4 - 27 Study the Rectification Effect of Single Graphene/PET Nanopore

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Solid state nanopores or nanochannels prepared in polymer[1,2] and semiconductor films[3] have shown interesting transport phenomena, because of their diameters at the nanoscale and positive or negative charges on their walls. Graphene is an ideal material for developing solid state nanopores not only due to its atomic scale thickness, high mechanical strength and chemical stabilities but also because of the impermeability of the pristine single layer graphene to all atoms and molecules except protons[4]. As the single Graphene/PET (G/PET) nanopore is the elementary building block for nanoporous membrane, the understanding and control of its individual ionic transport properties are also crucial in protein separation, water desalination, and bio-molecule detection using arrays of identical nanopores. Here, the single G/PET nanopore was successfully prepared by using ion irradiation technology and asymmetric etching method[5] and the corresponding ionic transport properties were investigated in detail.

The I-V measurements were performed on G/PET nanopore system and the obvious non-linear curves were confirmed with the KCl electrolyte concentration from 0.001 to 1 mol/L. Five typical I-V curves with KCl electrolyte concentrations ranging from 0.002 to 0.01 mol/L are picked out (shown in Fig. 1(a)). The G/PET nanopore system shows higher current at positive voltage and lower current at negative voltage, which means that the rectification effect happened in G/PET nanopore system. The rectification is used to evaluate the rectification ability of G/PET nanopore. In Fig. 1(b), the rectification ratio as a function of KCl electrolyte concentration from 0.001 to 1 mol/L at different voltages was depicted. It can be seen that the rectification ratio increases with decreasing the electrolyte concentration from 1 to 0.01 mol/L and reaches a maximum value of 14 at 0.01 mol/L under the 4 V bias voltage. After this point, the rectification ratio begins to decrease with further decreasing the electrolyte concentration. It is well known that the variation of rectification ratio at different electrolyte concentrations is linked to the thickness of DDL. The higher electrolyte concentration will result in thinner DDL thickness according to Debye-huckel theory and the corresponding lower rectification effect. Meanwhile, when the DDL begins to overlap in the pore tip area, the G/PET nanopore will exhibit the strongest ion rectification effect. In our case, the calculated thickness of DDL is around 3 nm with KCl electrolyte concentration of 0.01 mol/L and begins to overlap in the tip area (diameter of 6.2 nm). The DDL overlap effect on the nanopore conductance is more significant and that will influence the ionic conductance at the "on" and "off" states. As shown in Fig. 1(b), before the DDL overlapping, the rectification ratio in KCl exhibits a strong voltage dependence, *i.e.* the higher voltage was applied, the higher rectification ratio can be obtained. When decreasing the electrolyte concentration further, the larger DDL overlapping portion will be formed in the tip area and the voltage dependent rectification ratio disappeared.

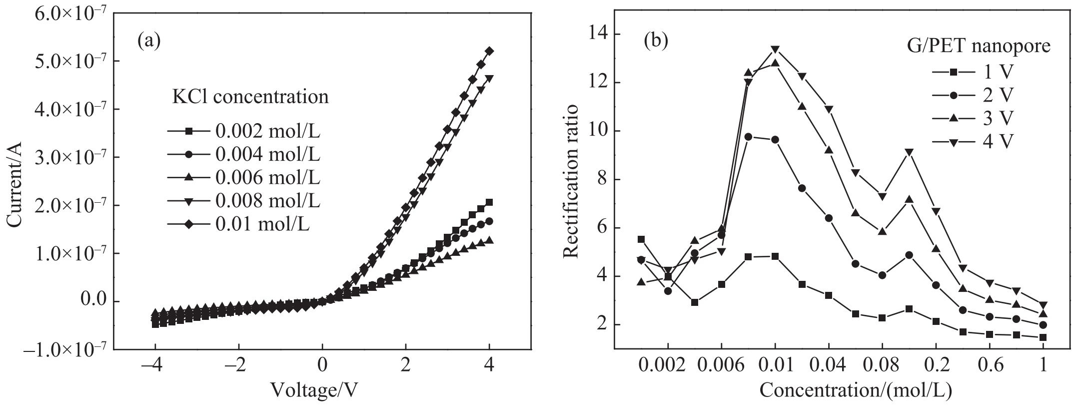

Fig. 1 Rectification of G/PET nanopore. (a) current-voltage curves of G/PET nanopore with an applied voltage ranging from -4 V to 4 V in KCl electrolyte with different concentrations, (b) The ion rectification ratio as a function of KCl electrolyte concentration at different applied voltages.

The effect of pH on rectification behavior was studied for a series of pH values and only hydrochloric acid was used to adjust the electrolyte pH from 2 to 5 in order to avoid introducing other anions in the system. In order to get better rectification effect in G/PET nanopore according to our previously results, the KCl electrolyte solution with concentration of 0.002 mol/L is used for further studies. Fig. 2 (a) gives the typical I-V curves of KCl electrolyte solution at different pH values. All the curves exhibit excellent ionic diode effect behavior in which the “on” state appears at positive voltage while the “off” state connects with negative voltage. The rectification ratio was also used to evaluate the rectification effect of G/PET at different pH conductions. The rectification ratio as function of pH value is shown in Fig. 2(b). The maximum rectification ratios in Fig. 2(b) is around 190. To the best of our knowledge, the rectification ratio of 190 is the highest value obtained in single nanopore system up to now.

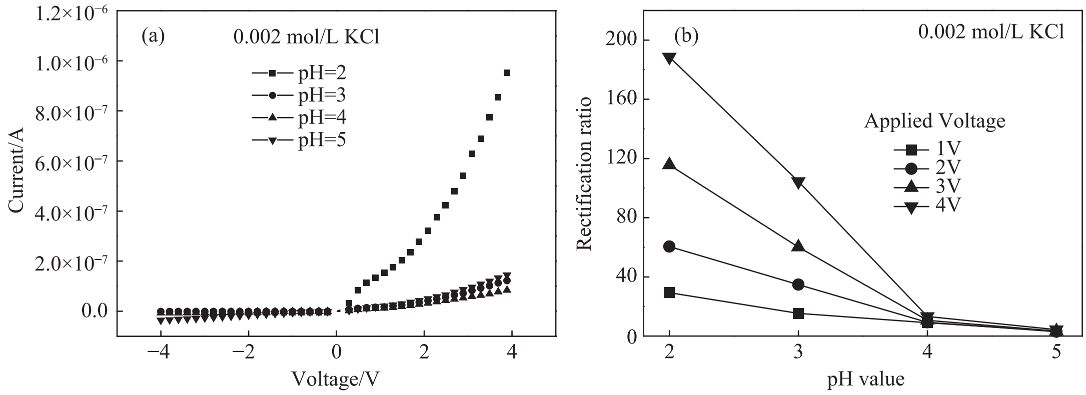

Fig. 2 (a) Current-voltage curves of G/PET nanopore with scan voltage from −4 V to 4 V at different pHs, (b) Rectification ratio of G/PET nanopore as function of pH value at different voltage bias. The KCl concentration used here is 0.002 mol/L.

In our current work, although the large rectification ratio up to 190 was obtained in G/PET nanopore in the acidic conditions, however, there are still some factors that can influence the ion rectification effect of G/PET nanopore, such as the tip and base size of the conical nanopore, graphene nanopore size, *etc.*, which are still unclear and need to be investigated in detail in the future. It is hoped that by optimizing the G/PET structure parameters, even larger rectification ratios could also be obtained and can be utilized in the future nanofluidic devices.

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4 - 28 Surface Modification and Damage of MeV-Energy Heavy Ion Irradiation on Gold Nanowires

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Recently, the irradiation effects in nanomaterials have been a hot topic in nanoscience. Although irradiation-induced damages have been studying for a long time, very limited research has been performed on the damages induced by MeV-energy heavy ions in gold nanowires(NWs). In this work, we report a study of the irradiation effects on single crystalline gold NWs, which are fabricated electrochemically in the etched ion track templates. The as-prepared gold NWs on the Au/Cu substrate were characterized by SEM after dissolving the polycarbonate (PC) template, as shown in Fig. 1(a). Gold NWs with diameters from 20 to 90 nm were fabricated to study the size dependence of irradiation damage induced by the heavy ions. To guarantee that the different NWs could obtain the same irradiation fluence, the NWs with different diameters were mixed together and transferred to the TEM grid, as shown in Fig. 1(b). In this way, the gold NWs with different diameters were presented on the same TEM grid and underwent the same ion irradiation. The gold NW with a diameter of 70 nm is shown in Fig. 1(c), presenting a smooth surface and excellent cylindrical shape. The crystal structure of the prepared NWs was also investigated by HRTEM. Fig. 1(d) exhibits the single crystalline structure and [111] growing direction of a 30 nm gold NW.