Supplementary Information for

Alternating Electric Fields Induced Ion Current Rectification and Electroosmotic Pump in Ultranarrow Charged Carbon Nanocones

Wen Li[a,b], Wensen Wang[a,b], Quangang Hou[a,b], Youguo Yan[a,b], Caili Dai*[c] and Jun Zhang*[a,b]

[a] School of Materials Science and Engineering, China University of Petroleum, 266580 Qingdao, Shandong, People's Republic of China

[b] Key Laboratory of New Energy Physics & Materials Science in Universities of Shandong, China University of Petroleum, 266580 Qingdao, Shandong, People's Republic of China

[c] School of Petroleum Engineering, State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao, Shandong 266580, People's Republic of China

Corresponding Authors

*E-mail: zhangjun.upc@gmail.com (Jun Zhang)

*E-mail: daicl@upc.edu.cn (Caili Dai)

Table S1 LJ and charge parameters employed in this work

Element	$C(sp^2)$	H_w	O_w	Cl^-	Na^+
ε (kcal/mol)	0.0859	0	0.102	0.0356	0.0874
σ (Å)	3.3997	0	3.188	4.478	2.439
q (e)	0 (graphene) -0.0114 (CNC)	0.415	-0.83	-1	+1

Brief description of the rectification mechanism in small and large conical channels. In negatively charged conical channels with tip exit larger than 5 ns, one polarity of voltages from tip to base causes ions to accumulate in the tip region within the channel, giving high conductivity state with high ion current from tip to base. The opposite polarity could lead to ion depletion and low conductivity state with low ion current from base to tip. This voltage polarity dependence of enrichment and depletion of ions causes the ion current rectification (ICR).[1-4]

In our ultranarrow CNC channels, the conventional theories for fluidic transport are no longer applicable because of the small channel scale (sub-2 nm).[5] In our negatively charged CNC channel, most of the passed ions are cations, and the transport of cations from base to tip side is easier because of larger exit and the corresponding higher likelihood of collecting ions from solution. Meanwhile, the transport of ions from base to tip side would be further enhanced through the electrostatic repulsion among the entered cations in the CNC channel. This gives the high ion current of the CNC channel from base to tip side. However, these effects do not work when ion flows from tip to base side because of the absence of confined space to accommodate multiple ions, giving low ion current.[6]

Detailed explanations for the different EOF mechanisms between ultranarrow and large charged conical channels. In our ultranarrow charged CNC channel, the transport of ions could drag part of the water molecules in their hydration shells passing through the CNC channel together. Therefore, the EOF efficiency is proportional to the ion current. High ion current state indicates high EOF efficiency.

In CNC channels with tip exit larger than 5 ns, one polarity of voltages causes ions to accumulate in the tip region within the channel, giving high conductivity state. The opposite polarity could lead to ion depletion and low conductivity state. As we all know, EOF mainly occurs in the electrical double layer. At high conductivity state (larger ion current), the high ion concentration would compress the thickness of the electrical double layer, which will decrease the EOF efficiency. At low conductivity state (smaller ion current), the low ion concentration will make the channel own thick electrical double layer, giving high EOF efficiency.

The calculation for Debye screening length.

The Debye screening length is calculated by the following equation:

$$\lambda_D = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{e^2 c_0}}$$

Where ε_0 is the permittivity of free space, ε_r is dielectric constant, k_B is Boltzmann constant, T is absolute temperature, e is elementary charge, C_0 is ion concentration.

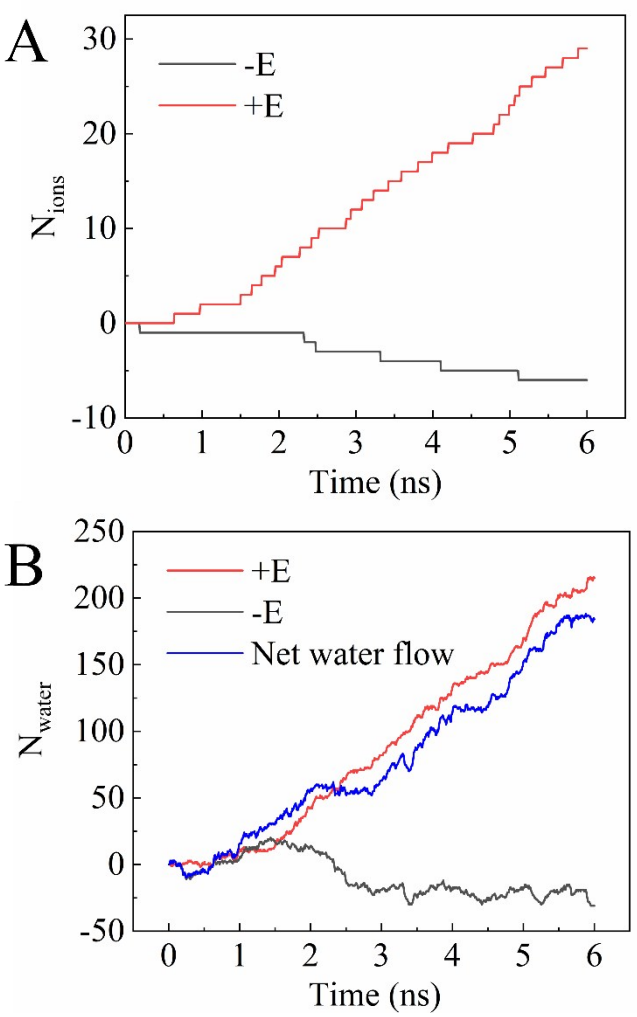

Fig. S1 The number of passed Na^+ ions (A) and water molecules (B) through the CNC channel under direct E of ±0.2/√2 V/nm (effective value of the alternating E shown in Fig. 2A).

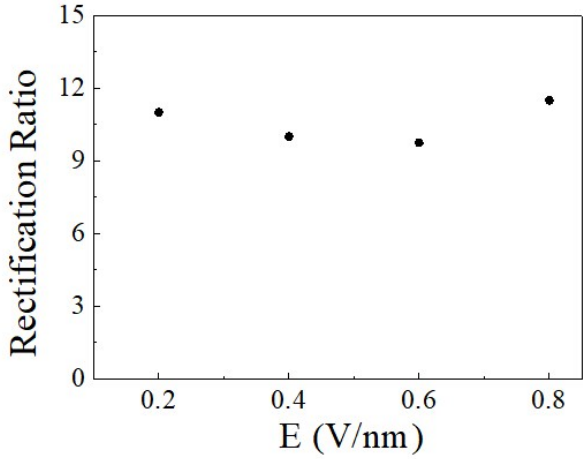

Fig. S2 The ion-current rectification ratio under symmetrical sinusoidal electric fields with different E_0 at constant period of 1 ns.

Pressure induced water flux in the ultranarrow CNC channel.

Fig. S3 shows the built system to study the pressures induced water flux in CNC channel. The channel is same to the channel shown in Fig. 1 in the main text. Compared with Fig. 1, another two rigid graphene slabs were placed in the rightmost and leftmost side, respectively, and driving pressures were applied on these two slabs. Larger pressure was applied on the left graphene slab and low pressure of 0.1 MPa were applied on the right slab. During simulation, constant forces (f) was applied on the carbon atoms of the leftmost and rightmost graphene slabs. Then, the pressure could be calculated using equation of P=N*f/S, where N is the number of carbon atoms on the graphene slab, f is the applied force on single carbon atom, and S is the sectional area of the system.

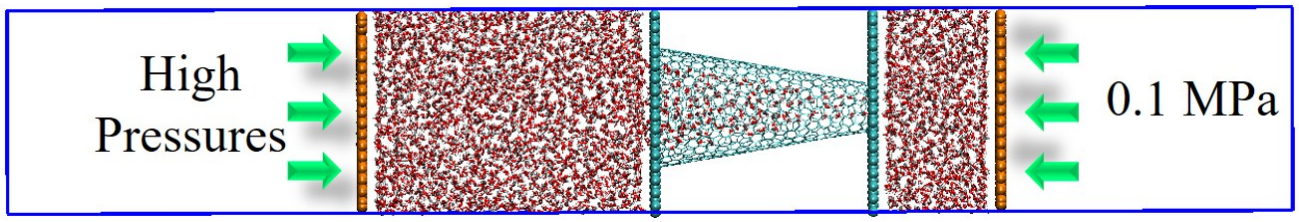

Fig. S3 The built system for pressures induced water flow in the ultranarrow CNC channel.

References

1 Z. S. Siwy, *Adv. Funct. Mater.* 2006, **16**, 735-746.

2 I. Vlassiouk, Z. S. Siwy, *Nano Lett.* 2007, **7**, 552-556.

3 L. J. Cheng, L. J. Guo, *Chem. Soc. Rev.* 2010, **39**, 923-938.

4 J. B. Cervera, Schiedt, P. Ramirez, *EPL (Europhysics Letters)* 2005, **71**, 35.

5 H. Daiguji, *Chem. Soc. Rev.* 2010, **39**, 901-911.

6 W. Li, Y. Yan, M. Wang, P. Král, C. Dai, J. Zhang, *J. Phys. Chem. Lett.* 2017, **8**, 435-439.