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AC Electroosmotic Pumping in Nanofluidic Funnels

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Abstract

We report efficient pumping of fluids through nanofluidic funnels when a symmetric AC waveform is applied. The asymmetric geometry of the nanofluidic funnel induces not only ion current rectification but also electroosmotic flow rectification. In the base-to-tip direction, the funnel exhibits a lower ion conductance and a higher electroosmotic flow velocity, whereas in the tip-to-base direction, the funnel has a higher ion conductance and a lower electroosmotic flow velocity. Consequently, symmetric AC waveforms easily pump fluid through the nanofunnels over a range of frequencies, e.g., 5 Hz to 5 kHz. In our experiments, the nanofunnels were milled into glass substrates with a focused ion beam (FIB) instrument, and the funnel design had a constant 5° taper with aspect ratios (funnel tip width to funnel depth) of 0.1 to 1.0. We tracked ion current rectification by current-voltage (*I*–*V*) response and electroosmotic flow rectification by transport of a zwitterionic fluorescent probe. Rectification of ion current and electroosmotic flow increased with increasing electric field applied to the nanofunnel. Our results support three-dimensional simulations of ion transport and electroosmotic transport through nanofunnels, which suggest the asymmetric electroosmotic transport stems from an induced pressure at the junction of the nanochannel and nanofunnel tip.

Graphical abstract

Keywords

AC electroosmotic pump; electroosmotic flow rectification; ion current rectification; nanofluidics; nanofunnel; focused ion beam milling

Small lateral dimensions, surface charge, and geometric asymmetry in nanochannel devices lead to a number of unique ion and fluid transport properties^{1–3} and applications in chemical

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analysis.^{4–5} Due to small lateral dimensions and surface charge in nanochannel devices, channel conductance is enhanced,⁶ electroosmotic flow is reduced,^{7–9} and electrokinetic mobilities of small molecules⁹ and DNA¹⁰ are reduced. In addition, nanofluidic devices with straight channels or pores exhibit concentration polarization and are able to concentrate small molecules¹¹ and peptides and proteins^{12–13} at the nanochannel and microchannel interface. With a geometric asymmetry, quartz nanopipettes,^{14–15} track-etched polymer membranes,^{16–18} silicon-based nanochannels,¹⁹ and nanoscale funnels²⁰ rectify ion current. Conical nanopores can also electrokinetically trap and concentrate particles due to the high electric field strength at the tips of the pores.^{21–22}

In addition to rectifying ion current, experiments^{23–24} and simulations²⁵ demonstrate that devices with an asymmetric geometry exhibit higher electroosmotic flow in the base-to-tip direction. In the simplest picture, this difference in electroosmotic velocity is due to the difference in ion enrichment and depletion states in the nanofunnel that occurs during ion transport. In the base-to-tip direction (high flow velocity, low ion conductance), the ion concentration is depleted in the funnel which yields a thicker electrical double layer and an increased electroosmotic velocity. In the tip-to-base direction (low flow velocity, high ion conductance), the ion concentration is enriched in the funnel which results in a thinner electrical double layer and a reduced electroosmotic velocity. In three-dimensional simulations of ion transport through nanofunnels,²⁵ an induced pressure gradient is generated at the abrupt geometrical transition from the nanochannel to the funnel tip when ion current flows in the tip-to-base direction. This induced pressure results in a recirculation of the fluid flow; consequently, fluid flow into the funnel tip is hindered. In the base-to-tip direction, this abrupt geometrical transition does not occur, and fluid flow does not recirculate. In contrast, in pressure-driven systems, nozzles exhibit the opposite effect where flow is higher in the tip-to-base direction than in the base-to-tip direction.²⁶

Here, our primary goal is to demonstrate AC electroosmotic pumping in nanofluidic funnels. We fabricated in-plane nanofunnels in glass substrates with a focused ion beam (FIB) instrument.^{27–28} The all-glass device enabled us to work at higher field strengths compared to our prior work on ion transport in nanofunnels.^{20,29} The nanofunnels were milled with a 5° taper along the axis of fluid transport²⁰ and with aspect ratios (funnel tip width to funnel depth) from 0.1 to 1.0. The ion current rectification ratio increased with aspect ratio, i.e., surface to volume ratio, and showed a maximum at electrolyte concentrations around 10 to 50 mM. Both the ratios of ion current rectification and electroosmotic flow rectification increased with increasing electric field strengths over a range from 90 to 2000 V/cm. A symmetric sinusoidal AC waveform with an amplitude of 10 V_{p-p} (peak to peak) and frequencies from 5 Hz to 5 kHz electroosmotically pumped fluids through the nanofunnels. Contrary to a previous design with integrated valves,³⁰ our AC electroosmotic pump is valveless and relies simply on the electroosmotic flow rectification in channels with an asymmetric geometry.

Experimental Section

Materials

We purchased sodium chloride and sodium hydroxide from Mallinckrodt, Inc.; rhodamine B and methanol from Sigma-Aldrich Co.; ammonium hydroxide from J.T. Baker; hydrogen peroxide from Macron Fine Chemicals; Microposit MF-319 developer from MicroChem Corp.; chromium etchants 8002-A and 1020 and buffered oxide etchant from Transene Co.; D263 mask blanks from Telic Co.; #1.5 cover glass from VWR Inc.; Anotop 10 syringe filters from Whatman GmbH; and 353NDT Epoxy from Epoxy Technology.

Device Fabrication

Microfluidic devices were fabricated by standard UV photolithography and wet chemical etching, as described previously.³¹ D263 glass substrates coated with 120 nm of Cr and 530 nm of AZ1518 photoresist were exposed to 200 mJ/cm² UV radiation through a photomask (HTA Photomask). Substrates were developed in MF-319 developer for 2 min and rinsed with water. The microchannel pattern was transferred to the chromium layer by etching for 8 min in chromium etchant 8002-A. Finally, microchannels were etched to a depth of 9.5 μm and width of 40 μm in buffered oxide etchant. Dimensions of the microchannels were determined with a stylus-based profiler (Dektak 6M, Veeco Instruments, Inc.). Access holes were sandblasted into the ends of the channels (AEC Air Eraser, Paasche Airbrush Co.) before removal of remaining photoresist with acetone and chromium with chromium etchant 1020. Substrates were cleaned with a solution of NH_4OH , H_2O_2 , and H_2O (2:1:2) at 70 $^\circ\text{C}$ for 20 min, sonicated in water, rinsed with water, and dried overnight in a 90 $^\circ\text{C}$ oven.

The nanofunnel and two nanochannels were milled directly into the glass substrates in the 80- μm long gap between the microchannels with a focused ion beam (FIB) instrument (Auriga 60, Carl Zeiss GmbH) controlled by the NanoPatterning and Visualization Engine (NPVE; FIBICS, Inc.).^{27–28} With a 30-kV ion beam at 50 pA, the nanofunnel and two nanochannels were milled to depths of 50, 110, 260, and 520 nm with doses of 0.25, 0.5, 1, and 2 nC/ μm^2 , respectively. For the nanofunnels, these depths yielded aspect ratios (funnel tip width to funnel depth) of 1.0, 0.5, 0.2, and 0.1, respectively. The funnel and channels were milled with the assistance of an electron flood gun (FG 15/40, SPECS, GmbH) at 5 eV and 20 μA , which compensated for positive charge build-up on the substrate surface. The scanning electron microscope (SEM) on the FIB instrument and an atomic force microscope (AFM; MFP-3D, Asylum Research, Inc.) were used to determine widths and depths, respectively, of the nanofunnel and nanochannels. Prior to bonding, the substrate was hydrolyzed in a solution of 1 M NaOH for 15 min at room temperature, and the #1.5 cover glass was hydrolyzed in a solution of 1 M NaOH at 70 $^\circ\text{C}$ for 15 min. The substrate and cover glass were then sonicated in water, rinsed with water, brought into contact with each other, dried overnight at 90 $^\circ\text{C}$, and annealed in a furnace at 545 $^\circ\text{C}$ for 12 h. Glass reservoirs were epoxied over sandblasted holes.

Ion Current Rectification Measurements

Channels were sequentially filled with methanol, methanol/water (1:1), water, 100 mM NaOH, water, and concentrations of NaCl between 0.1 and 100 mM. All solutions were

filtered through 20-nm syringe filters. We used a picoammeter/voltage source (6487 Keithley Instruments, Inc.) to collect current-voltage (I–V) curves from nanofunnels with aspect ratios of 0.1, 0.2, 0.5, and 1.0. We tested three devices of each aspect ratio. For the current-voltage (I–V) measurements, the working electrode was placed on the base side of the funnel in the solution 1 reservoir, and the counter electrode, which was held at ground, was placed on the tip side of the funnel in the solution 2 reservoir (see Figure 1). Silver-silver chloride wire electrodes made electrical connections to the solution reservoirs. The potential applied at the funnel base was swept from –10 V to +10 V in triplicate, then from +10 V to –10 V in triplicate at 0.1 V/step for 1 s/step to generate six I–V curves.

Electroosmotic Flow Measurements

In the nanofunnel devices, we measured the electroosmotic velocity by monitoring the arrival time of a zwitterionic dye (rhodamine B). The length of the nanofunnel and two nanochannels milled between the microchannels was 80- μm long. The detection point was positioned in the nanochannel 65 μm from the microchannel containing the dye, approximately halfway between the end of the nanofunnel and the micro- and nanochannel junction. The 65- μm distance allowed sufficient time to make an accurate electroosmotic flow measurement, especially at high field strengths. The arrival time of the dye was monitored on an inverted optical microscope (IX71, Olympus, Inc.), and a green helium-neon laser focused to a spot with a 60 $\times$ objective at the detection point was used to excite the dye.⁸ The fluorescence was collected by the objective, spectrally filtered with a TRITC filter cube (U-N41002, Olympus, Inc.), spatially filtered with a 100- μm pinhole, detected with a photomultiplier tube (H5783-01, Hamamatsu Photonics), amplified (SR570, Stanford Research Systems, Inc.), and recorded through a multifunction data acquisition card (PCI-6032, National Instruments Corp.) with a LabVIEW program (National Instruments Corp.).

A positive potential (0.3–10 V) from an analog output card (PCI-6713, National Instruments Corp.) controlled through the LabVIEW program was applied through a silver-silver chloride electrode to a solution reservoir containing rhodamine B dye, and a silver-silver chloride electrode inserted into the other solution reservoir was held at ground. For each set of measurements, the average field strength in the nanofunnel was stepped from lowest (90 V/cm) to highest (2000 V/cm). The arrival time of the dye front in the nanochannel was fitted with a sigmoidal curve and corresponded to the half-height of the fitted curve. For the highest to lowest field strengths, arrival times of the rhodamine B solution at the detection point ranged from 0.034 to 0.98 s in the base-to-tip direction and 0.068 to 1.04 s in the tip-to-base direction, respectively. With a diffusion coefficient³² of $4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, rhodamine B diffuses the 65 μm to the detection point in ~ 5.3 s, which is 5.1 times slower than the arrival time of the rhodamine B at the lowest field strength (1.04 s).

AC Electroosmotic Pumping Measurements

To measure the net transport of the rhodamine B in the nanochannels under an AC electric field, we applied an AC waveform from the LabVIEW card. In each measurement, we used a symmetric sinusoidal waveform of 10 V_{p-p} (peak to peak) and varied the frequency from 1

Hz to 50 kHz. The arrival time of the dye front in the nanochannels was fitted with a sigmoidal curve and corresponded to the half-height of the fitted curve.

Results and Discussion

Nanofunnel Design

Figure 1b shows an AFM image of a nanofunnel fabricated between two nanochannels that bridge the 80- μm gap between the two V-shaped microchannels. Each funnel was 11.3 μm long (Figure 1a), and the two nanochannels were each $\sim 35 \mu\text{m}$ long and connected the funnel tip and base to the microchannels. All funnels used in this study were $50 \pm 3 \text{ nm}$ wide at the tip and $1.03 \pm 0.1 \mu\text{m}$ wide at the base, and each funnel had a taper of 5° . The funnels were milled to uniform depths of 50 ± 4 , 110 ± 10 , 260 ± 20 , and $520 \pm 20 \text{ nm}$. The two connecting nanochannels were $1.02 \mu\text{m}$ wide and milled to the same depths as the nanofunnels. With the funnel tip width of 50 nm , the funnels with depths of 50 , 110 , 260 , and 520 nm had aspect ratios (funnel tip width to funnel depth) of 1 , 0.5 , 0.2 , and 0.1 , respectively.

Effect of Funnel Geometry and Electrolyte Concentration on Ion Transport

We tested various funnel aspect ratios to see how well a funnel with a narrow tip width and larger depth (aspect ratio = 0.1) rectified ion current compared to a funnel with a similar tip width and depth (aspect ratio = 1). We characterized the ion current rectification in nanofunnels with funnel aspect ratios of 0.1 , 0.2 , 0.5 , and 1 and electrolyte concentrations from 1 to 100 mM . The potential of the working electrode was stepped at 0.1 V/step for 1 s/step from -10 to 10 V in triplicate and then swept from 10 to -10 V in triplicate at the same rate. Figure 2 shows an average I - V curve for three funnels filled with 10 mM NaCl , which demonstrates ion current rectification. When counterions (cations) are moving in the base-to-tip direction with a positive potential applied at the base, a depletion zone forms in the funnel, and a low conductance state exists. When the potential at the base is negative and counterions move in the tip-to-base direction, an enrichment zone forms in the funnel, a high conductance state occurs, and current is enhanced.

Figure 3 shows the variation of the rectification ratio achieved in nanofunnels with aspect ratios of 0.1 , 0.2 , 0.5 , and 1 . Although all devices demonstrated some degree of ion current rectification, the rectification ratio increased as the aspect ratio approached 1 . Devices with an aspect ratio of 1 have the highest surface-to-volume ratio at the funnel tip, which is needed to drive ion current rectification. We did not test funnels with aspect ratios > 1 because the funnel width dictates the degree of ion current rectification.²⁹ Because aspect ratios of 0.5 and 1 produced similar rectification ratios, we used funnels with an aspect ratio of 0.5 for electroosmotic flow measurements. The deeper channels had a lower hydrodynamic resistance than the shallower channels; consequently, the deeper channels were easier to fill and to exchange NaCl solutions.

Figure 4 shows the variation of the rectification ratio with NaCl concentration for devices with an aspect ratio of 0.5 . NaCl concentrations between 0.1 and 100 mM were tested, and the ion current rectification ratio exhibited a maximum around 10 to 50 mM NaCl . We

performed all electroosmotic flow measurements at a NaCl concentration of 50 mM due to the higher conductivity and high rectification ratio.

Electroosmotic Flow Rectification

With a DC potential applied, we measured the electroosmotic velocity both from the funnel base to tip and from the funnel tip to base on three nanofunnel devices. Although the flow velocities in both directions increased linearly with increasing field strength, the slope of this increase was different for each direction of transport. The electroosmotic velocity was higher in the base-to-tip direction, and the electroosmotic flow rectification reached a maximum of 2 at the highest field strength (Figure 5). Both the ion current and electroosmotic flow rectification increase as a function of average electric field strength in the nanofunnel (Figure 6).

AC Electroosmotic Pump

The ability of these nanofunnels to rectify electroosmotic flow suggests that net transport of fluid occurs in one direction under an AC field. This asymmetric flow ratchets the fluid through the funnel with each half-cycle of the AC field and depends on the amplitude and frequency of the waveform. We used a sinusoidal waveform of 10 V_{p-p} (peak to peak) for all measurements and varied the frequency of the waveform from 1 Hz to 50 kHz. Figure 7 shows the variation of the AC flow velocity with the frequency of the applied waveform. We note that at frequencies below 5 Hz, the fluid velocity in the channels was fast enough that the fluorescent probe reached the detection point on the first half-cycle. Measurements at lower frequencies would necessitate a longer channel, lower amplitude waveform, or both. Further, AC pumping at frequencies > 5 kHz was not observed.

To understand the limits of AC pumping at frequencies > 5 kHz, we consider the charge relaxation rate and the distances the ions travel in the funnel during formation of the enrichment and depletion regions. The charge relaxation time of a liquid³³ is $\tau = \epsilon/\sigma$ where ϵ is the permittivity of water and σ is the conductivity of the medium. For $\epsilon = 7.1 \times 10^{-12}$ A s V⁻¹ cm⁻¹ and $\sigma = 5 \times 10^{-3}$ S cm⁻¹ for 50 mM NaCl, the charge relaxation time is estimated to be 1.4 ns, which is much faster than the 50 μ s of a half-cycle at 10 kHz. Consequently, charge relaxation is not expected to contribute to the rectification of electroosmotic flow. Next, we calculate the distance traveled by the ions during formation of at least a partial enrichment or depletion region within the funnel. The distance traveled by each ion is $l = \mu_{ep}Et$ where μ_{ep} is the electrophoretic mobility, E is the average electric field strength in the funnel, and t is the time during a half-cycle at 10 kHz. For $\mu_{ep} = 5.2 \times 10^{-4}$ cm²V⁻¹s⁻¹ for Na⁺, $\mu_{ep} = 7.9 \times 10^{-4}$ cm²V⁻¹s⁻¹ for Cl⁻, $E = 590$ V/cm with 10 V_{p-p} applied, and $t = 50$ μ s, the distances traveled are 0.15 μ m for Na⁺ and 0.23 μ m for Cl⁻. As expected, the distances traveled by the ions are a small fraction of the funnel length of 11.3 μ m, which, in turn, are insufficient to establish electroosmotic flow rectification.

Because our device had only a single nanofunnel, we were not able to measure the backpressure during operation. To estimate the operating backpressure, we use the Darcy-Weisbach equation³⁴ for pressure loss with laminar flow (p):

$$\Delta p = \frac{32\rho V^2 L}{ReD} \quad (1)$$

where ρ is the fluid density, V is the volumetric flow rate, L is the channel length, Re is the Reynolds number, and D is the hydraulic diameter of the channel. For a straight nanochannel with cross-sectional dimensions of 110 nm deep and 1.0 μm wide, the hydraulic diameter is 200 nm. For the 80- μm long channel, the operating backpressure is calculated to be 10.8 kPa in DC mode and 4.5 kPa at 5 Hz and 0.9 kPa at 5 kHz in AC mode.

Conclusion

We demonstrated that nanofluidic funnels with an asymmetric geometry rectify both ion current and electroosmotic flow, but in opposite directions. The electroosmotic flow rectification can be exploited to efficiently pump fluids through the funnels with a symmetric sinusoidal AC waveform applied. This AC electroosmotic pump is a valveless design that simply requires a geometrical asymmetry and surface charge to effect net fluid transport in the base-to-tip direction. Further, we found that funnels fabricated with an aspect ratio close to 1 rectify current best, and the degree of ion current and electroosmotic flow rectification increases with field strength.

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References

1. Schoch RB, Han J, Renaud P. *Rev. Mod. Phys.* 2008; 80:839–883.
2. Zangle TA, Mani A, Santiago JG. *Chem. Soc. Rev.* 2010; 39:1014–1035. [PubMed: 20179822]
3. Haywood DG, Saha-Shah A, Baker LA, Jacobson SC. *Anal. Chem.* 2015; 87:172–187. [PubMed: 25405581]
4. Kovarik ML, Jacobson SC. *Anal. Chem.* 2009; 81:7133–7140. [PubMed: 19663470]
5. Piruska A, Gong M, Sweedler JV, Bohn PW. *Chem. Soc. Rev.* 2010; 39:1060–1072. [PubMed: 20179825]
6. Stein D, Kruithof M, Dekker C. *Phys. Rev. Lett.* 2004; 93:035901. [PubMed: 15323836]
7. Jacobson, SC.; Alarie, JP.; Ramsey, JM. *Proceedings of the Micro Total Analysis Systems Symposium*. Ramsey, JM.; van den Berg, A., editors. Dordrecht, The Netherlands: Kluwer Academic Publishers; 2001. p. 57-59.
8. Haywood DG, Harms ZD, Jacobson SC. *Anal. Chem.* 2014; 86:11174–11180. [PubMed: 25365680]
9. Pennathur S, Santiago JG. *Anal. Chem.* 2005; 77:6782–6789. [PubMed: 16255574]
10. Menard LD, Ramsey JM. *Anal. Chem.* 2013; 85:1146–1153. [PubMed: 23234458]
11. Pu Q, Yun J, Temkin H, Liu S. *Nano Lett.* 2004; 4:1099–1103.
12. Wang Y-C, Stevens AL, Han J. *Anal. Chem.* 2005; 77:4293–4299. [PubMed: 16013838]
13. Kim SJ, Wang YC, Lee JH, Jang H, Han J. *Phys. Rev. Lett.* 2007; 99:044501. [PubMed: 17678369]
14. Wei C, Bard AJ, Feldberg SW. *Anal. Chem.* 1997; 69:4627–4633.
15. Umehara S, Pourmand N, Webb CD, Davis RW, Yasuda K, Karhanek M. *Nano Lett.* 2006; 6:2486–2492. [PubMed: 17090078]

16. Siwy Z, Fulinski A. *Phys. Rev. Lett.* 2002; 89:198103. [PubMed: 12443155]
17. Siwy ZS. *Adv. Funct. Mater.* 2006; 16:735–746.
18. Kovarik ML, Zhou K, Jacobson SC. *J. Phys. Chem. B.* 2009; 113:15960–15966. [PubMed: 19908894]
19. Karnik R, Duan C, Castelino K, Daiguji H, Majumdar A. *Nano Lett.* 2007; 7:547–551. [PubMed: 17311461]
20. Perry JM, Zhou K, Harms ZD, Jacobson SC. *ACS Nano.* 2010; 4:3897–3902. [PubMed: 20590127]
21. Lee S, Zhang YH, White HS, Harrell CC, Martin CR. *Anal. Chem.* 2004; 76:6108–6115. [PubMed: 15481960]
22. Kovarik ML, Jacobson SC. *Anal. Chem.* 2008; 80:657–664. [PubMed: 18179245]
23. Bishop GW, Lopez MM Jr, Rajasekaran PR, Wu X, Martin CR. *J. Phys. Chem. C.* 2015; 119:16633–16638.
24. Jin P, Mukaibo H, Horne LP, Bishop GW, Martin CR. *J. Am. Chem. Soc.* 2010; 132:2118–2119. [PubMed: 20121145]
25. Hlushkou D, Perry JM, Jacobson SC, Tallarek U. *Anal. Chem.* 2012; 84:267–274. [PubMed: 22111623]
26. Stemme E, Stemme G. *Sens. Actuators, A.* 1993; 39:159–167.
27. Harms ZD, Haywood DG, Kneller AR, Selzer L, Zlotnick A, Jacobson SC. *Anal. Chem.* 2015; 87:699–705. [PubMed: 25489919]
28. Harms ZD, Selzer L, Zlotnick A, Jacobson SC. *ACS Nano.* 2015; 9:9087–9096. [PubMed: 26266555]
29. Perry JM, Harms ZD, Jacobson SC. *Small.* 2012; 8:1521–1526. [PubMed: 22415976]
30. Brask A, Snakenborg D, Kutter JP, Bruus H. *Lab Chip.* 2006; 6:280–288. [PubMed: 16450039]
31. Zhuang Z, Starkey JA, Mechref Y, Novotny MV, Jacobson SC. *Anal. Chem.* 2007; 79:7170–7175. [PubMed: 17685584]
32. Culbertson CT, Jacobson SC, Ramsey JM. *Talanta.* 2002; 56:365–373. [PubMed: 18968508]
33. Ramos A, Morgan H, Green NG, Castellanos A. *J. Phys. D: Appl. Phys.* 1998; 31:2338–2353.
34. Elger, DF.; Crowe, CT.; Roberson, JA.; Williams, BC. *Engineering Fluid Mechanics*. 10th. Hoboken, NJ: John Wiley & Sons, Inc; 2013.

Figure 1.

(a) Schematic of the nanofunnel integrated into the microfluidic device with two V-shaped microchannels. The nanofunnels were 50-nm wide at the tip, 1.0- μm wide at the base, and 11.3- μm long with depths of 50, 110, 260, and 520 nm. (b) Atomic force microscope image of a 5° nanofunnel with an aspect ratio of 0.5 (funnel tip width to funnel depth).

Figure 2.

Average current-voltage (I-V) curve for nanofunnels filled with 10 mM NaCl. The potential applied at the funnel base was swept at 0.1 V/step for 1 s/step with the funnel tip held at ground. Error bars at every 5th point are $\pm\sigma$ for six I-V curves on three nanofunnels ($n = 18$).

Figure 3.

Variation of the ion current rectification ratio with aspect ratio for nanofunnels with potentials of ± 10 V applied. The rectification ratio is the absolute value of current measured at the negative applied potential (e.g., -10 V) divided by the current measured at the positive applied potential (e.g., $+10$ V). The aspect ratio is the funnel tip width to funnel depth. Error bars are $\pm\sigma$ for six I–V curves on three funnels for each aspect ratio ($n = 18$).

Figure 4.

Variation of the ion current rectification ratio with NaCl concentration for nanofunnels with potentials of ± 10 V applied. The funnel had an aspect ratio = 0.5. Error bars are $\pm\sigma$ for six I-V curves on three funnels for each NaCl concentration (n = 18).

Figure 5.

Variation of the electroosmotic velocity in the base-to-tip and tip-to-base directions with average field strength in the nanofunnel. The funnel had an aspect ratio = 0.5, and the NaCl concentration was 50 mM. Error bars are $\pm\sigma$ for three measurements on three funnels at each field strength (n = 9).

Figure 6.

Variation of the electroosmotic flow (EO) rectification ratio (left) and ion current rectification ratio (right) with the average electric field strength in the nanofunnel. Electroosmotic flow in the funnels rectifies in the base-to-tip direction whereas the ion current rectifies in the tip-to-base direction. The nanofunnel had an aspect ratio = 0.5, and the NaCl concentration was 50 mM. Error bars are $\pm\sigma$ for three flow measurements on three funnels ($n = 9$) and for six current measurements on three funnels ($n = 18$).

Figure 7.

Variation of the AC electroosmotic pump velocity with AC frequency for a symmetric sinusoidal waveform with an amplitude of $10 V_{p-p}$ applied to the nanofunnel. Net transport of rhodamine B is due to a higher electroosmotic velocity in the base-to-tip direction than the tip-to-base direction. The nanofunnel had an aspect ratio = 0.5, and the NaCl concentration was 50 mM. Error bars are $\pm\sigma$ for three measurements on three funnels at each frequency ($n = 9$).