Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for:

Macroscopic movement of electrolyte-droplet reveals the characteristics of microscopic ion dynamics

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Experimental & Methods

Preparation and electrical characterization of the ionovoltaic device

N-type Si wafers ((100) with edge (110) (110), resistivity 8500 Ω·cm, MTI corporation) with a naturally deposited oxide layer (approximately 1-2 mm thickness) were used as electrode. The contact angle of the wafer was found to be about 80º (Fig. S1). NaCl (≥99.0%, Samchun chemicals), KCl (≥99.0%, Junsei chemicals), and $MgCl_2$ (≥98.0%, Sigma-Aldrich) crystals were dissolved in deionized water (18.2 $M\Omega \cdot cm$, Direct Q® 3 UV, Merck). Each electrolyte-droplet was dragged by the width of a 1 cm Si wafer or a slide glass using a custom machine consisting of a motor. Due to their relative hydrophilicity of the wafer and glass compared to the substrate, the droplet was successfully dragged by the motor. The output voltage and current generated by the ion-electron interaction were measured by a Keithley 2182A nanovoltmeter and a 6485 picoammeter, respectively.

Measurement of the Force-distance curve

Force-distance curves were recorded by a Park Systems NX10 (Park Systems), and we used an N-type OMCL-AC160TS cantilever (Olympus, resistivity = 0.1-0.4 Ω·cm, spring constant = 26 N/m). N-type Si wafers ((100) with edge (110) (110), resistivity 1000 Ω·cm, MTI Corporation) were immersed in various concentrations of NaCl aqueous solution, respectively (from 10^{-6} M to 10^{-1} M).

Derivation of the characteristic equation

From Figure 2a in the manuscript, the output current and voltage are expressed as follows,[1]

$$I = I_i - I_p, \qquad (S1)$$

$$V = V_i - IR_{s+c}, \qquad (S2)$$

$$R_p + R_{s+c} = R_{semi}, \qquad (S3)$$

where $V_i = I_p R_p$.

Combining eqs 2, S1 and S2 produces

$$I = \frac{\varepsilon}{d} W v \left(\frac{c}{c_0}\right)^{\beta} \sum_i \psi_i - \frac{\left(V + IR_{s+c}\right)}{R_p} \qquad (S4)$$

Substituting eq S3 into S4 yields the characteristic equation of the device:

$$I = -\frac{1}{R_{semi}}\left(V - vlR_{\square}\frac{\varepsilon}{d}\left(\frac{c}{c_0}\right)^{\beta} \sum_i \psi_i(v,c)\right) \qquad (S5)$$

We assume the electrolyte-droplet has a rectangular shape, whose width and length are respectively W and l. Therefore, the short-circuit current I_{sc} becomes

$$I_{sc} = vl\frac{W}{L}\frac{\varepsilon}{d}\left(\frac{c}{c_0}\right)^{\beta} \sum_i \psi_i(v,c) \qquad (S6)$$

where $R_{semi} = \frac{L}{W} R_{\square}$.

Derivation of eq 7 using the modified Poisson-Boltzmann model[2-5]

The modified Boltzmann distribution describes the net local ion density as follows,

$$n_+ = \frac{n_0 e^{-\frac{q\psi(z)}{k_B T}}}{1 + 4a^3 n_0 \sinh^2\left(\frac{q\psi(z)}{2k_B T}\right)}, \qquad (S7)$$

and

$$n_- = \frac{n_0 e^{\frac{q\psi(z)}{k_B T}}}{1 + 4a^3 n_0 \sinh^2\left(\frac{q\psi(z)}{2k_B T}\right)}. \qquad (S8)$$

n_+ and n_- are respectively the local number density of cation and anion. The ions are treated as hard spheres with a finite ion size.

The local charge density of ions with z being normal to the solid surface, $\rho_{ion}(z)$, determines the amount of the accumulated charges ($\sigma_{semi} = -\int \rho_{ion} dz - \sigma_{surf}$). The amount of ionic charge that contributes to the accumulation of charge in the semiconductor is given by $\int_z \rho_{ion} dz$. The integration range refers to the effective distance over which charges interact within the semiconductor. Poisson's equation replaces charge density with potential distribution as follows.

$$\int_z \rho_{ion} dz = \int_z -\varepsilon\varepsilon_0 \frac{d^2\psi(z)}{dz^2} dz \qquad (S9)$$

According to the modified Poisson-Boltzmann model, the derivative of surface potential to the normal distance to the surface z is

$$\frac{d\psi(z)}{dz} = \sqrt{\frac{2k_B T}{\varepsilon\varepsilon_0 a^3} \ln\left(1 + 2\nu \sinh^2\left(\frac{q\psi_0}{2k_B T}\right)\right)}. \qquad (S10)$$

a is the diameter of the hydrated cation. $\nu = 2a^3 n$ is a packing parameter. n is the number density of bulk ions. Thus,

$$\int_Z \rho_{ion} dz \cong \varepsilon\varepsilon_0 \left(\frac{d\psi(z)}{dz}\bigg|_{z=0} - \frac{d\psi(z)}{dz}\bigg|_{z=1/\kappa} \right). \qquad (S11)$$

Here, we assume the Debye length $1/\kappa$ as the effective thickness of the EDL where the ions in the EDL attract the electrons at the semiconductor,[6] and set the electrical potential at the Debye length as a decreased surface potential in magnitude by $1/e$ (i.e., $\psi(1/\kappa) = \psi_0/e)$.

Insertion of Eq S10 into Eq S11 gives

$$\int_Z \rho_{ion} dz \cong \sqrt{\frac{2\varepsilon\varepsilon_0 k_B T}{a^3}} \left\{ \sqrt{\ln\left(1 + 2\nu \sinh^2\left(\frac{q\psi_0}{2k_B T}\right)\right)} - \sqrt{\ln\left(1 + 2\nu \sinh^2\left(\frac{q\psi_0}{2ek_B T}\right)\right)} \right\}.$$

$(S12)$

Hence, the OCV of the ionovoltaic device is

$$V_{OC}(v,c) \cong vlR_{\square}\left(\frac{c}{c_0}\right)^{\beta} \left[\sqrt{\frac{2\varepsilon\varepsilon_0 k_B T}{a^3}} \left\{ \sqrt{\ln\left(1 + 2\nu \sinh^2\left(\frac{q\psi_0}{2k_B T}\right)\right)} - \sqrt{\ln\left(1 + 2\nu \sinh^2\left(\frac{q\psi_0}{2ek_B T}\right)\right)} \right\} + \sigma_{surf} \right]$$

$(S13)$

which is the eq 7 in the main text.

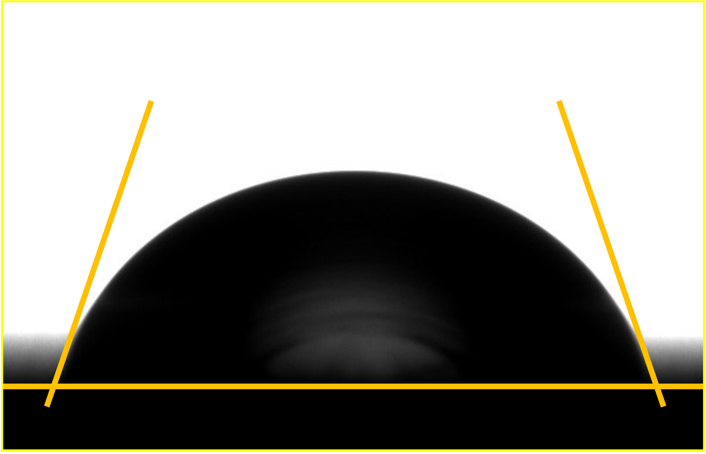

Fig. S1 Measurement of DI water contact angle on silicon substrate (ρ = 8500 Ω·cm).

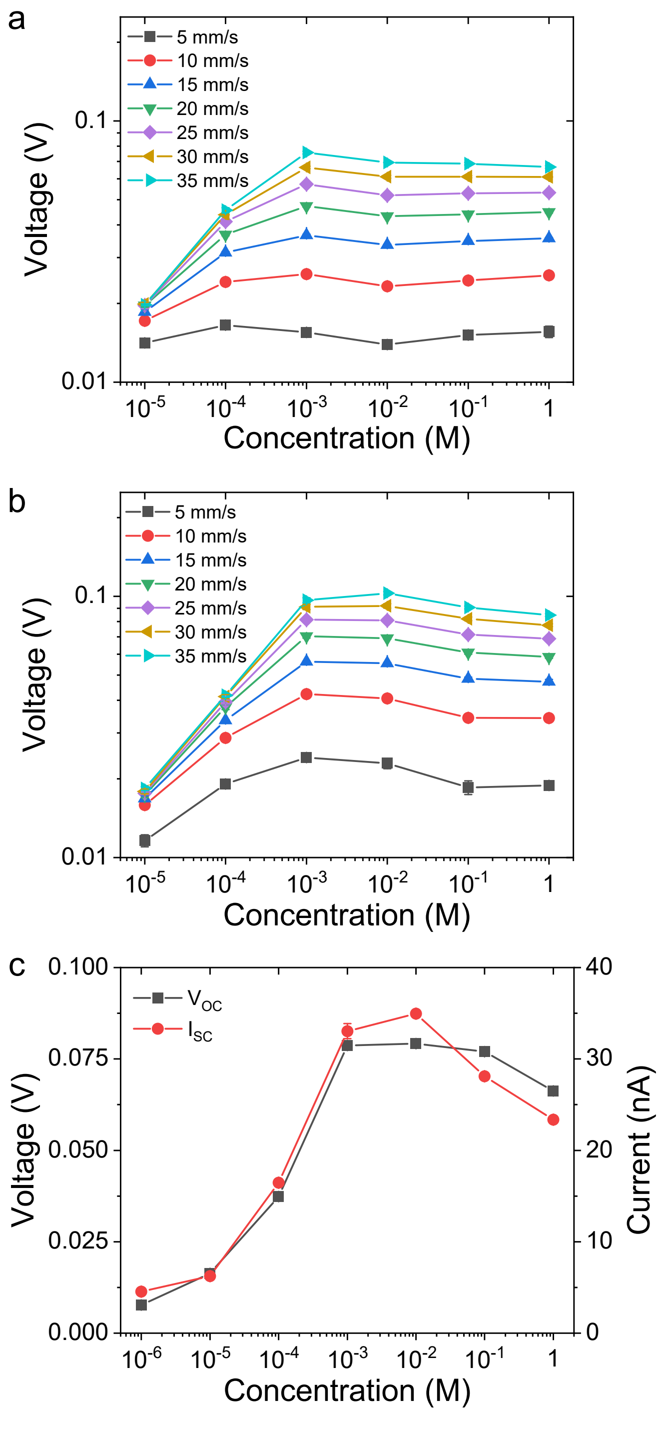

Fig. S2 Measured open-circuit voltage as a function of the concentration of **(a)** KCl and **(b)** $MgCl_2$ electrolyte-droplet at different velocities. The volume of the droplets is 100 μL. **(c)** Measured open-circuit voltage (V_{OC}) and short-circuit current (I_{SC}) with respect to NaCl droplet concentration when the droplet flows at 25 mm/s. The volume of the droplet is 100 μL.

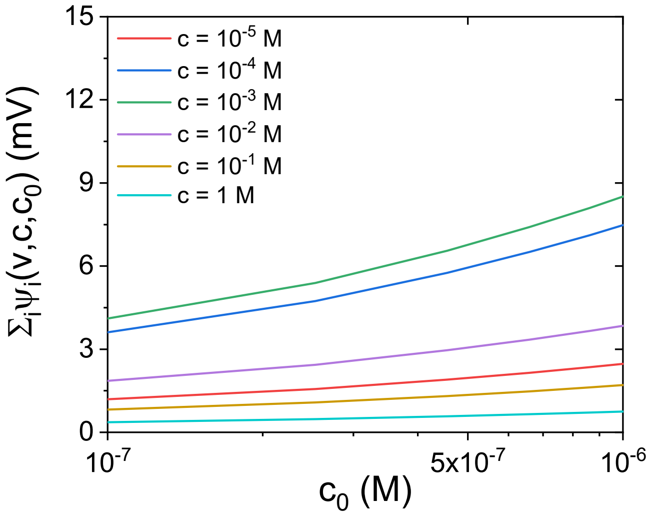

Fig. S3 Dependence of the potential $\sum_i \psi_i(v,c,c_0)$ on the reference concentration c_0 calculated from eq 2. The value of β is fixed as 0.32.

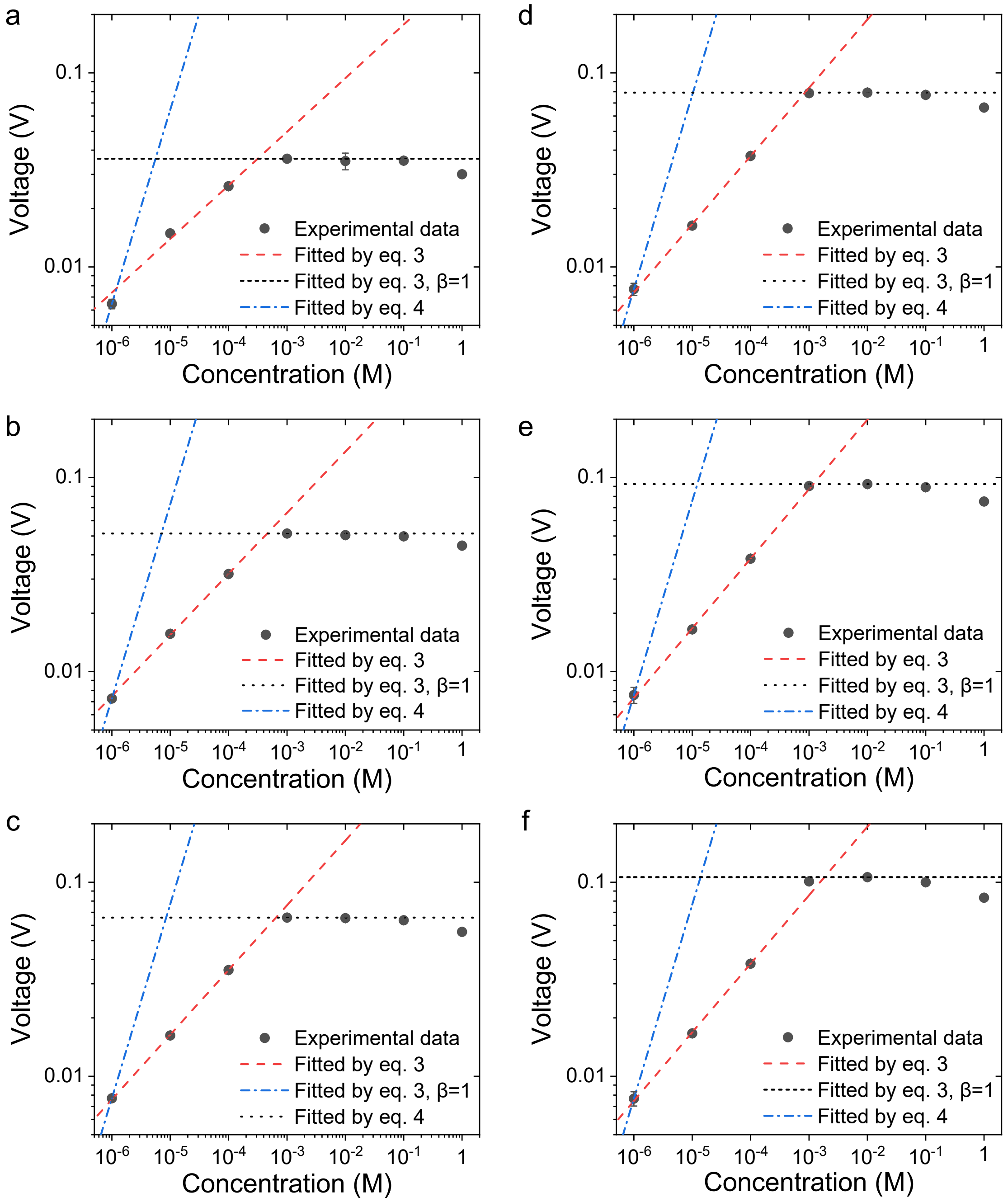

Fig. S4 Measured OCV as a function of NaCl droplet concentration. The fitted line by eq 3 (red dashed line), the one by eq 3 when $\beta = 1$ (blued dash-dotted line), and the one by eq 4 (black dotted line) are described, respectively. Droplet flows at **(a)** 10 mm/s, **(b)** 15 mm/s, **(c)** 20 mm/s, **(d)** 25 mm/s, **(e)** 30 mm/s, and **(f)** 35 mm/s. The volume of the droplet is 100 μL.

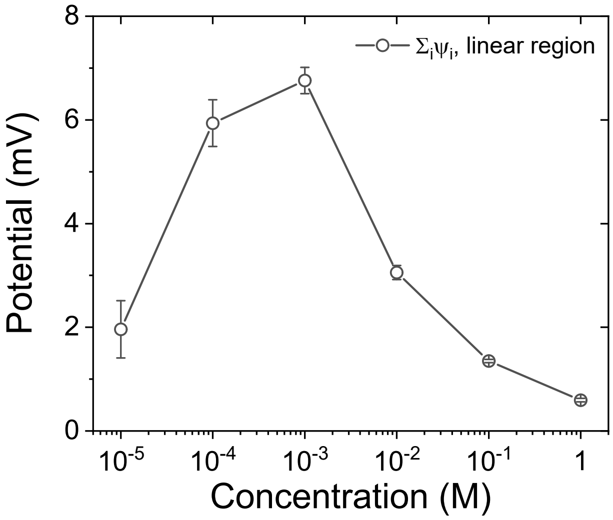

Fig. S5 Averaged interfacial potential $\sum_i \psi_i(v,c)$ as a function of the electrolyte-droplet concentration when $c_0 = 5 \times 10^{-7}$ M. The magnitude of the averaged $\sum_i \psi_i(v,c,c_0)$ is calculated from the slope of the linear region in Fig. S6a for given concentrations using eq 3. The value of β is regarded as 0.32.

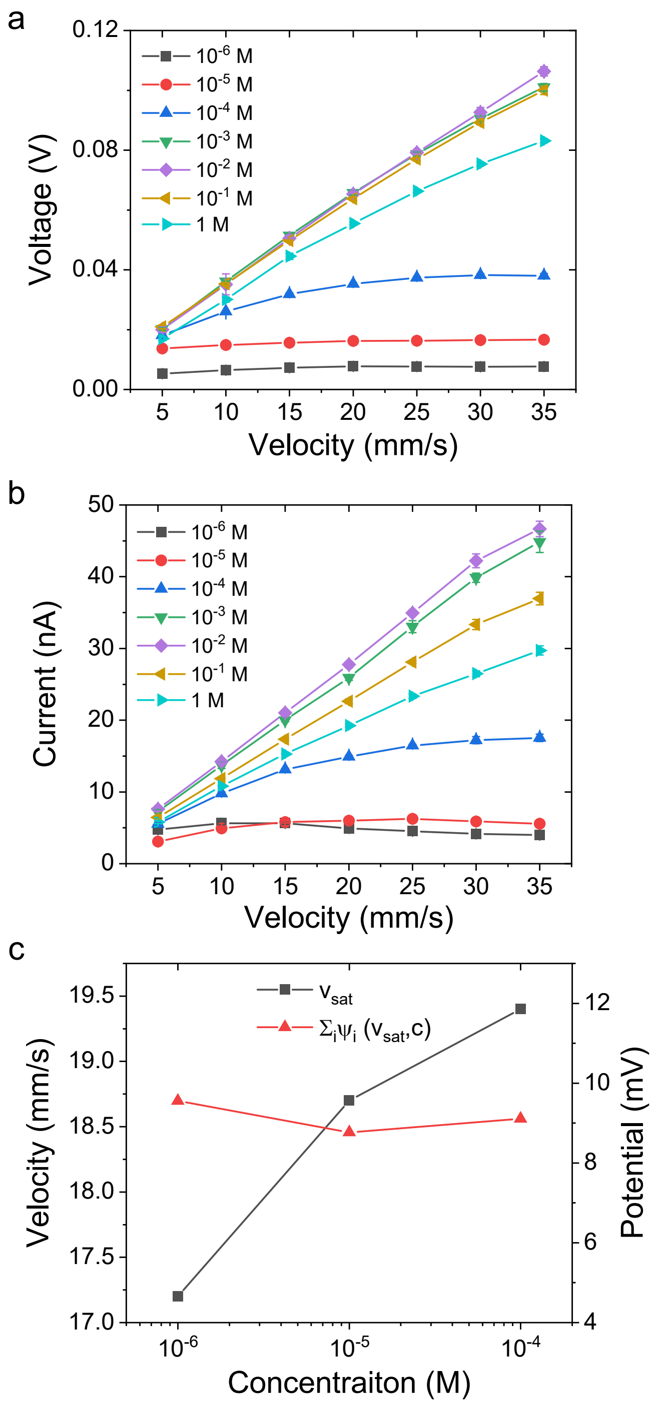

Fig. S6 (a) Measured open-cicuit voltage as a function of the velocity of NaCl electrolyte-droplet. **(b)** Measured short-circuit current of the device as a function of the velocity of the NaCl electrolyte-droplet. The volume of the droplets of all measurement is 100 μL. **(c)** Yielded v_{sat} (gray) and $\sum_i \psi_i(v_{sat}, c)$ (red) as a function of the droplet concentration.

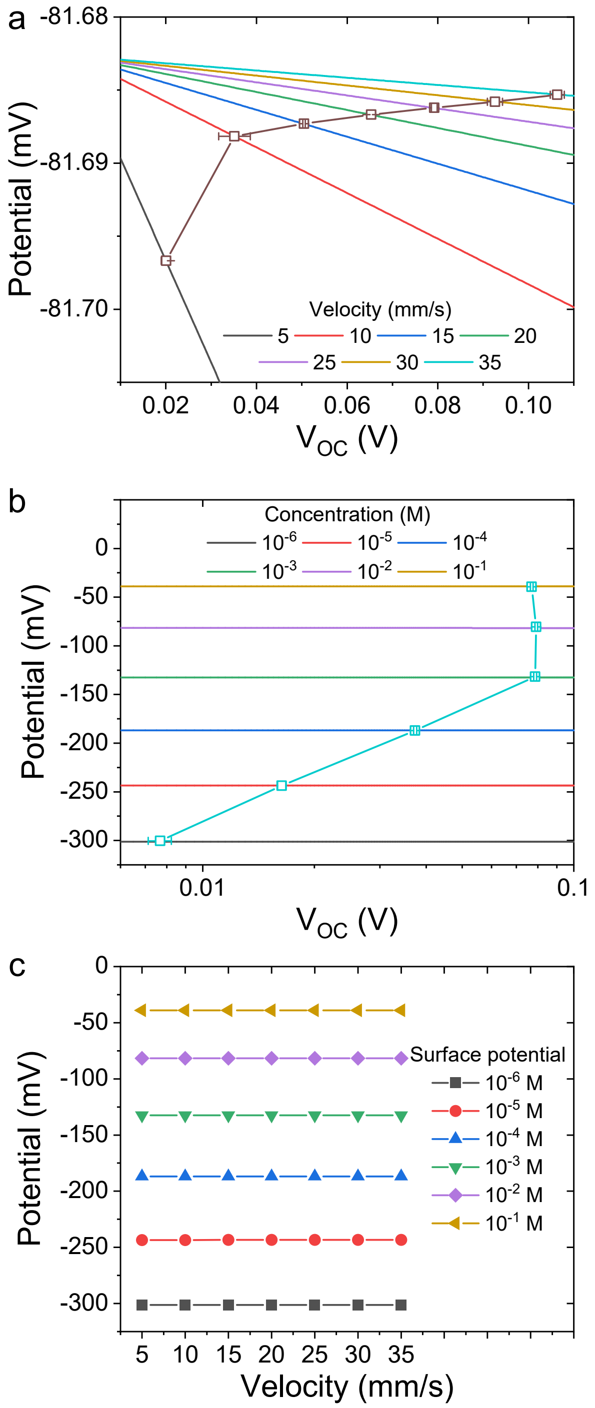

Fig. S7 **(a)** Surface potentials calculated by eq 7 in the manuscript for a 10^{-2} M NaCl electrolyte-droplet flowing along the semiconductor surface at various velocities. **(b)** Surface potentials calculated by eq 7 in the manuscript for NaCl electrolyte-droplets flowing along the semiconductor surface at 25 mm/s with concentrations ranging from 10^{-6} to 10^{-1} M. **(c)** Surface potentials estimated by eq 7 as a function of the droplet velocity from 10^{-6} to 10^{-1} M. In all cases, a 100 μL NaCl electrolyte-droplet flows along the semiconductor surface covered by native oxide (SiO_x), whose surface charge density is assumed to be $-0.02\ C/m^2$.[7]

References

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