Supplementary Information (SI) for ChemComm.

Supplementary Materials

A Switchable and Facile Ionic Diode Modulated by Polyethylene Glycol

Fei Zheng[1,2,3,4], HongLuan Li[1,2], Jun Yang[1,2], Haiyan Wang[1,2], Guangle Qin[1,5], Dapeng Chen[1,5], Jingjie Sha[1,2*]

1. Jiangsu Key Laboratory for Design and Manufacture of Micro-nano Biomedical Instruments, Southeast University, Nanjing 211189, China

2. School of Mechanical Engineering, Southeast University, Nanjing 211189, China

3. Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom

4. School of Nanoscience and Nanotechnology, University of Chinese Academy of Sciences, Beijing 101408, China

5. Jiangsu Automation Research Institute, Lianyungang 222000, China

[*]Correspondence to: Jingjie Sha, E-mail: major212@seu.edu.cn;

Table of Contents

Supplementary Note 1: Materials and Methods

Nanopore fabrication

Quartz glass capillaries, with inner and outer diameters of 0.7 mm and 1.0 mm respectively, were sourced from Sutter Instruments (Catalog number QF100-70-7.5, California, USA). These capillaries were reduced to nanoscale dimensions using a laser-heated pipette puller (P-2000, Sutter Instrument, California, USA). For most experiments, nanopores were pulled to a diameter of 25 ± 5 nm (mean ± standard deviation) with a cone semi-angle of 0.03 ± 0.01 radians. The parameters for this pulling process were HEAT=760, FIL=4, VEL=29, DEL=140, and PULL=175 (Supplementary Note 6), as detailed in the P2000 manual. After fabrication, the capillary was cut to the desired length and placed into a custom PMMA microfluidic device (Supplementary Note 2). The glass pipette was positioned between two reservoirs using a gasket, with the two cells clamped tightly to ensure proper insulation. The PMMA material used was polymethyl methacrylate from Sigma-Aldrich (Missouri, USA). The device underwent plasma treatment for 5 minutes to make the nanopore surface hydrophilic, after which the nanopores were flushed with an electrolyte solution (1× Tris-HCl buffer, pH 8.0).

Nanopore characterization

The pulled glass nanopores were imaged using a scanning electron microscope (SEM) (Helios NanoLab™ 600i, FEI, USA). Prior to imaging, the nanopipettes were coated with a thin gold layer a few nanometers thick through sputtering. They were then mounted onto a sample holder and positioned at an angle of 60 degrees or more for optimal imaging. The imaging process was performed at 3 kV with a working distance of 4.2 mm.

I-V (Current-Voltage) characterization

Nanopore measurements were carried out using a patch clamp amplifier (Axopatch 700B, Molecular Devices, CA, USA) in voltage-clamp mode, with current signals digitized at a sampling rate of 250 kHz (Axon Digidata 1550A, Molecular Devices, CA, USA) and processed using a low-pass filter set to 10 kHz. Data was recorded using the pClamp 10 software (Molecular Devices, CA, USA). Two Ag/AgCl electrodes, prepared by oxidizing Ag wires in a 10% NaClO solution, were placed in the *cis* and *trans* reservoirs to establish an electric circuit across the nanopore. Prior to sample measurements, the current-voltage characteristics of the nanopores were scanned from -600 mV to 600 mV to determine pore diameter. Current readings were analyzed using Clampfit software, while Python scripts were employed for further data analysis. I-V measurements of the KCl solution, both before PEG addition and after flushing PEG, were performed for each experiment (Supplementary Note 6).

Materials

The following commercial reagents were used in the experiments: 100× Tris-HCl buffer solution (Solarbio, Catalog number T1150-100), ≥99% pure Potassium chloride for molecular biology (Sinopharm, Catalog numbers 7447-40-7), and Polyethylene Glycol 1500 (Sigma-Aldrich, Catalog numbers 81210). Solutions and buffers used for nanopore measurements, prepared from these reagents, were filtered twice through 0.22 µm Millipore syringe filter units (MF-Millipore™, Sigma-Aldrich, Catalog number GSWP02500).

Supplementary Note 2: Experimental Setup

The experimental setup, illustrated in Figure S1, is designed to study ion transport through a glass pipette with a nanoscale channel at its tip. It consists of two reservoirs, labeled *cis* and *trans*, filled with an electrolyte solution to maintain a conductive medium for ion movement. The glass pipette acts as a bridge between the reservoirs, with its nanoscale channel facilitating ion flow under an applied voltage. A gasket is placed at the junction of the pipette and reservoirs to ensure a sealed environment, which is crucial for directing ion transport solely through the nanoscale channel and minimizing external interference. Silver/silver chloride (Ag/AgCl) electrodes are inserted into both reservoirs, connected to a voltage source to apply a membrane potential across the glass pipette.

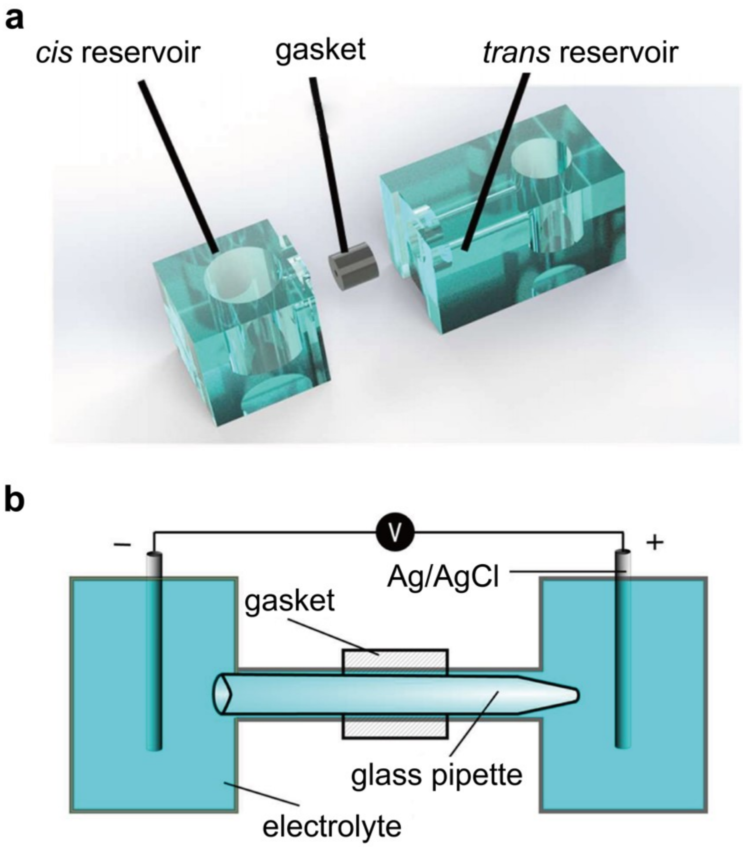

Figure S1. Schematic of the experimental setup for ion transport studies through a glass nanopore. (a) The 3D illustration of the experimental assembly, showing the *cis* and *trans* reservoirs connected by a glass nanopore. A gasket is placed between the reservoirs to maintain a sealed environment. (b) Cross-sectional diagram of the setup, with a glass nanopore filled with the electrolyte solution, connected to Ag/AgCl electrodes in both reservoirs.

Supplementary Note 3: I-V Characteristic Measurements

The I-V characteristic measurement, depicted in Figure S2, was performed to assess the ion transport properties through the nanopore using 0.05 M KCl and 50% w/v PEG. Panel (a) shows a series of current-time traces recorded at different applied voltages, ranging from -800 mV to +800 mV in 50 mV increments. Each voltage step was applied for 4 seconds, and the current was recorded during the middle 2 seconds of each interval. Ionic currents were measured using a patch-clamp amplifier. The staircase-like arrangement of the traces reflects the gradual change in ionic current with each voltage step, indicating stable ion transport through the nanopore. Panel (b) presents the current-voltage (I-V) curve derived from the data in panel (a), showing a nonlinear, rectifying behavior typical of ion transport through a nanopore. Each red circle on the curve represents the average current recorded at each voltage step.

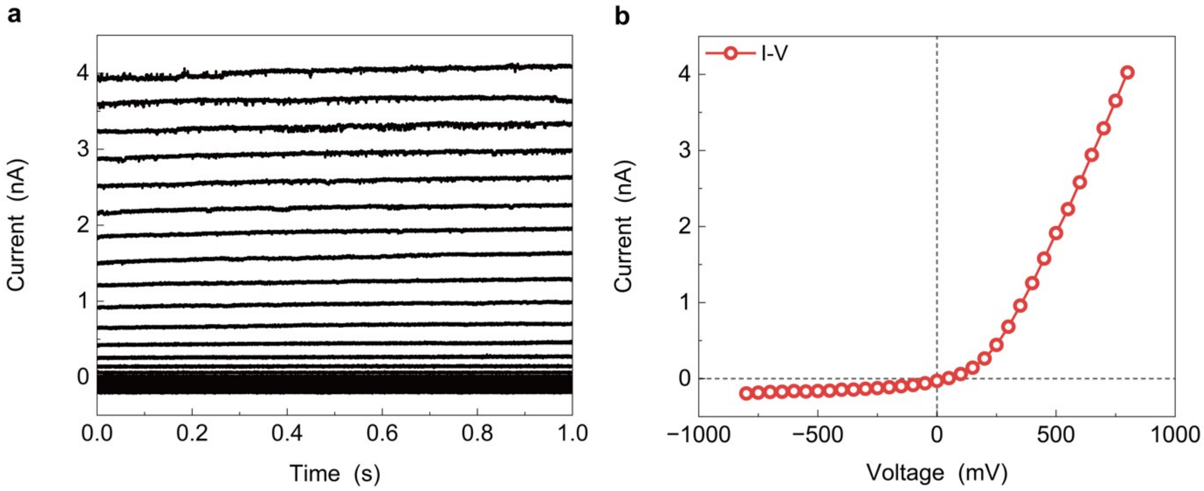

Figure S2. I-V characteristic measurement of ion transport through a nanopore. (a) Current-time traces recorded at varying applied voltages in 0.05 M KCl and 50% w/v PEG. Each trace corresponds to a different voltage step, illustrating stable ionic currents through the nanopore. (b) Current-voltage (I-V) curve showing the nonlinear rectifying behavior of the nanopore. The red circles represent the average of measured current values at each voltage step.

Supplementary Note 4: Long-Time Recording of the Current-Time Trace

To further analyze the stability and behavior of ion transport through the nanopore over extended periods, we recorded the current-time trace for 300 seconds under constant applied voltage conditions. As shown in Figure S3, the ionic current remained stable throughout the duration of the recording, maintaining an average value around 1.3 nA with minimal fluctuation. This demonstrates that the ionic diode system retains consistent performance over time, and no significant ion blockades or disturbances were observed during the long-term measurement. The consistent current flow suggests that the PEG-modulated system does not degrade or lose efficiency during prolonged operation, underscoring its reliability for potential long-term applications.

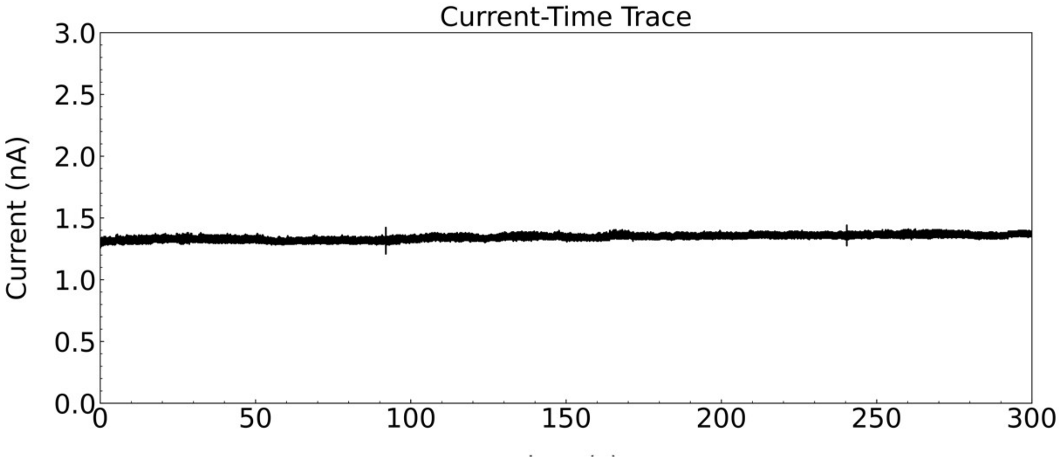

Figure S3. Long-time recording of the current-time trace. The ionic current was recorded for 300 seconds under constant applied voltage conditions.

Supplementary Note 5: Voltage-Step Response of the PEG-Modulated Ionic Diode

To further investigate the dynamic response of the PEG-modulated ionic diode, a voltage-step experiment was conducted, as shown in Figure S4. The applied voltage was varied in a stepwise manner, ranging from 250 mV to 400 mV in an increment of 50 mV, with each step maintained for 1.5 second. The corresponding current response of the ionic diode was recorded throughout the voltage steps. The top panel of Figure S4 displays the applied voltage over time, while the bottom panel shows the resulting ionic current response. As observed, the current exhibits a clear and consistent response to each voltage step, demonstrating the diode's ability to adjust to rapid voltage changes.

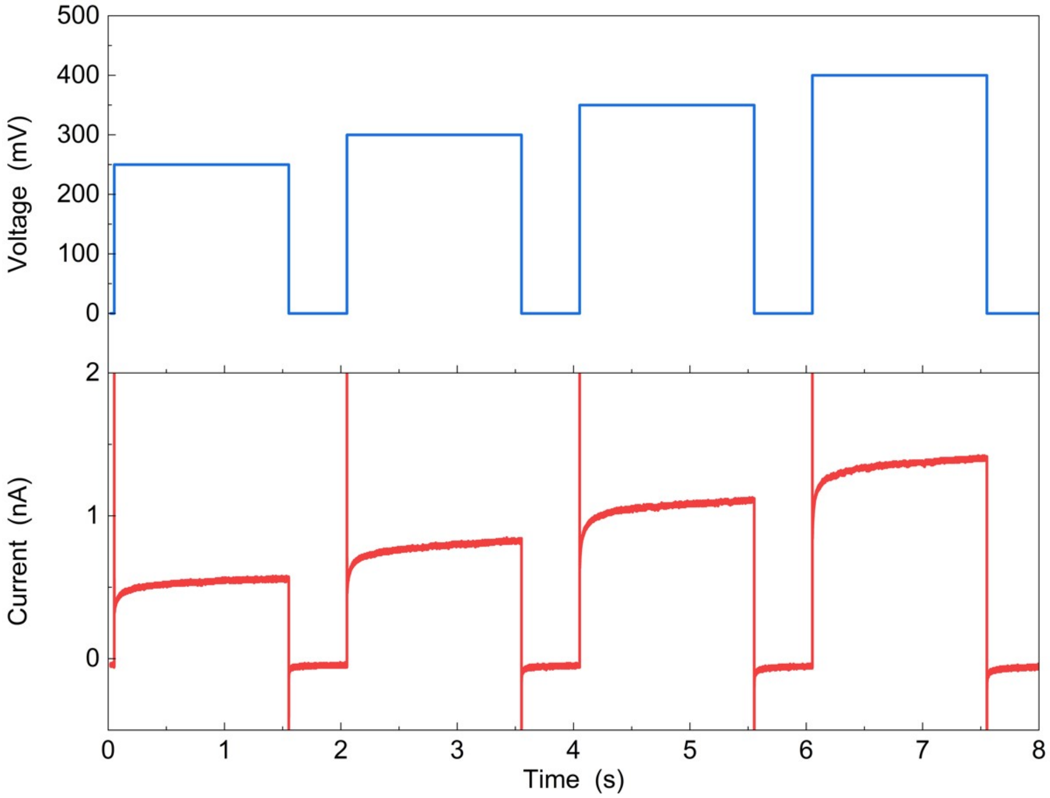

Figure S4. Voltage-step response of the PEG-modulated ionic diode.

Supplementary Note 6: I-V Characteristics Measured Before Adding PEG and After Flushing PEG

Control I-V measurements were performed to evaluate the stability of the nanopore following the addition of PEG. After completing the PEG experiments, the chambers and nanopores were thoroughly flushed with a pure KCl solution, and the I-V curve was re-measured, as shown in Figure S5. The I-V curves obtained before the addition of PEG and after flushing with KCl solution display a high degree of consistency across all applied voltages, indicating that the nanopore remains stable and unaffected by the presence of PEG throughout the experiments.

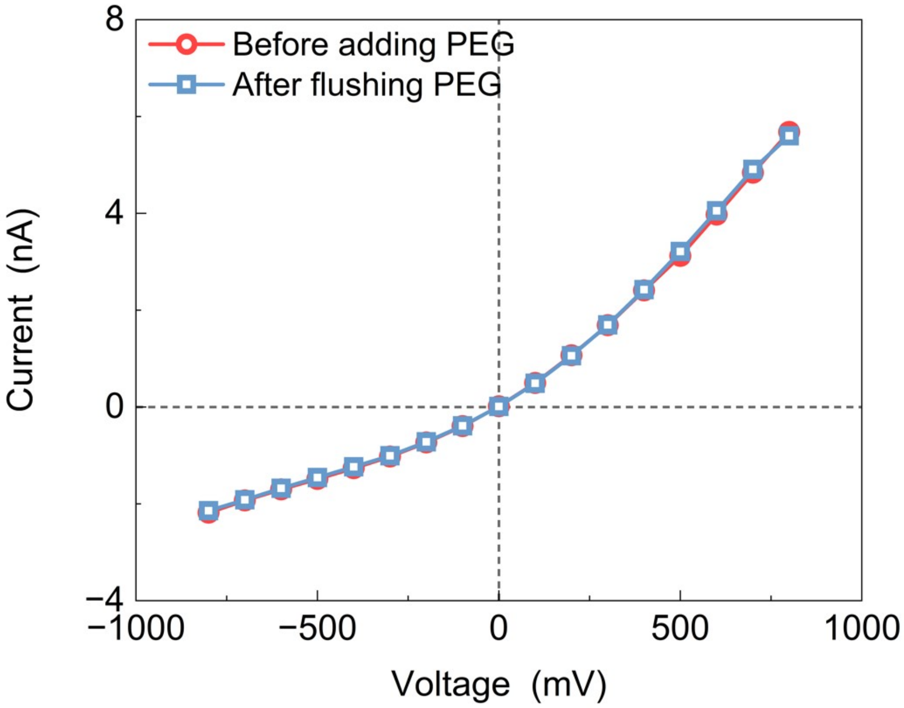

Figure S5. I-V characteristics measured before adding PEG and after flushing PEG. The I-V curves were recorded in a pure KCl solution both before the addition of PEG (red circles) and after flushing PEG with KCl (blue squares).

Supplementary Note 7: Pulling Parameters of Glass Nanopores

Table S1. Pulling parameters for the glass nanopipette used in this work. To obtain nanopores with varied diameters, the Pull parameter was modified while other parameters were keeping unchanged.

Heat	Filament	Velocity	Delay	Pull
760	4	29	140	175