

Supporting Information for

**Identification of droplet-flow-induced electric energy on
electrolyte-insulator-semiconductor structure**

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Experimental (method) Section

Fabrication of the energy transducer: Here the silicon dioxide and the poly(4-vinylphenol) (P4VP) were deposited by the plasma-enhanced CVD (PECVD) and the dip coating process, respectively. First of all, various insulator thin films were prepared. The 10 nm HfO_2 (or Al_2O_3) layers were deposited onto the Si wafers ((100) Undoped with resistivities: 8500 ± 500 ohm-cm, MTI Corporation) by atomic layer deposition (ALD, IPS Nano-ALD 2000) with $\text{Hf}[\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]_4$ (or $\text{Al}(\text{CH}_3)_3$) source. The SiO_2 layers were deposited onto the Si wafers by Plasma-enhanced chemical vapor deposition (PECVD, Unaxis, VL-LA-PECVD) with SiH_4 and N_2O gas. Poly(4-vinylphenol) (P4VP) precursor was a blend of Poly(4-vinylphenol), Propylene glycol monomethyl ether acetate, and Poly(melamine-coformaldehyde) methylated/butylated (Sigma aldrich) with mass ratio 1:0.5:98.5. The P4VP films were dip-coated at $100 \mu\text{m/s}$ after ultraviolet ozone (UVO, $\lambda = 185$ and 254 nm , 100 mW/cm^2) exposure for 30 min, and then dried at 200°C for 20 min. Then, 1H,1H,2H,2H-Perfluorooctyl-trichlorosilan (FOTS, Sigma aldrich) was deposited on the insulator by chemical vapor deposition (CVD) after ultraviolet ozone (UVO, $\lambda = 185$ and 254 nm , 100 mW/cm^2) exposure for 30 min. The UVO treated film and an open glass vessel containing about $30 \mu\text{L}$ of FOTS were put in a sealed desiccator under vacuum for 10 min at room temperature. Afterward, the sample was annealed 120°C for 15 min to remove untreated fluorosilane.

Characterization of the fabricated transducer: The output voltage and current characteristics for all devices were measure using Keithley 2182A nanovoltmeter and 6485 picoammeter, respectively. To measure the output electric signal (Figure 1d), a load resistor was serially connected to the both ends of the semiconductor. To make the water droplet flow at constant

specific velocity with a constant length of water droplet, water droplet was dragged by Si wafer using custom machine. From the linear relation between the output performance and freely rolling water droplet by gravity, it is confirmed that no effect is occurred on the generated electric signal by dragging Si wafer (Figure S2, Supporting Information). In figure 2, the measured output voltage and current according to various load resistances were displayed on IV curve. The error bar represents the deviation of the measured value twice for each of the three devices. For the measurement in Figure 2 and 3, all experiments were performed with FOTS as a SAM and Si ($\rho=8500\pm500\ \Omega\cdot\text{cm}$) as a semiconductor. In Figure 3, the thicknesses of the P4VP layers were measured by ellipsometer (Woollam M-2000). W represents the width of the device as well as the width of the droplet. In other words, because the droplet flows with a width of 1 cm while being slightly pressed on the transducer having a width of 1 cm, the width of the droplet is equal to the width of the transducer. The acid solution was made with hydrochloric acid and the base solution was made with sodium hydroxide (Fig. S7).

DFT calculations: We obtained the charge population and potential profile with Density Functional Theory (DFT) calculations which is one of the most widely used electronic structure computation method for physical, chemical, and material system. All DFT calculations are performed with the TURBOMOLE^[32] package version 7.0.2. and Vienna ab-initio simulation package (VASP).^[33-36] The hybrid functional of the Perdew-Burke-Ernzerhof^[37,38] exchange-correlation functional, PBE0 (containing 25% HF portion), is used with general dispersion correction^[39] for density functional calculation for long-range correction. To efficiently simulate the experimental system, we constructed the model system by combining SAM molecular structure with independently optimized periodic Si slab. This

procedure preserves the geometric properties while reducing the computational cost. Because the Si layer maintains a well-defined lattice structure, the Si layer is optimized using the periodic boundary condition (PBC) of the VASP package. 3x3 Si (100) plane was adopted to mimic the experimental environment and projector augmented wave potential ^[40] was used with the energy cutoff set to 400 eV. Also, Brillouin zone integration was sampled by 6 x 6 k mesh. The SAM structure was assumed to be unaffected by neighboring SAM molecules due to the stability of the structure. Therefore, structural optimization was performed with the TURBOMOLE package without PBC environment. SAM structure is optimized within continuum solvation model, COSMO (Conductor-like Screening Model) ^[41,42], with the dielectric constant 80 to model water solvation environment (implicit solvent), and the average medium was simulated. 6-311++G (2d,2p) basis set was used. To mimic the ionic current inducement for the system, a point charge (+1) scanning along z-axis was performed.

Note 1 | DFT calculations of electron accumulation by cation adsorption A schematic of the EIS structure and the vertical potential profile as calculated by density functional theory (DFT) calculations are shown in **Figure S1a**. The z-position, $r=0$, indicates the water-dielectric layer interface. Here, silicon is used as a semiconductor, with a self-assembled monolayer (SAM) consisting of perfluorooctyltrichlorosilane (FOTS) serving as a dielectric layer. A positive point charge in water represents alkali metal ions as a cation. The potential profile across the dielectric layer is mainly determined by the dipole moment of the molecules constituting the SAM. The features of exponential potential-decay in the bulk water and semiconductor regions follow conventional characteristics of each interface. The electron density was also calculated when the cation was adsorbed onto the solid surface (Figure S1b). Further, at dielectric layer-semiconductor interface, the charge variation, $\Delta Q = Q(r) - Q(\infty)$, per the charge of the adsorbed cation depending on the distance between the solid surface and the cations is calculated (Figure S1c). The distance variation represents the adsorption (or desorption) of cations. As the cation approaches the solid surface, more electrons accumulate at the dielectric layer-semiconductor interface. Detailed simulation methods are introduced in the method section.

Note 2 | Experimental evidences of excluded hypotheses The effect of electrostatic charges as an operation mechanism of the transducer, such as the electron transfer and the effect of initially charged droplet were excluded on the grounds of following reasons. First, the DC electric signal is generated in our work while electrostatic interaction produces pulsed signal. Second, to obtain electric signal induced by electrostatic force, two different electrode is needed. While we used single semiconductor as an electrode. Further, because the electric signals were merely generated by flowing de-ionized (DI) water ($18.2 \text{ M}\Omega\cdot\text{cm}$) droplet with

respect to the 0.01 M NaCl solution droplet in Figure S2, the hypotheses of the mass (e.g. water molecules, ions, and functional groups of solid surface) transfer between water and solid surface also be excluded.

Note 3 | Derivation of the characteristic equation The equivalent circuit of the transducer is shown in Figure S3. R_w , and R_p are the resistance of the water droplet and the overlapped area of Si wafer with water. R_{s+c} is a sum of contact resistance and the resistance of the other (non-overlapped) area of Si wafer with water. I is an output current of the transducer. I_i and I_p are the current flowing along the R_w (resistance of water droplet) and R_p respectively; $R_p + R_{s+c} = R_{semi}$. C_b and C_f are the capacitors made by adsorbed cations and attracted electrons at the front and back side of the water droplet. Q_b and Q_f are the charges on the C_b and C_f respectively. In the circuit, two upper plates of two capacitors and R_w represent water droplet. Two lower plates of two capacitors, R_{s+c} and R_p represent Si wafer. Here, I_i is current due to the flow of ions that is generated by adsorption of the ions to the front side which is desorbed from the rear side of the droplet. The currents (I and I_p) flowing through the Si wafer are the currents produced by the flow of electrons induced by the adsorbing ions. The ions and electrons do not flow across the capacitors, but the flow of ions induces the flow of electrons. In other words, in equivalent circuit, the current flowing around two capacitors is not DC charge transport across ideal capacitors but a current flow of electrons induced by ion adsorption. From the equivalent circuit it is evident that the output current and voltage are given by following equations;

$$I = I_i - I_p, \quad (9)$$

$$V = V_i - IR_{s+c}, \quad (10)$$

where V_i is voltage on R_p ($V_i = I_p R_p$).

The current along the R_w is

$$I_i = \frac{dQ_f}{dt} = \sum_i \psi_i \frac{d}{dt} \left(\frac{\varepsilon A}{d} \right) = \frac{\varepsilon}{d} W v \sum_i \psi_i, \quad (11)$$

where $i=S, SAM, \text{ and } D$.

Eliminating I_i , I_p , and V_i produces

$$I = \frac{\varepsilon}{d} W v \sum_i \psi_i - \frac{(V + I R_{s+c})}{R_p}. \quad (12)$$

Substituting the relation, $R_p + R_{s+c} = R_{semi}$, into the equation (12) produces the characteristic equation of the transducer, which relates the parameters of the transducer to the output current and voltage:

$$I = -\frac{1}{R_{semi}} \left(V - v l R_{\square} \frac{\varepsilon}{d} \sum_i \psi_i \right). \quad (13)$$

Here, as the water droplet was dragged by wafer, the water droplet is slightly pressed by the wafer, so the shape of the droplet actually moves in a rectangular shape with a slightly rounded vertex. Therefore, we assumed that the droplet is a rectangular shape with a width of W and a length of l in order to establish a theoretical model that matches the experimental results. When water droplets such as real raindrops flow over a solid surface, the shape of the water droplets is not perfectly spherical but rather oval or elongated. If the derived characteristic equation is applied to a circular droplet, the term expressed as a simple product ($W * v$) should be expressed as an integral form.

Note 4 | Derivation of the short-circuit current According to the characteristic equation, the short-circuit current is expressed by the following:

$$I_{SC} = -\frac{1}{R_{semi}} \left(-vlR_{\square} \frac{\varepsilon}{d} \sum_i \psi_i \right) = vl \frac{R_{\square}}{R_{semi}} \frac{\varepsilon}{d} \sum_i \psi_i \quad (14)$$

Substituting the relation, $R_{semi} = \frac{L}{W} R_{\square}$, into the equation (14) produces

$$I_{SC} = vl \frac{W}{L} \frac{\varepsilon}{d} \sum_i \psi_i. \quad (3) \text{ in manuscript}$$

Note 5 | Dependence on pH and salt concentration of water droplet As the ion concentration (NaCl) increased, the magnitude of the generated electric signal increases and then gradually decreases after a specific concentration (Fig. S6). In the concentration range where the electric signal increases according to the ion concentration, we assume that as the concentration of adsorbed ions increases, the amount of electrons accumulated in the Si layer increases and the amount of current flowing in the Si layer increases accordingly, in light of our hypothesis. Interestingly, this device shows a trend of decreasing after a maximum with a certain ion concentration using NaCl salts. The experimental results (Fig. S7 in revised supporting information) show that the effect of pH is similar to that of salt concentration. Further studies are needed to clarify these causes.

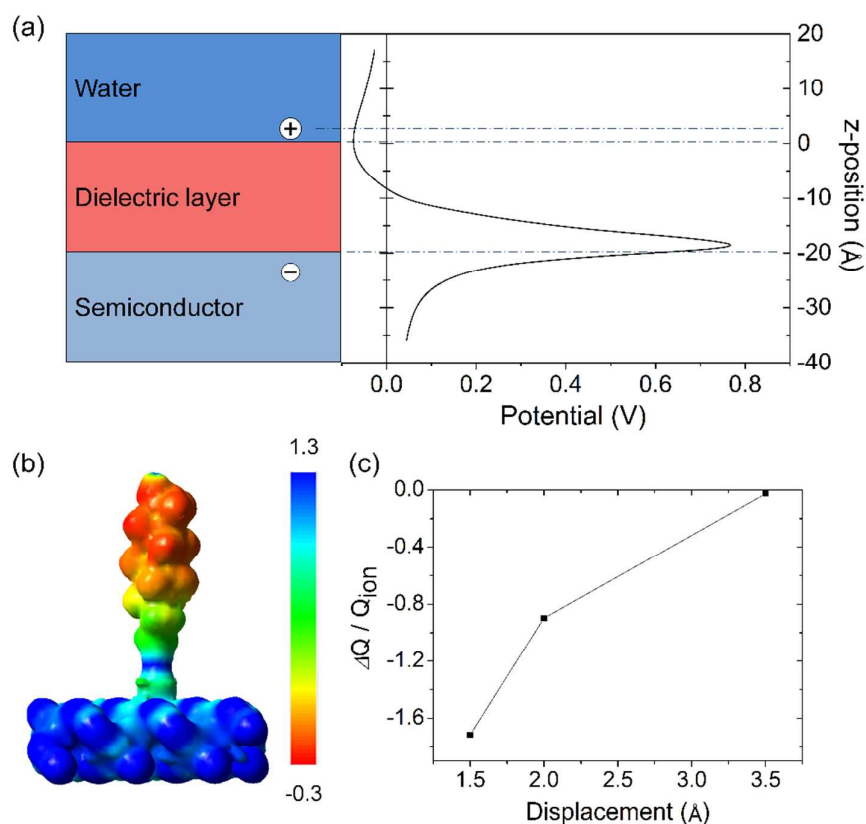


Figure S1. DFT calculation of the potential profile and charge distribution across the EIS structure. (a) Calculated potential profile of the EIS structure as the function of out-of-plane z-position (r). Silicon and SAM (FOTS) were used as the semiconductor and dielectric layer for the calculation, respectively. The white circle with the plus sign represents an alkali metal ion. An attracted electron is also illustrated. The two interfaces and the cation position are marked by the dashed line. (b) Calculated electron density of the EIS structure when the cation was located at $r=1.5\text{Å}$. The unit is e/a_0^3 , where a_0 is the Bohr radius. (c) DFT calculation results of the charge variations at the dielectric layer-semiconductor interface depending on the distance between the cation and the solid surface.

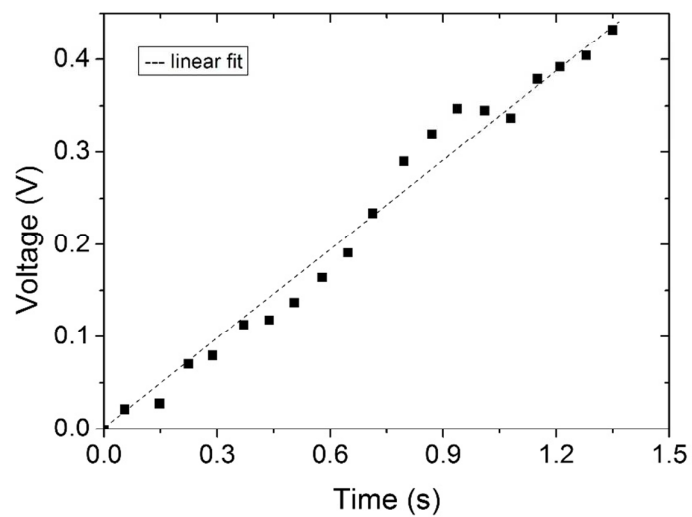


Figure S2. Measured open-circuit voltage as the 0.01 M NaCl solution droplet (150 μL) freely rolled on the transducer by gravity.

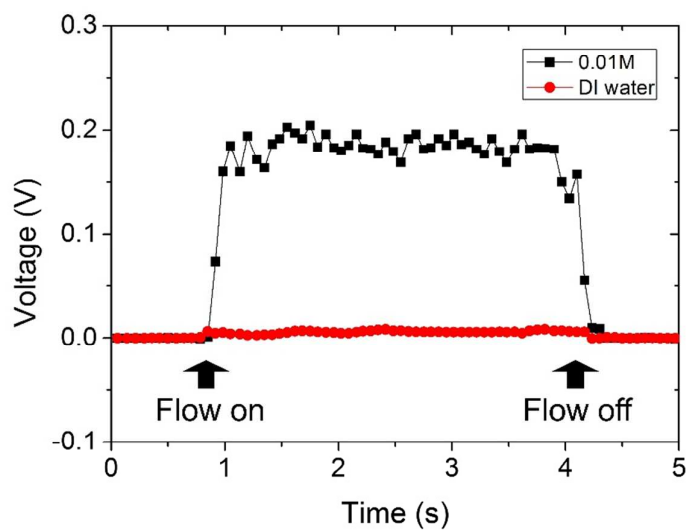


Figure S3. Measured open-circuit voltage as the 0.01 M NaCl solution droplet (pH=6.8) and deionized water droplet flew at 3cm/s. Volume of the droplets is 150 μ L.

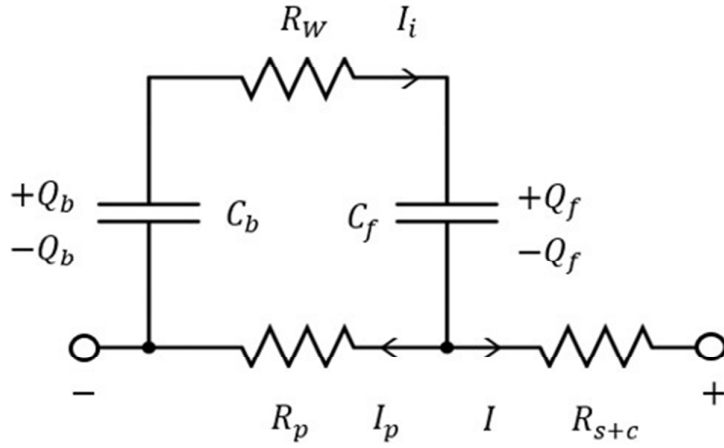


Figure S4. Equivalent circuit of the transducer. R_w , and R_p are the resistance of the water droplet and the overlapped area of Si wafer with water. R_{s+c} is a sum of contact resistance and the resistance of the other (non-overlapped) area of Si wafer with water. I is an output current of the transducer. I_i and I_p are the current flowing along the R_w and R_p respectively; $R_p + R_{s+c} = R_{semi}$. C_b and C_f are the capacitors made by adsorbed cations and attracted electrons at the front and back side of the water droplet. Q_b and Q_f are the charges on the C_b and C_f , respectively.

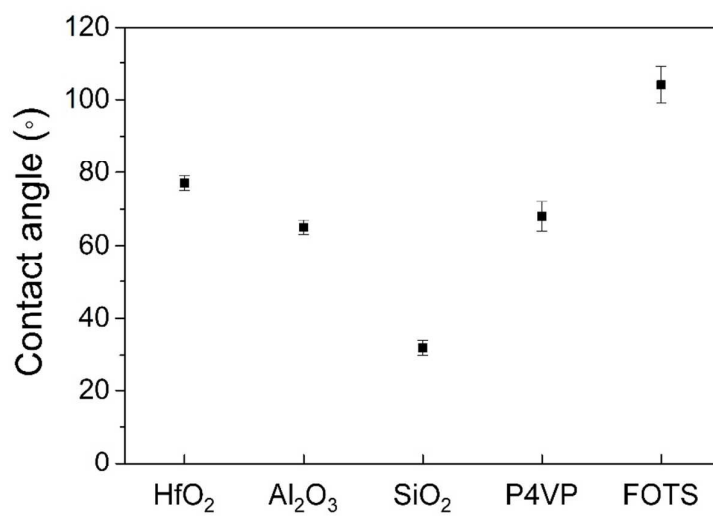


Figure S5. Contact angles were measured on various surfaces using de-ionized water. Water contact angles recorded on four different spots.

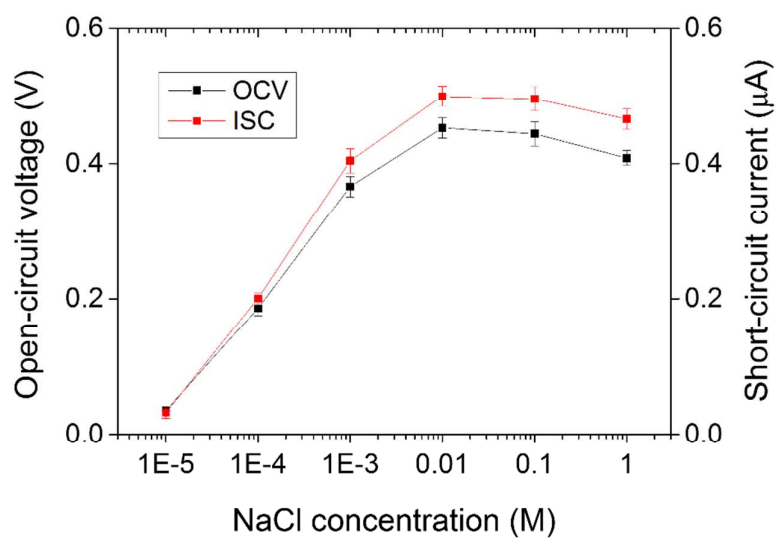


Figure S6. Measured open-circuit voltage and short-circuit current according to the NaCl concentration. Water droplet flew at 4cm/s. Volume of the droplets is 200 μ L. Hafnium oxide (10 nm) was used as a dielectric layer.

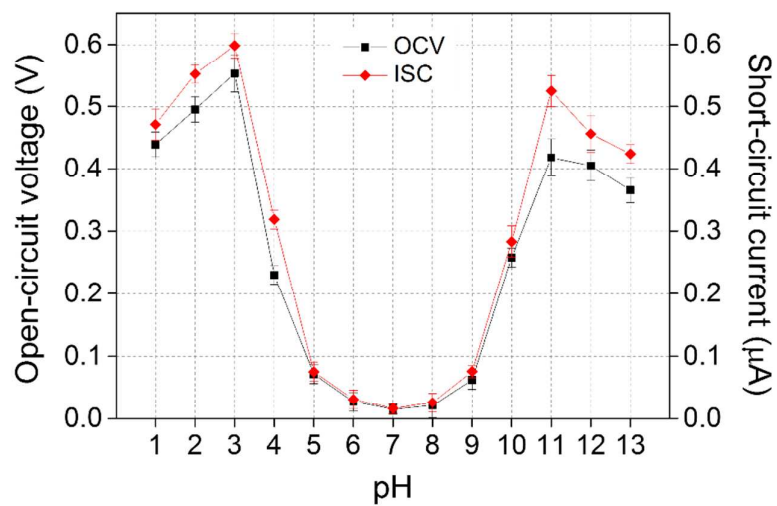


Figure S7. Measured open-circuit voltage and short-circuit current according to the pH of the water droplet. Water droplet flew at 4cm/s. Volume of the droplets is 200 μ L. Hafnium oxide (10 nm) was used as a dielectric layer.

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