Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting Information for

Periodic oscillation of ion conduction of nanofluidic diodes using a chemical oscillator

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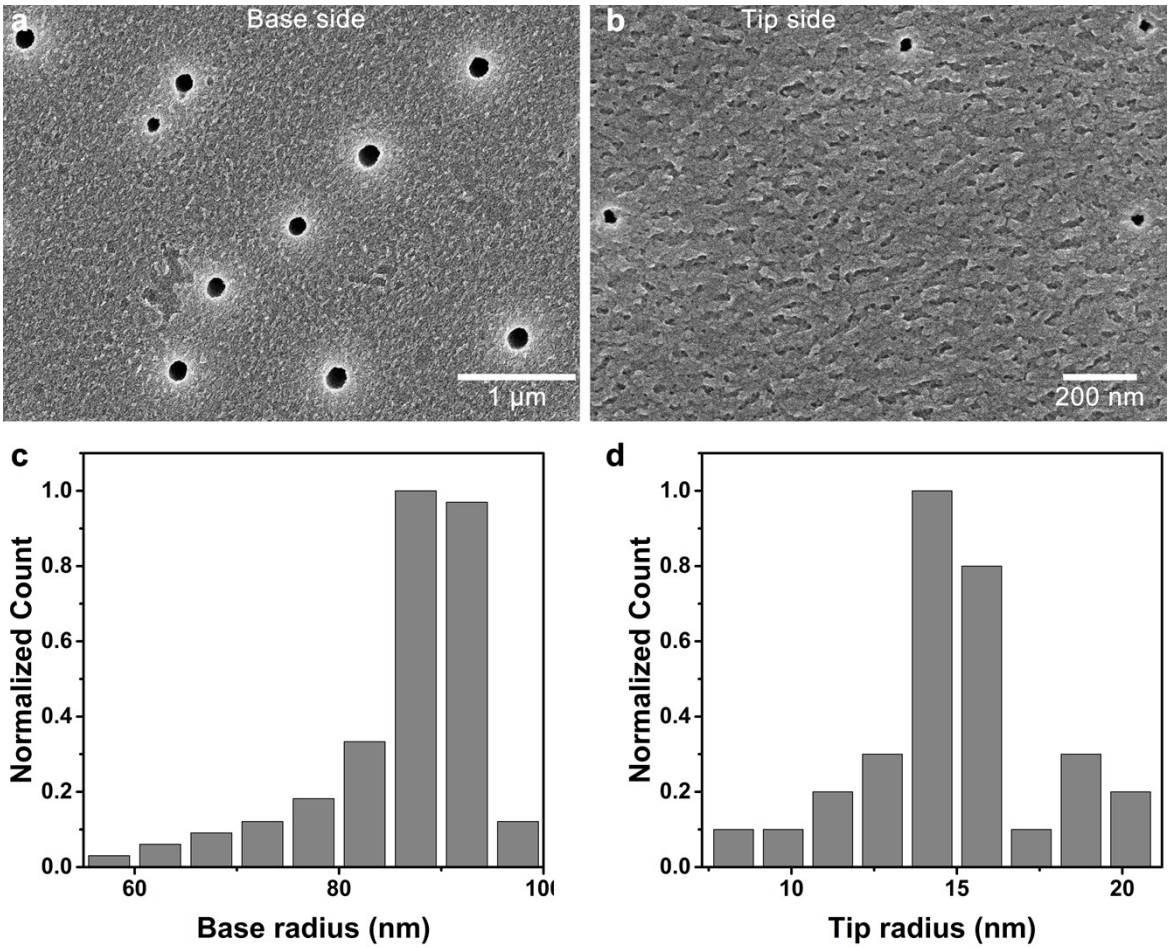

Figure S1. SEM images of (a) the base side and (b) the tip side the bullet-shaped nanochannels etched for about 3 min. Statistic radii of the bases (c) and tips (d) of the nanochannels. Tip radii range from 7 to 21 nm and average tip radius is 14 ± 3 nm, while base radii vary from 55 to 100 nm and mean base radius is 86 ± 9 nm.

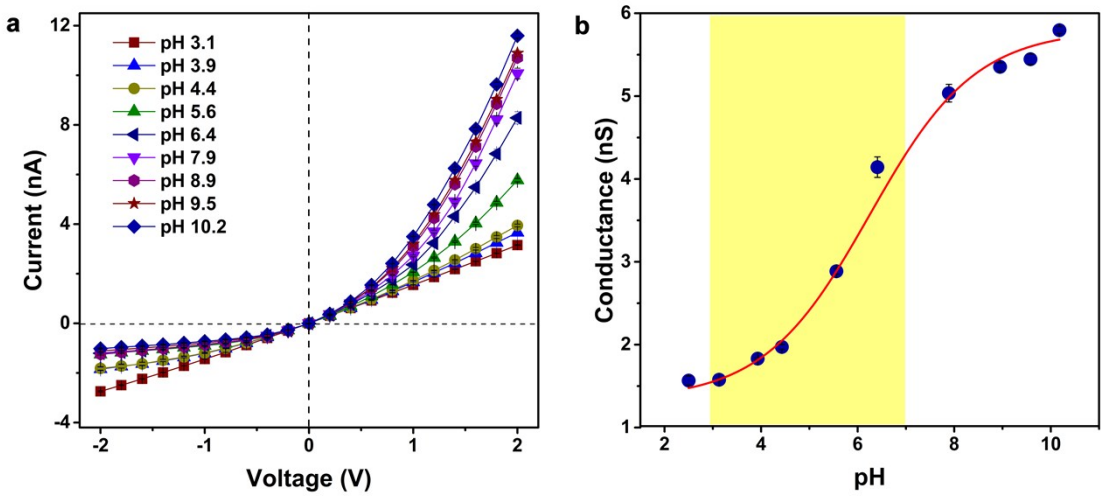

Figure S2. pH-responsive property of the bullet-shaped nanochannel measured in 0.1 M KCl solutions with different pH values at room temperature. (a) Current-voltage (I-V) curves of the channel under different pH conditions. The nanochannel exhibited asymmetric I-V curves under high pHs because the nanochannel surface was negatively charged under these conditions. Ionic currents at positive voltages increased with pH increasing from 3 to 10. (b) Ion conductance of the nanochannel as a function of the pH values.

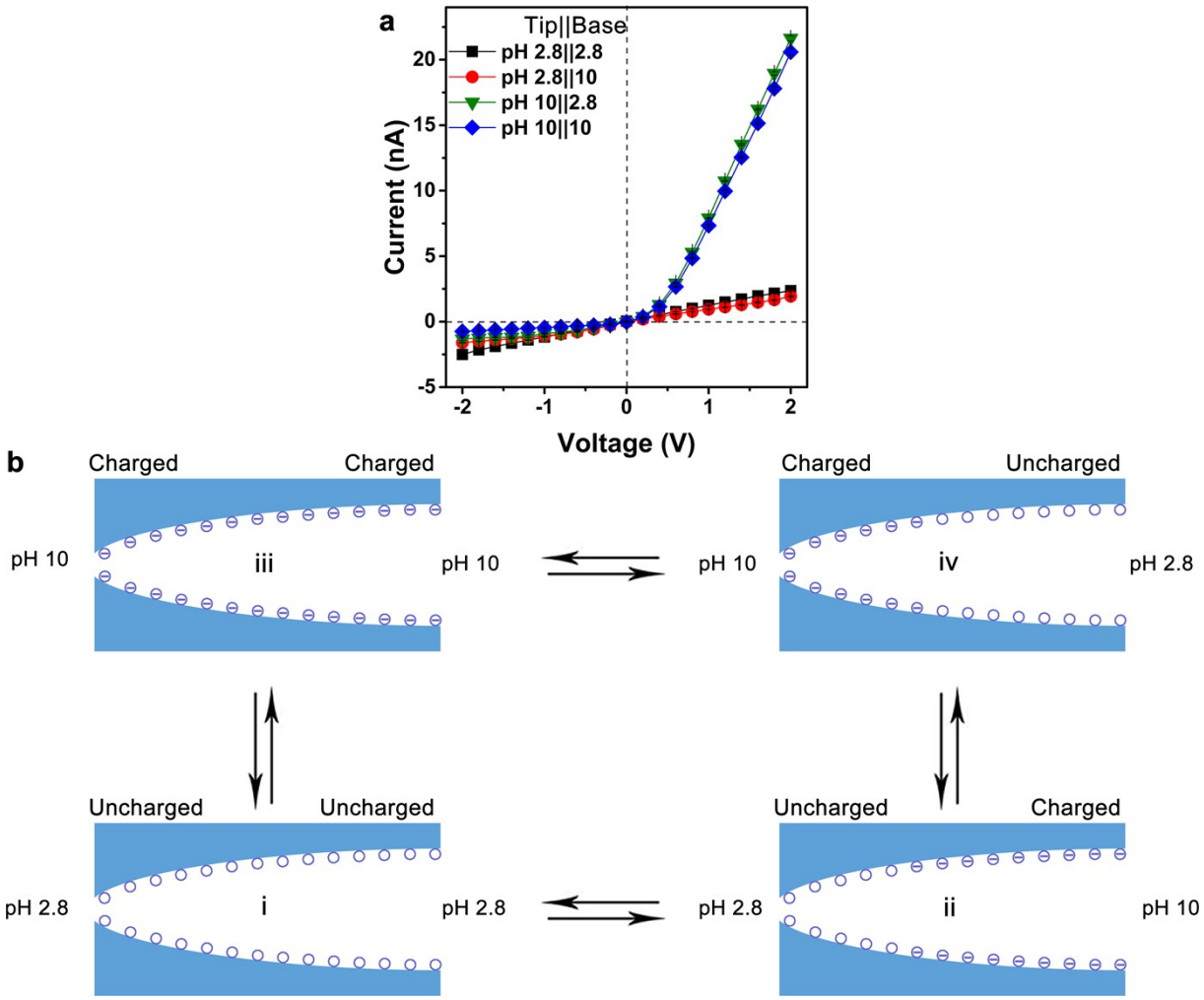

Figure S3. Ion transport property of the bullet-shaped nanochannel was mainly dependent on the surface property of the tip region of the nanochannel. a) I-V properties of the bullet-shaped nanochannel measured in 0.1 M KCl solutions with symmetric and asymmetric pH values on the tip and base sides of the channel (indicated by pH tip||base: pH 2.8||2.8 (■); pH 2.8||10 (●); pH 10||10 (◆); pH 10||2.8 (▼)) at room temperature. b) Schematic illustration of the surface property of the nanochannel under symmetric and asymmetric pH conditions: i, pH 2.8||2.8; ii, pH 2.8||10; iii, pH 10||10; iv, pH 10||2.8. Experimental I-V curves of the channel under pH 2.8||2.8 and pH 2.8||10 conditions are very close, and I-V curves of the channel under pH 10||10 and pH 10||2.8 conditions are also similar. These experimental results demonstrate that the ion transport property of the bullet-shaped nanochannel is mainly determined by the surface charge density of the small tip region of the nanochannel, which is consistent with the ion transport property observed in the conical nanochannel.[1, 2]

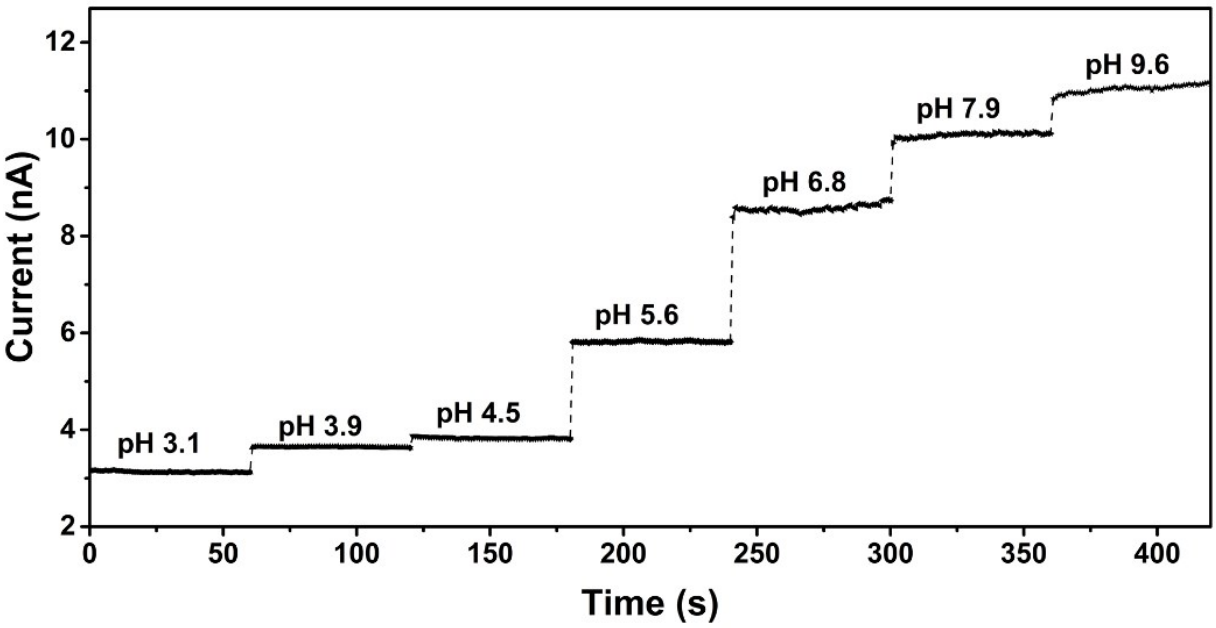

Figure S4. Un-continuous ionic current changes of the bullet-shaped nanochannel measured under conventional manually-operated pH switching system: pH switching is achieved by manually adding different 0.1 M KCl solutions with different pH values into the electrochemical cell.

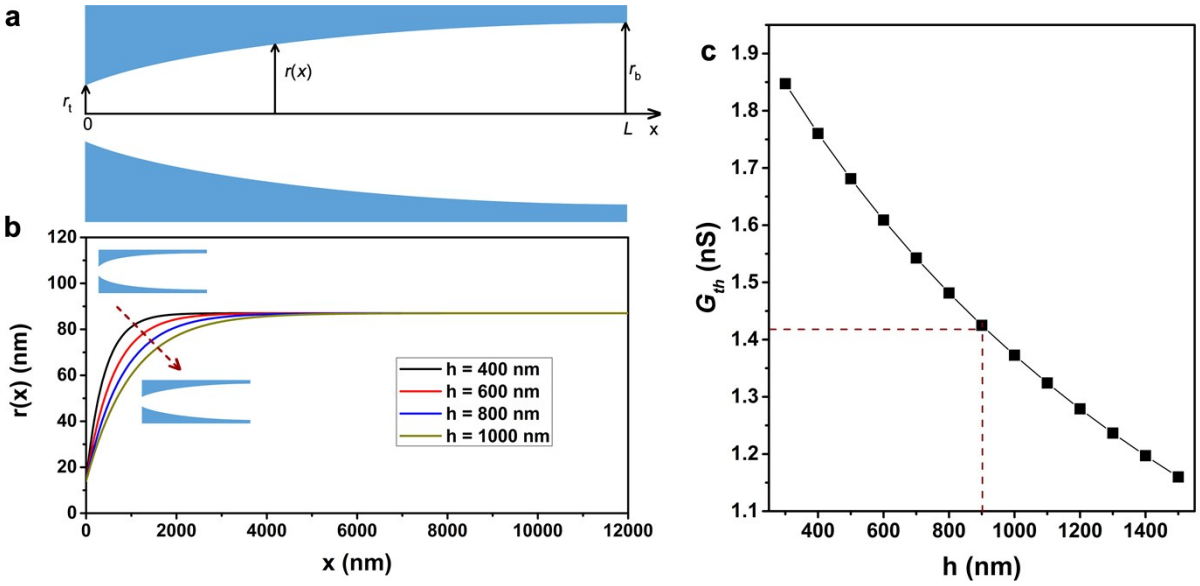

Figure S5. (a) Scheme of the bullet shaped nanochannel. (b) Theoretical radius profiles of the channel observed from equation S1. (c) Dependence of theoretical ion conductance of the nanochannel on equation S2 on *h*.

As the nanochannel is bullet-shaped, its average radius profile could be theoretically described by equation S1.[3, 4]

$$r(x) = r_b - (r_b - r_t)\exp(-\frac{x}{h}) \qquad \text{(S1)}$$

where $r_t = r(x = 0) = 14$ nm, $r_b = r(x = L) = 86$ nm, L is length of the nanochannel corresponding to membrane thickness (about 12 μm), and h is a geometrical parameter characterizing the curvature of the nanochannel profile,[5] named as *curvature radius*, which is defined from 300 to 1000 nm in accordance with previous works. The dependence of the radius profile the bullet-shaped nanochannel is shown in Figure S5b. Theoretical average resistance (R) of the uncharged bullet-shaped nanochannel can be calculated by equation S2.

$$R_{th} = \frac{1}{\pi k}\int_0^L \frac{dx}{\left[r_b - (r_b - r_t)\exp(-\frac{x}{h})\right]^2} \qquad \text{(S2)}$$

where k is the specific conductivity of the reacted solution (k of the reacted solution at 40 °C was 1.12 ± 0.02 S.m^{-1}, k of the continuously-fed solution was varied as show in Figure S6c). The conductance (G) of the nanochannel is calculated by $G_{th} = 1/R_{th}$. The experimental conductance value of the uncharged nanochannel is G_{exp} = 1.41 ± 0.05 nS (measured in pH 4.0 reacted solution). The theoretical conductance is calculated based on k = 1.12 S.m^{-1}, r_b = 86 nm, r_t = 14 nm, h = 300-1500 nm and L = 12 μm. Dependence of G_{th} on h is shown in Figure S5c. The conductance of the nanochannel decreases with increasing h value from 300 to 1000 nm. When h = 900 nm, the theoretical conductance value (1.42 nS) is close to the average experimental conductance value (1.41 ± 0.05 nS). Therefore, the theoretical ion conductance of the the nanochannel induced by ion-conductivity variation in the continuously-fed reaction solution could be calculated by equation S3. The calculated resultwas shown in Figure 2, red line.

$$G_{th}(k) = 1/R_{th} = \pi k / \int_0^{12000} \frac{dx}{\left[86 - 72\exp(-\frac{x}{1000})\right]^2} = 1.27(\text{nm}) \times k(S.m^{-1}) \qquad \text{(S3)}$$

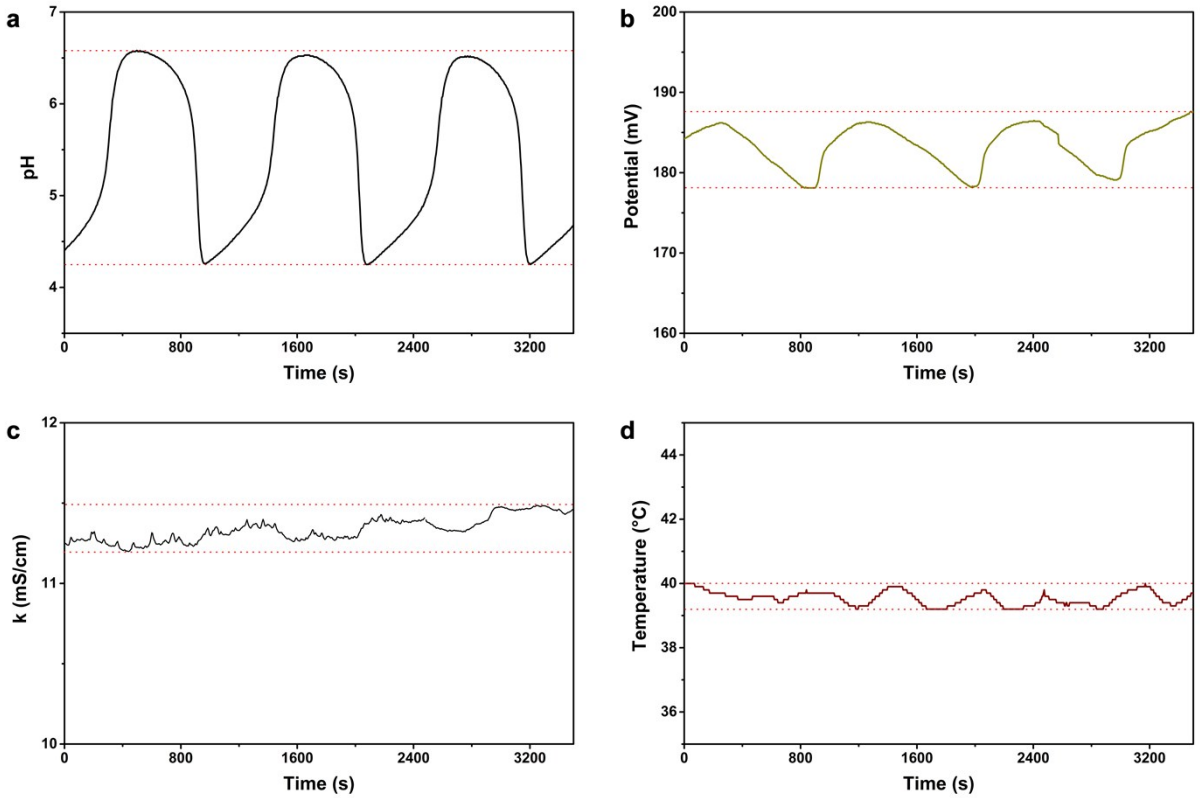

Figure S6. (a) pH, (b) potential, (c) ion conductivity, and (d) temperature oscillations of the continuously-fed reacting solution at 40 °C.

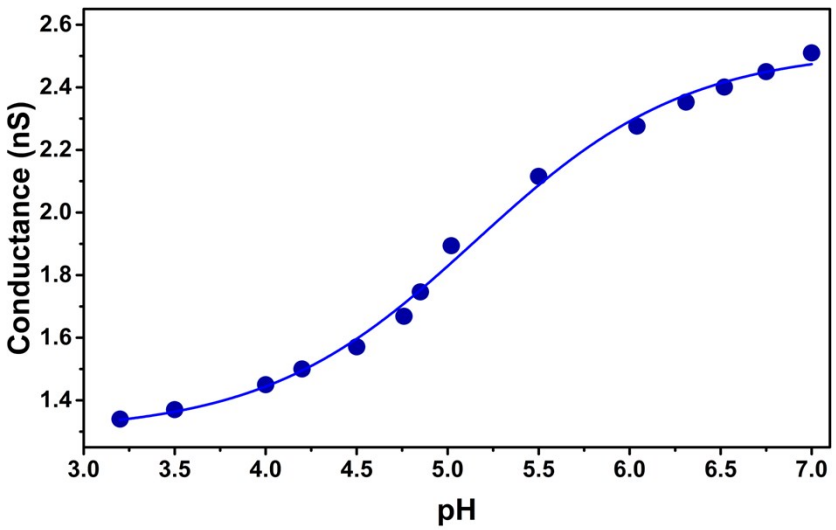

Figure S7. Dependence of experimental ion conductance value of the nanochannel on the pH value of the reacted solution at 40 °C. pH of the tip side varied from 3 to 7, while pH of the base side was maintained at 10. pH of the reacted solution is adjusted by adding 1 M HCl solution.

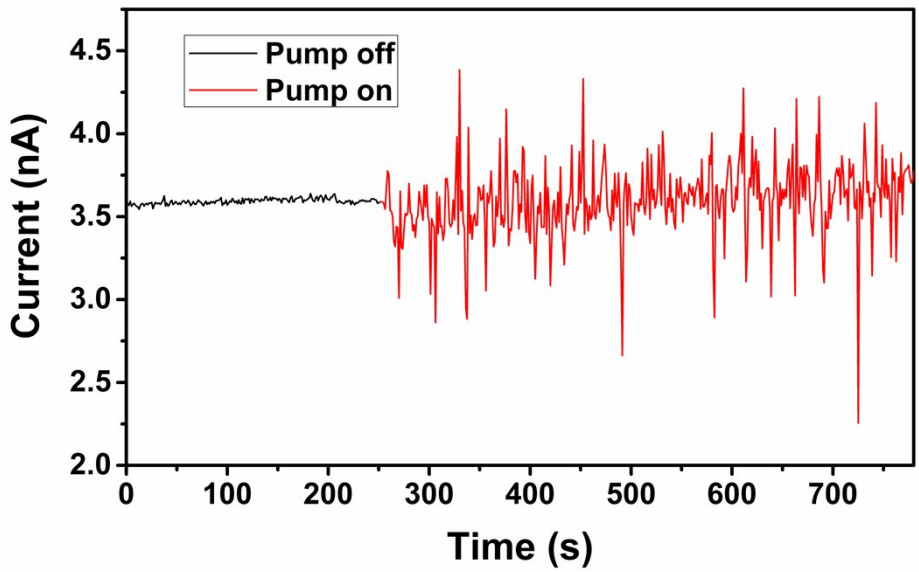

Figure S8. Influence of the pump on the peristaltic pump on the ion current noise of the nanofluidic system. The noise could be reduced by shutting down the peristaltic pump

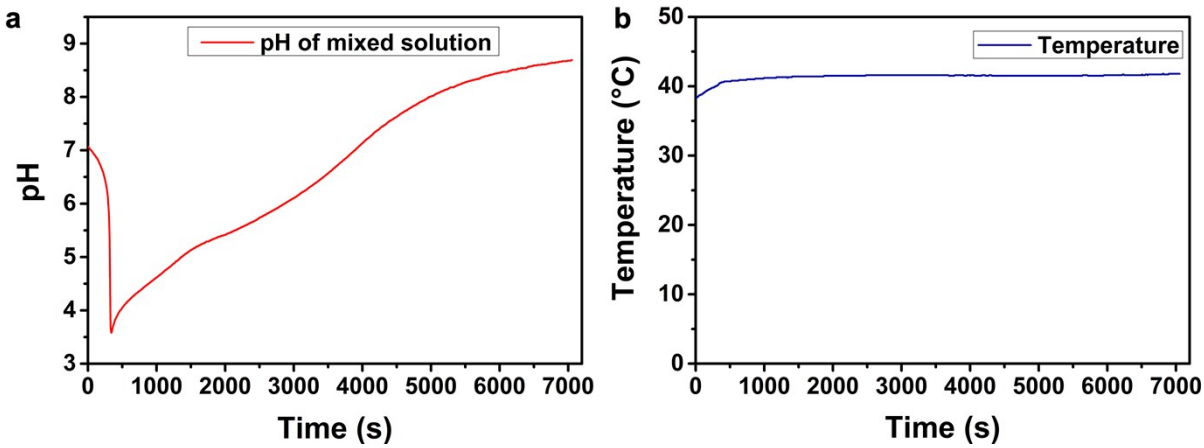

Figure S9. (a) pH and b) temperature changes of the closed (un-fed) mixed solution at 40 °C. After mixed about 3 hours, the pH value of the mixed solution was stable at about 10.

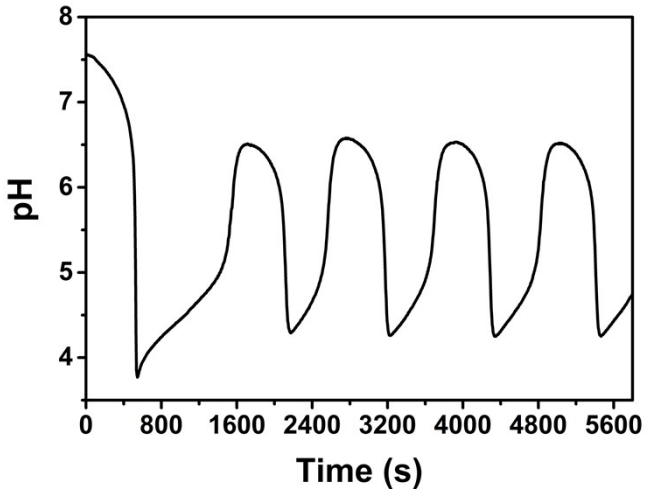

Figure S10. pH oscillation of the continuously-fed reaction solution at 40 °C. Initial pH of the reaction was above 7, the pH dramatically decreased firstly to below 4 driven by the H^+-

producing process, and then pH increased slowly to 6.6 driven by the H^+-consuming process. After that, pH stably oscillated between 4.2 and 6.6 with a period of 1070 s.

References

1 I. Vlassiouk, T. R. Kozel and Z. S. Siwy, *J. Am. Chem. Soc.*, 2009, **131**, 8211.

2 L. Wang, W. Guo, Y. B. Xie, X. W. Wang, J. M. Xue and Y. G. Wang, *Radiat. Meas.*, 2009, **44**, 1119.

3 P. Ramirez, P. Y. Apel, J. Cervera and S. Mafe, *Nanotechnology*, 2008, **19**, 315707.

4 H. Zhang, X. Hou, L. Zeng, F. Yang, L. Li, D. Yan, Y. Tian and L. Jiang, *J. Am. Chem. Soc.*, 2013, **135**, 16102.

5 P. Y. Apel, I. V. Blonskaya, O. L. Orelovitch, P. Ramirez and B. A. Sartowska, *Nanotechnology*, 2011, **22**, 175302.