Electronic Supplementary Information

A bidirection-adjustable ionic current rectification system based on a biconical micro-channel

Fengxia Chang, Cheng Chen, Xia Xie, Lisha Chen, Meixian Li, Zhiwei Zhu*

Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

**To whom correspondence should be addressed. E-mail: zwzhu@pku.edu.cn.*

Contents

1. Materials and Instruments

Potassium chloride (KCl) and sodium dodecyl sulfate (SDS) were of analytical grade and purchased from Beijing Chemical Works (Beijing, China). Polyethyleneimines (PEIs, linear, M. W. 25000) was purchased from Alfa Aesar Chemical Company (Singapore). Hexadecyl trimethylammonium chloride (CTAC) was purchased from J&K chemicals (Beijing, China). All aqueous solutions were prepared with pure water obtained from Wahaha Group Co. Ltd. (Hangzhou, China). All chemicals were used as received without further purification.

Current-voltage curves were obtained with CHI 760 electrochemical workstation (Shanghai, China). An Ag/AgCl electrode was inserted inside of the left cone of the channel as working electrode. Another Ag/AgCl electrode was placed in another conical region to be an auxiliary/reference electrode. After a LSV scan, the connection between electrodes and electrochemical work station was changed and another current-voltage curve was recorded with the Ag/AgCl electrode in the right cone acting as working electrode. The experimental data may vary from each other a little because of fluctuations in the fabrication and modification, so the results have been repeated at least 3 times using the similar size of channels. But for every well-engineered ICR system, the repeatability of experimental data is very good.

The diameter of the micro-channel was estimated with Olympus BX-51 optical microscope (Japan). And the microscope image was obtained with the same instrument. The pH value was measured with a pH meter (PHSJ-3F, Shanghai Precision and Scientific Instrument, China).

2. Fabrication and Modification of Biconical Micro-channel

The biconical micro-channel was fabricated by a CO_2-laser-based pipette puller (P-2000, Sutter Instrument Co., USA). And the quartz capillaries (0.7 mm inner diameter and 1.0 mm outer diameter) were from the same company of the puller.

The program used in the fabrication of biconical micro-channel is shown as follows:

(Cycle 1) heat=760, filament=2, velocity=44, delay=128, pull=0;

(Cycle 2) heat=740, filament=2, velocity=41, delay=128, pull=0.

The modification procedure was as follows. First, 1 μL H_2O was injected into the right cone using a microsyringe followed by 5 μL PEIs (1 g/L) aqueous solution injected into the left cone. Here H_2O was placed in the channel to prevent PEIs spreading in the channel evenly in order to obtain an asymmetrically modified biconical channel. Next, the channel was placed in air for 30 min so that PEIs can interact with the inner walls. Finally, the channel was baked at 120 °C for 2 h to remove H_2O.

CTAC and SDS were separately added into the working electrolyte of 1 mM KCl. The mixed solution was sucked into the biconical micro-channel from left orifice with an aurilave on the right orifice. Acidic solutions were prepared with HCl.

3. Refreshing of the Modified Biconical Micro-channel

To remove PEIs layer, H_2SO_4 solution (3 M) was injected into the channel, and then the channel was baked at 80 °C for 14 h. With strong acidic solution in the channel, the dissociated silanol groups on the inner surface were protonated, which cut down the electrostatic interaction between PEIs and the inner surface. So PEIs layer would be removed and the channel was refreshed. After that, the channel was washed with H_2O and then baked to remove H_2O. LSV was implemented with the refreshed channel with KCl solution in it and the results (Fig S1) showing no rectification proved that PEIs was removed successfully.

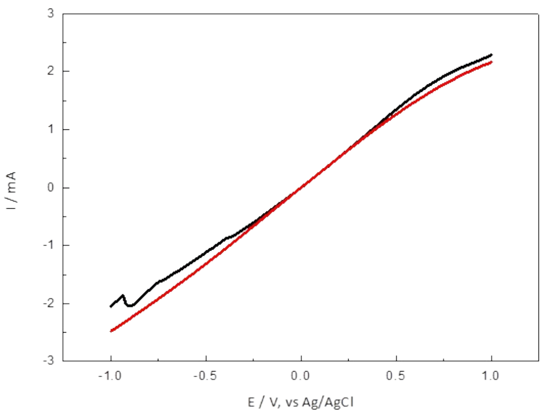

Fig. S1 Linear sweep voltammograms (LSVs) measured with the refreshed biconical micro-channel as working electrodes situated in the two cones of the channel separately. The concentration of KCl: 0.1 M. Scan rate: 10 mV s^{-1}.

The modification layer of surfactant CTAC or SDS on the inner surface can be removed easily by directly washing with H_2O.

4. The influence of Diameter of Biconical Channels on ICR

LSVs were obtained with biconical channels ranging from 60 to 120 μm. The current-voltage curves and their rectification ratios did not present any regular change or to be affected by the diameter of the narrowest section of the channel. The cause may be that the diameter is much larger than the diffuse double layer (DDL) thickness, and the disparity among the channels is not distinguished enough as in Liu's work[1] in which the disparity of diameters reached three magnitudes. Thus the channels can't introduce significant difference on the DDL with diameter ranging in the mentioned scope.

5. The Influence of KCl Concentrations on ICR

KCl solutions with different concentrations were injected to a PEIs modified biconical channel and for each concentration two current-voltage curves were obtained as the working electrode is in the two conical regions of the channel, respectively. The two rectification ratios (*R*) of each curve were calculated by

$$R = \left| \frac{i_{+1V}}{i_{-1V}} \right|$$

Here i_{+1V} and i_{-1V} are the current values at +1V and -1V, respectively.

Based on this equation, the ratio is larger than one for positive rectification and less than one for negative rectification. So for the two curves of a concentration, one ratio is larger than one as the working electrode is in the modified conical region and the other one is less than one as the working electrode is in the bare cone.

The ratios of different KCl concentrations are presented in Fig. S2. And there is no significant difference when the concentration varies. Also, Mayer's work[2] in which micropores were used to generate ICR demonstrates that electrolyte concentration does not affect ICR when the diameter is up to 500 times larger than the DDL thickness. So it can be concluded that ICR is independent on KCl concentration in this biconical micro-channel.

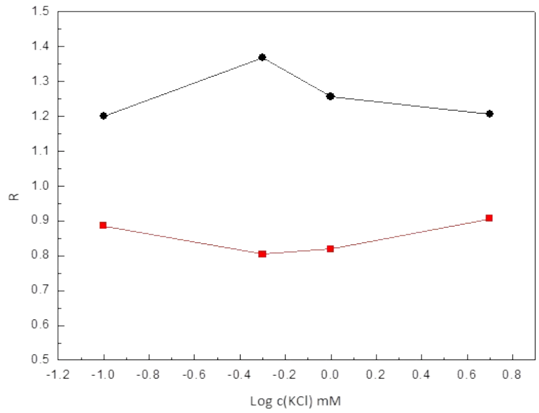

Fig. S2 Dependence of ionic current rectification ratio on KCl concentration for PEIs coated biconical channel which is modified asymmetrically. Black dots stand for rectification ratios of curves obtained when the working electrode is located in the modified cone of the channel. Red squares were obtained when the working electrode is located in the bare cone of the channel.

6. Consecutive LSV Scans for the CTAC Modified Biconical Channel

To test the stability of the CTAC modified ICR system, 5 consecutive LSV scans were applied with the modified biconical system. As show in Fig. S3, even if with 5 continuous cycles of scans, the rectification curves still coincide with the first scan very well. As the results of experiments, this ICR system has strong stability and high reliability.

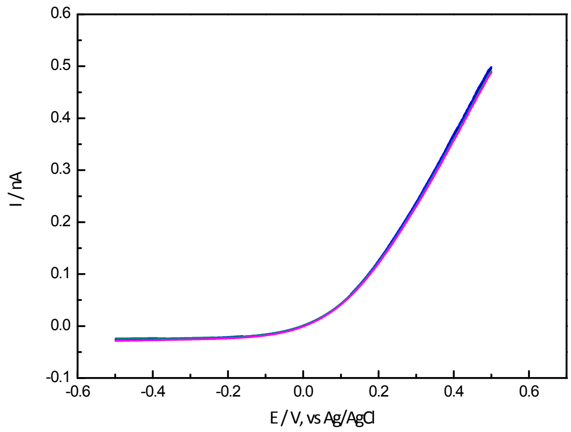

Fig. S3 5 consecutive LSV scans for the biconical channel with solution containing 0.1 mM CTAC and 1 mM KCl.

References

1. S. Liu, Y. Dong, W. Zhao, X. Xie, T. Ji, X. Yin, Y. Liu, Z. Liang, D. Momotenko and D. Liang, *Analytical chemistry*, 2012, **84**, 5565-5573.

2. E. C. Yusko, R. An and M. Mayer, *ACS Nano*, 2009, **4**, 477-487.