Supporting information

Bioinspired solid-state hydrogel nanofluidic ionic diodes: nano-confined network tuning and ion transport regulating

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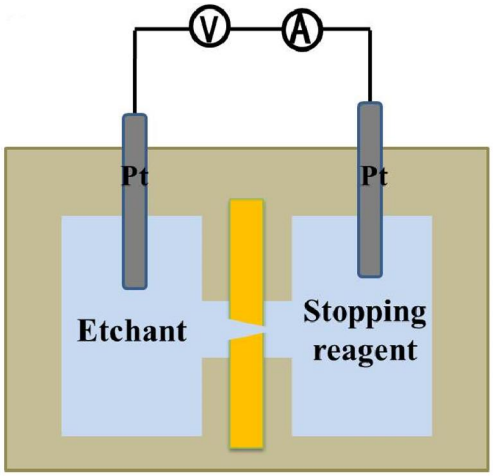
Experimental Section

Nanochannel Fabrication: Polyimide (PI) membrane (12 μm thick) was irradiated with single swift heavy ions (Au, 11.4 Mev) in the Universal Linear Accelerator (UNILAC) (GSI, Darmstadt, Germany). The conical nanochannels were prepared by using track-etching method. In order to obtain a uniform diameter of the nanochannel and shorten the etching time, both sides of the PI membrane were irradiated with UV for an hour, respectively. The polymer membrane was mounted between two halves of electrochemical cells (Scheme S1). First, the device, the etching and stopping solutions were preheated at 60 °C for 30 minutes. 1 M KI for stopping and 13% NaClO for etching were separately added to both sides of membrane. The platinum electrodes were used to apply a constant voltage of 1 V to monitor the changes in current during etching. After a certain period of time, the detection current suddenly increased, which was due to the channel conduction. When the current reached the desired value, the appropriate nanochannel could be obtained. Then, the stopping solution is used to wash the both sides of the cell. Finally, the membrane is taken out and washed with MilliQ water.

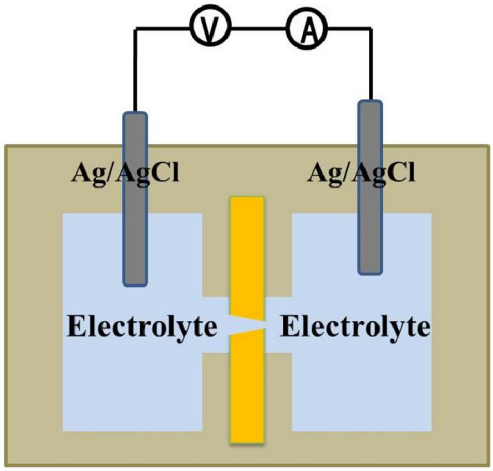


Scheme S1. The device for nanochannel preparing.

Hydrogel Nanofluidic Diodes Fabrication: The etched polyimide (PI) nanochannel membrane was sandwiched between two PTFE flanges, agarose and potassium chloride aqueous solution were added to the glass electrochemical cell. The Ag/AgCl electrodes were fixed in both sides of the glass electrochemical cell. When the temperature reaches 90 °C, the agarose melts to form a sol, further cooled at room temperature to form a hydrogel, and the process can be recycled. Unless otherwise specified, the agarose was

2 wt% and the electrolyte solution was 0.1 M KCl. The polymer PI membrane was single conical nanochannel. The equipment was fixed on the hot table to prevent shaking. While used magnetic slowly stirring, to avoid the generation of bubbles and heated at 90 °C for 2 h. White agarose powder with constant heating and stirring, gradually dissolved to form a transparent melt. Cooled at room temperature, the sol gradually solidified to form a white hydrogel nanofluidic diode. In order to increase the ion current flux to light the LED, the polymer PI membrane (density of 1×10^6 cm^{-2}) and the KCl solution (1 M) were used to prepare the diode.

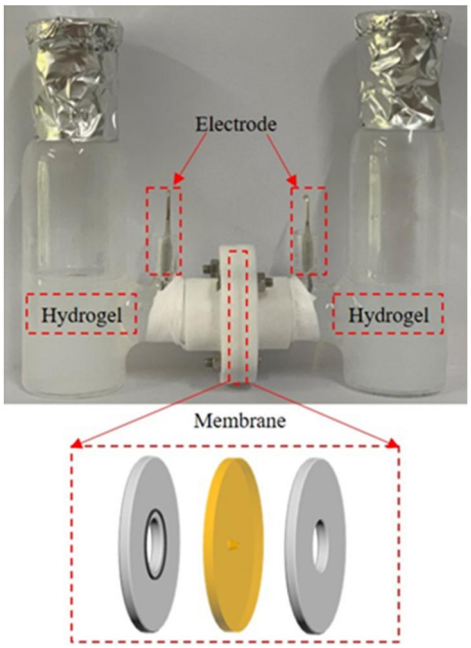
Current Measurement: Ionic current of the nanofluidic diodes were measured with a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH, USA). The *I-V* curve was first measured in aqueous solutions (Scheme S2). Then the ion transport behaviors of the hydrogel-filled diodes were measured with a H-shaped electrochemical cell (Scheme S3). Unless otherwise specified, current measurements were made at room temperature. Ag/AgCl electrodes were used to record transmembrane current (anode facing the base side of the nanochannel). Experiments were performed with a scanning voltage varying from -2 to +2 V.



Scheme S2. The device for current measurement of the nanochannel in aqueous solutions.

Since a single nanochannel is difficult to locate on a single-channel membrane under a scanning electron microscope (SEM), a multichannel membrane with channel density of ~10^6 pore/cm^2 was prepared under the same condition as the single nanochannel

membrane. SEM measurements were taken in the field-emission mode using a Hitachi S-4800 microscope at an acceleration voltage of 5 kV to get the diameter of the large opening. The tip diameter was estimated using the following equation: $d_{Tip} = \frac{4LI}{\pi k(c)UD}$, where d_{Tip} is the diameter of the tip side; L, I, U, and D are the length of the channel(~12 μm), the current, the applied voltage, and the diameter of the base side, respectively. k(c) is the specific conductivity of the electrolyte. For 1 M KCl solution at 25°C, k(c) = 0.11173 $\Omega^{-1} \cdot cm^{-1}$.



Scheme S3. The device for current measurement of the hydrogel-filled nanochannel

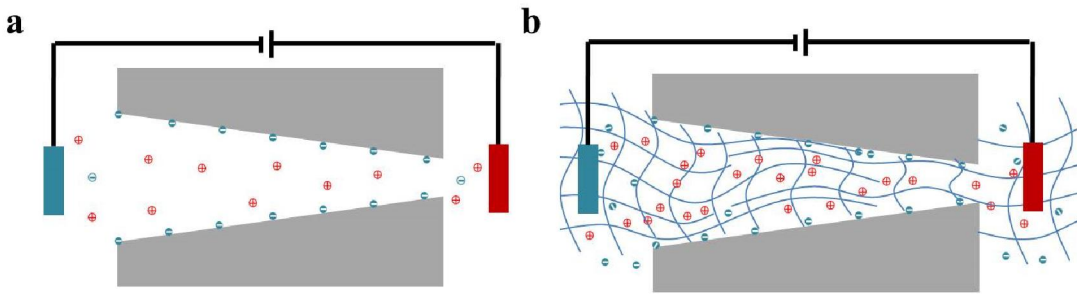


Fig. S1. Schematic illustration of the ion transport properties of the nanochannel between (a) aqueous and (b) hydrogel system.

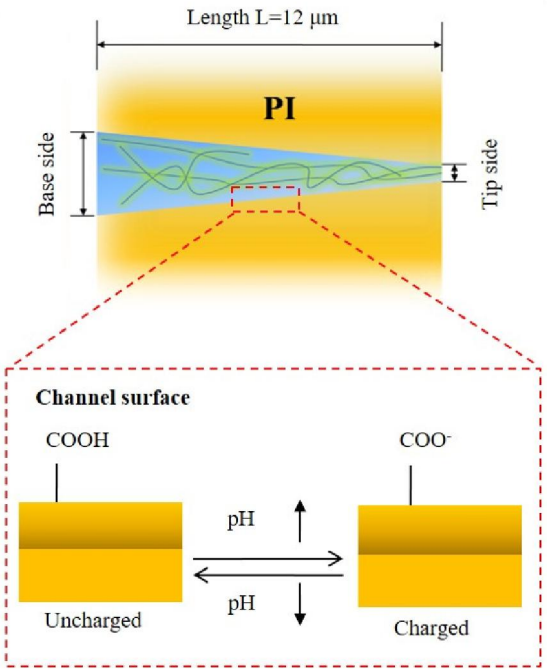


Fig. S2. Microscopic schematic of hydrogel diode and the chemical composition of nanochannel internal surface.

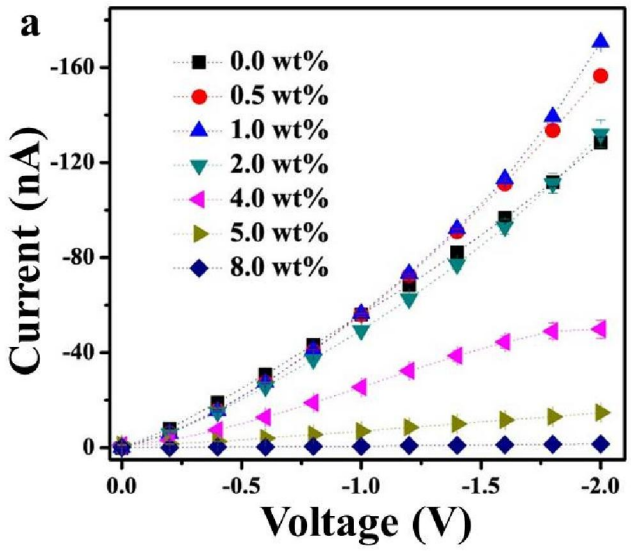


Fig. S3: *I-V* curve of different agarose concentration.

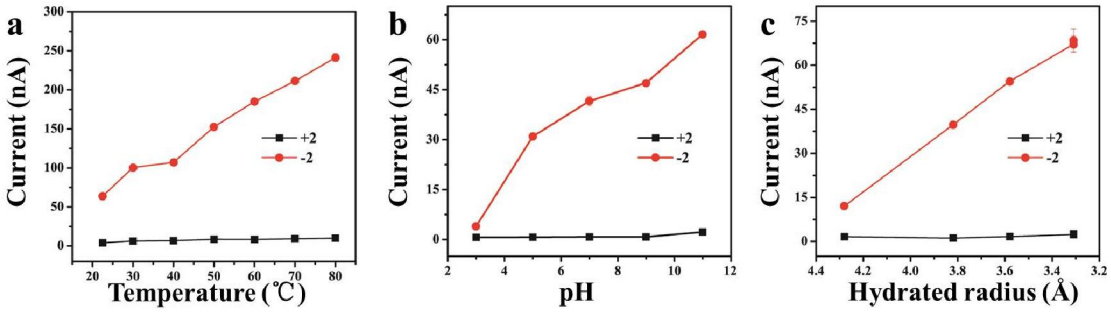


Fig. S4: Influencing factor on ionic current (corresponding voltage +2 V and -2 V).

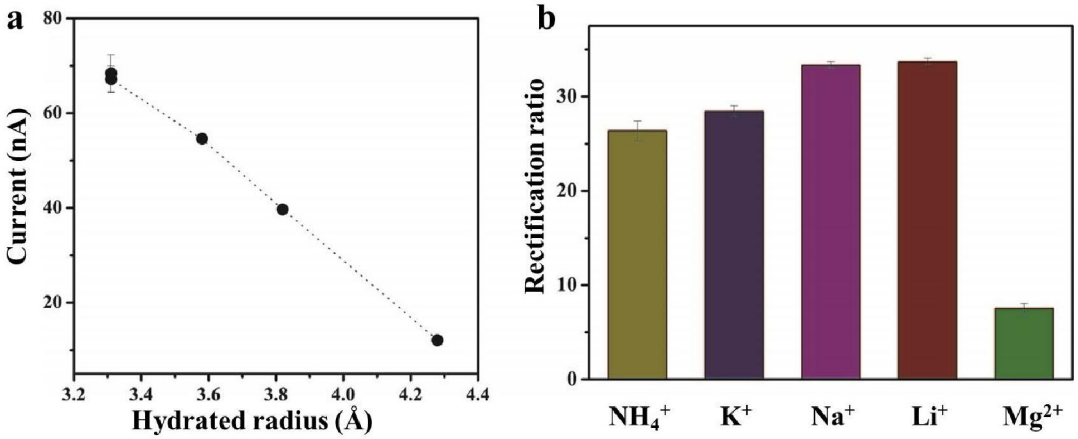


Fig. S5: Ion current and rectification ratio of different hydrated radius.

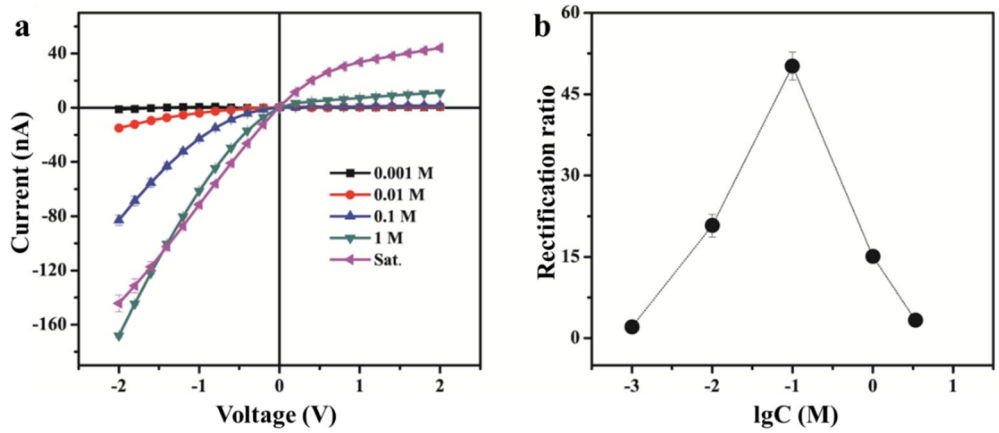


Fig. S6: *I-V* curve and rectification ratio corresponding of gradient electrolyte concentration (0.001 M, 0.01 M, 0.1 M, 1 M, and saturated).

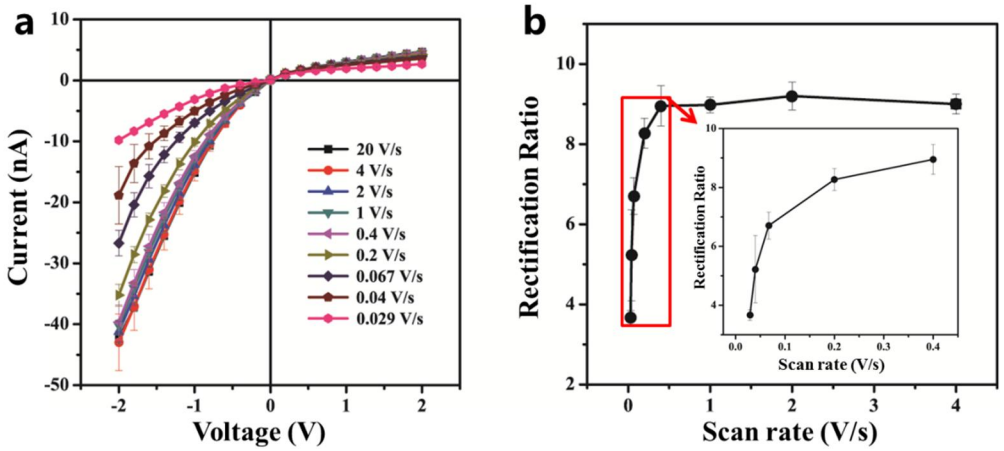


Fig. S7: *I-V* curve and rectification ratio corresponding of different scan rate.

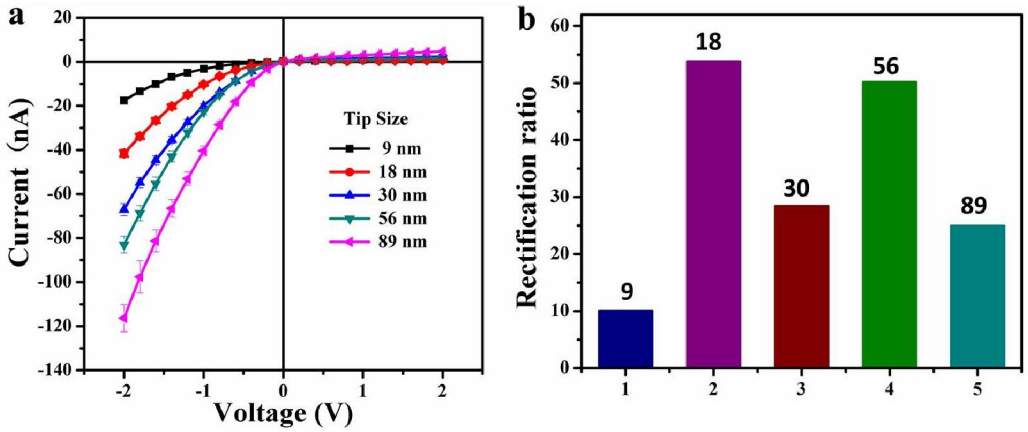


Fig. S8: The current of the gel diode increases gradually with the increase of the aperture of the small port, and the rectification ratio has no relation with the size of the small hole.

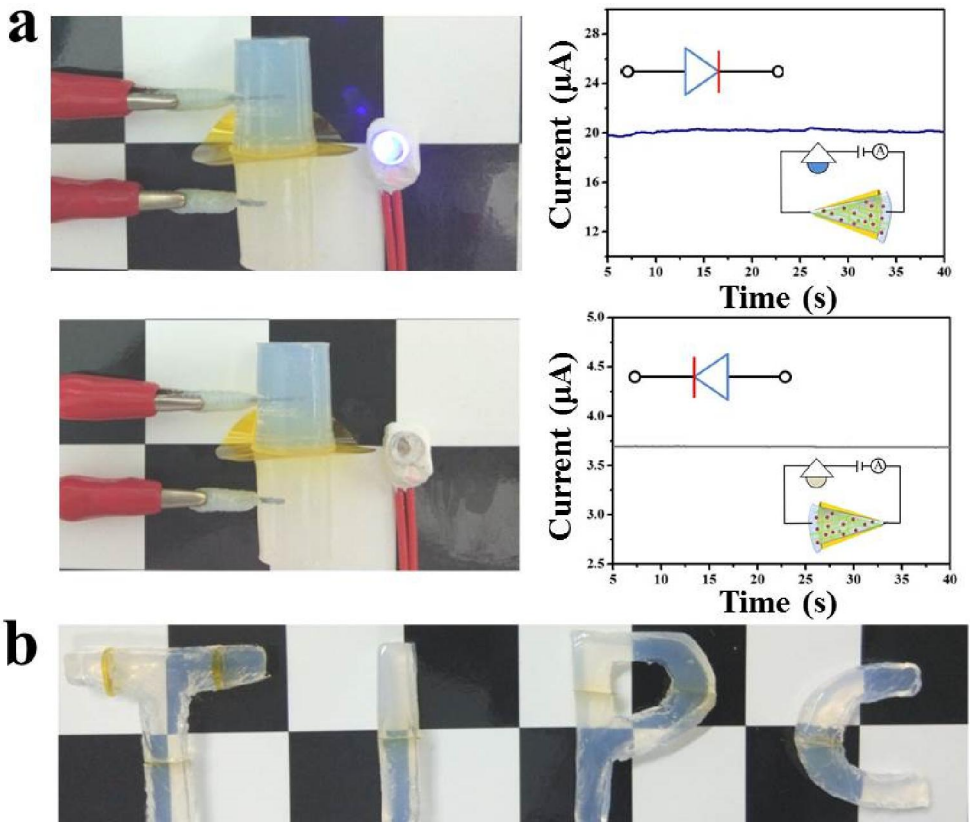


Fig. S9. The application of hydrogel ionic diode to unidirectional conduction, input voltage 5 V.