposition cycles. As a result, a conical-shaped nanopore with an Al_2O_3 coating layer was obtained. In our experiments, two types of the polymer foils were used, i.e., polycarbonate (PC) and PET. The PET nanopores with various diameters were deposited by 25 cycles of Al_2O_3 , respectively. Commercial PC nanoporous foils were deposited for 300 cycles.

C. Ionic current recordings

A foil with a single conical nanopore was mounted onto the center of our home-designed cell. Two chambers were filled with KCl solutions, and Ag/AgCl electrodes were used on both sides, respectively, to measure the ionic current. The ionic current was acquired by a picoammeter (Model 6487, Keithley Instruments Inc., Cleveland, OH). The voltage applied across the nanopore was scanned from -1 V to $+1\text{ V}$ with a step of 0.1 V for majority of the experiments. For some stability tests, the voltage was scanned from -5 V to $+5\text{ V}$. Milli-Q water ($18.2\text{ M}\Omega\cdot\text{cm}$) was used in all experiments for preparing the KCl aqueous solutions and rinsing the equipment. The concentration of KCl was 0.1M or 1.0M .

III. RESULTS AND DISCUSSION

Track-etched PET nanopores are negatively charged in aqueous solution due to the presence of surface carboxylate groups on the pore wall.¹¹ In order to get various rectification behaviors, we chose aluminum oxide to modify the nanopore surface, because aluminum oxide has a nominal isoelectric point at pH 9.0,²⁷ and thus it is weakly positively charged in neutral solutions (the surface charge density is about 2 mC/m²).²⁸ Therefore, pronounced discrepancy of the ionic current-voltage curves should appear if partial of or the entire nanopore is coated with aluminum oxide as compared to the uncoated nanopore.

In our experiments, we tried to verify that aluminum oxide can be indeed deposited into the nanopore by our ALD method. 300 ALD cycles of Al₂O₃ were deposited on commercial nanoporous PC foils (nanopore diameters are around 400 nm). After the deposition, we gently wiped the surface of the PC foil with sand paper to remove the Al₂O₃ layer deposited on the outer surface of the PC foil, and then immersed the PC foils into methylene chloride to dissolve the PC template and expose the ALD Al₂O₃ layer deposited inside the nanopores. As shown in scanning electron microscopy (SEM) images (Fig. 1), micrometer-long Al₂O₃ nanotube array was obtained. As shown in Fig. 1(b), the wall thickness of the Al₂O₃ nanotubes was about 60 nm, so the deposition rate was 0.2 nm per ALD cycle. We also noticed that the length of the obtained Al₂O₃ nanotubes was only about 2 μ m, which is much shorter than the length of the nanopores (i.e., 5 μ m, as this is the thickness of the PC foils), suggesting that only partial of nanopores was covered by ALD Al₂O₃. This is because we limited the precursor delivery of TMA during the ALD process, and the amount of the precursor was only enough to cover the area near the nanopore entrance, but not deep inside. With this strategy, we could use ALD to partially change the surface charge distribution inside the nanopore in order to obtain nanofluidic diodes with different charge polarity patterns. Hence, next, as schematically illustrated in Fig. 2, we used ALD to deposit Al₂O₃ from only one side of the PET conical nanopores to cover only one end by the positive charged Al₂O₃ layer.

A. Al₂O₃ deposited at the tip side

Fig. 3 shows the current-voltage (*I*-*V*) curves measured in 0.1M KCl and 1M KCl for a single conical PET nanopore before and after 25 cycles of the ALD Al₂O₃ deposition at the tip side. Prior to the ALD, the diameters of the tip and the base were 10 nm and 455 nm, respectively. After the deposition, the ionic current significantly decreased at both positive and negative biases. Especially at -1 V, the ionic current decreased from -0.7 nA to -0.1 nA for 0.1M KCl, and from -2.7 nA to -0.18 nA for 1M KCl, which was more than one order of magnitude. This decrease in current was due to the shrinkage of the tip entrance after the deposition. From the 1M KCl data, we calculated the tip diameter of the nanopore before and after deposition Al₂O₃ by Eq. (1) and found that D_{tip} decreased from 10 nm to 0.66 nm. The deposition rate

FIG. 1. SEM images for 60-nm-thick Al₂O₃ nanotubes. Polymer membrane was dissolved with methylene chloride after the deposition.

FIG. 2. Changes of surface charge distribution on the pore wall of conical nanopore after various regional modifications with Al_2O_3 .

calculated from these data was 0.187 nm per ALD cycle, which is comparable with the previously obtained growth rate (i.e., 0.2 nm per cycle).

We use the rectification degree Q , as defined in Eq. (2), to denote the rectification behavior of the nanopores

$$Q = |I_{-1V}/I_{+1V}|. \quad (2)$$

For the uncoated nanopore measured in 0.1M KCl, the ionic current under negative bias was larger than the current under the positive bias with same absolute value ($Q = 3.47$). This can be explained by the enrichment and depletion theory, where the ionic concentration inside a negatively charged nanopore enriches/depletes as a negative/positive bias is applied.^{9,29} According to the same theory, the rectification effect should inverse its polarity (i.e., $Q < 1$), if the polarity of the surface charge near the tip is switched to positive,³⁰ and, indeed, the rectification degree, Q , became 0.79 after the Al_2O_3 deposition (surface became positively charged), as shown in Fig. 3(a). This indicated that our regional modification of the nanopore surface was indeed successful, and the ionic selectivity switched from cation-selective to anion-selective.

We also noticed that for the measurements performed in 1M KCl, the rectification degree Q changed from ~ 1 (almost no rectification) to 0.22 after the Al_2O_3 deposition, as extracted from the I - V curves shown in Fig. 3(b). With the Al_2O_3 coating, the rectification in 1M KCl was 3 times stronger than that in 0.1M KCl. We attribute this phenomenon to the matching-up of the nanopore size and Debye screening length in solution, i.e., the rectification effect becomes most pronounced when the nanopore radius matches up the Debye screening length.³¹ The Debye screening length is calculated from the following equation:³²

$$\lambda_D = \sqrt{\frac{\epsilon k_B T}{2q^2 N_A c}}, \quad (3)$$

where ϵ is the solution dielectric constant, k_B is the Boltzmann constant, T is the temperature, q is the charge an ion carriers, N_A is the Avogadro number, and c is the ionic concentration of monovalent electrolyte (in mol/m^3). At room temperature (298 K), the calculated Debye screening length is 0.97 nm for 0.1M KCl and 0.31 nm for 1M KCl. Prior to the Al_2O_3 deposition, the tip diameter of the nanopore was 10 nm (i.e., 5 nm in radius), which was an order of magnitude larger than the Debye screening length for 1M KCl. Thus, the surface charge effect was largely screened by the ions inside the nanopore and a linear I - V curve was observed. However, after 25 cycles of ALD Al_2O_3 , the tip diameter decreased to 0.66 nm (i.e., 0.33 nm in radius), which was very close to the Debye length in 1M KCl (i.e., 0.31 nm), and much closer as compared with that in 0.1M KCl (i.e., 0.97 nm). Therefore, a strong reverse rectification effect was found in 1M KCl.

Additionally, we noticed that the I - V curves for the modified nanopore were much smoother than those of the uncoated nanopore. This implied that the ALD Al_2O_3 coating may also be beneficial for reducing the fluctuation of the ionic concentration inside the nanopore.

FIG. 3. Current-voltage characteristic curves of a conical nanopore in 0.1M KCl (a) and 1M KCl (b), respectively. The applied voltage was from -1 V to $+1$ V. The tip side of nanopore was modified with 25 cycles of the Al_2O_3 deposition. The diameter of tip was decreased from 10 nm to 0.66 nm after deposition. The blue and red lines represent before and after deposited Al_2O_3 film, respectively.

B. Al_2O_3 deposited at the base side

Prior to the deposition, the diameters of the tip and the base ends were 61 nm and 471 nm, respectively. After 25 cycles of Al_2O_3 deposition (about 4.6 nm in thickness) from the base side, we found that the rectification degree of the nanopore had an appreciable increase (Fig. 4): i.e., Q changed from 8.6 to 17.2 for 0.1M KCl and from 1.5 to 3.7 for 1M KCl, but the polarity of rectification direction remained the same. This is because the polarity of the surface charge near the tip side, which determines the ionic selectivity, was still negative, as no deposition occurred near the tip side. The enhancement of the rectification degree originated mainly from the slight decrease of current under positive bias, which is quite consistent with our previous observations.²⁰

C. Al_2O_3 deposited at both sides

Fig. 5 shows the I - V curves measured in 0.1M KCl for a PET conical nanopore ($D_{\text{tip}} = 9.5$ nm and $D_{\text{base}} = 569$ nm) before and after 25 cycles of Al_2O_3 deposition from both sides. Interestingly, the Al_2O_3 coated nanopore showed some peculiar gating behavior, as the current remained close to zero until the applied voltage exceeded 300 mV. So far, we were uncertain about the exact reasons to this behavior, but one possibility might be that the deposited Al_2O_3 almost blocked the tip opening of the nanopore and resulted in the voltage

FIG. 4. Current-voltage characteristic curves of a conical nanopore in 0.1M KCl (a) and 1M KCl (b). The applied voltage was from -1 V to $+1$ V. The base side of nanopore was modified with 25 cycles of the Al_2O_3 deposition. The thickness of Al_2O_3 film was about 4.6 nm. The diameter of tip was 61 nm. The blue and red lines represent before and after deposited Al_2O_3 film, respectively.

FIG. 5. Current-voltage characteristic curves of a 9.5 nm conical nanopore in 0.1 M KCl when both sides were modified with 25 cycles of the Al_2O_3 deposition.

dependence of the ionic current, as similar behaviors were found in small double conical nanopores. Nevertheless, this behavior might be useful for future designing nanofluidic devices.

D. Stability of the Al_2O_3 modified nanopores

A tip side modified nanopore (D_{tip} was 0.93 nm after 25 cycles of ALD) was used to test the stability of the Al_2O_3 modified nanopores. I - V curves after immersed in 1 M KCl for certain periods were recorded. As the immersing time increased from 0 h to 20 h, the ionic current under positive bias gradually decreased while the current under negative bias did not change too much (Fig. 6), and the rectification degree changed from 0.21 to 0.65 (i.e., the rectification effect became weaker) accordingly. This is likely due to the gradual dissolution of the deposited several-nanometer-thick Al_2O_3 in aqueous solution.

High voltage may even accelerate this dissolution process. As shown in Fig. 7, using the same nanopore as used in Sec. III A, the current-voltage curves were stable when applied voltage was below 2 V, and the polarity-inversed rectification behavior was consistent (i.e., $Q < 1$). But, if the external voltage exceeded 5 V, the Al_2O_3 modified nanopore quickly broke down: negative current had a steep increase and rectification direction switched back to that of the uncoated case (i.e., $Q > 1$), suggesting that the Al_2O_3 coating was likely dissolved. Further study to stabilize this ALD coating at high voltage is still ongoing.

FIG. 6. Current-voltage characteristic curves of the 0.93 nm conical nanopore with various immersing times in 1 M KCl. The tip side of nanopore was modified with 25 cycles of the Al_2O_3 deposition.

FIG. 7. Current-voltage characteristic curves of the 0.66 nm conical nanopore under various applied voltages in 1M KCl.

IV. CONCLUSIONS

We have investigated the modification of the polymer nanopores with the atomic layer deposition method. Various patterns of the inner surface charge distribution were obtained by ALD of Al_2O_3 with designed thickness. The direction/polarity and the degree of the ionic current rectification can be tuned by this method. Additionally, the stability of the ALD Al_2O_3 modified nanopores were also studied and the results indicated that long-time immersing in electrolyte could lead to the dissolution of the Al_2O_3 coating, and high applied voltage could accelerate this dissolution process, both of which are not favored for maintaining the diode behavior of the nanofluidic system. We believe that the results reported in this work are useful for designing sophisticated high-quality nanofluidic devices, though more efforts are still much needed to develop methods for modifying the nanopore surface.

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