Supplementary Information Self-propelled droplet-based electricity generation

Chaoran Liu^{a,c}, Jing Sun^b, Yu Zhuang^b, Jie Wei^b, Jing Li^b, Linxi Dong^a, Dongfang Yan^d, Alice Hu^b, Xiaofeng Zhou^{*c}, Zuankai Wang^{*b}

^aCollege of Electronics and Information, Hangzhou Dianzi University, Hangzhou 310018, China.

^bDepartment of Mechanical Engineering, City University of Hong Kong, Hong Kong 999077, China.

^cScience and Technology on Microsystem Laboratory, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China.

^dCollege of Computer Science and Engineering, Chongqing Three Gorges University, 780 Shalong Road, Chongqing 404100, China.

1. The energy conversion based on Electrical double layer (EDL)

EDL forms on the droplet overlapping area on the electrodes. Capacitances of the energy conversion electrodes are shown in Fig. 3a. Here, C_P , C_N and C_0 are the capacitances of positive electrode-droplet capacitor, negative electrode-droplet capacitor and inter-electrode capacitor, respectively. ε is the effective electrical permittivity of the medium between dielectric layer and hydrophobic layer. The sum of thickness of dielectric layer and hydrophobic layer is *d*. S_P and S_N are the overlapping areas of water droplet with positive and negative electrodes, respectively. The ratio of capacitances values is

$$\frac{C_0}{C_P + C_N} = \frac{\varepsilon_0 \frac{S_0}{d_0}}{\varepsilon_P \frac{S_P}{d_P} + \varepsilon_N \frac{S_N}{d_N}} \approx 5.1 \times 10^{-10}; (\varepsilon_P = \varepsilon_N = \varepsilon, d_P = d_N = d)$$
(S1)

The ratio of capacitances values shows that C_0 is negligible.

The interfacial electrical capacitance was proportional to the area of overlap from the motion of the water droplet. And water on the hydrophobic layer acted as an induction medium to attract the opposite charges on the electrodes. Charges ware arranged at the solid/liquid interface, and accumulated on the positive capacitor, $q_P = C_P V_P = \varepsilon S_P V_P / d$ and negative capacitor, $q_N = C_N V_N = \varepsilon S_N V_N / d$ to maintain the balance of the chemical potentials on the surface, determined by the overlapping area between the water droplet and electrodes ¹. Here, V_P and V_N are the voltage of the two capacitances. Accompanying the self-propulsion motion, interfacial electrical capacitances and the accumulated electric charges varied according to the position of droplet. The variation of electric charges generated a potential difference and an output voltage between two electrodes.

To further understand the EDL effect at the liquid/solid interfaces, we conduct density functional theory (DFT) calculations to simulate the charge transfer between water droplet and SiO₂ dielectric layer (Fig. S1). All the DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP). We adopt planewave basis set expansion with an energy cut-off of 400 eV base on the projector augmented-wave (PAW) method. Brillouin zone integration was sampled by a $3 \times 3 \times 1$ k mesh. To simplify our calculation, we choose a periodic unit which consists of six water molecules placed on the underlying SiO₂ dielectric substrate with a base size of 15*15*5 Å and is also sufficiently large enough to effectively study the water molecules-solid interaction. To avoid the perturbation from adjacent units, the distance between each unit is set to be 20 Å. The atomic positions in the unit are fully optimized until the system of interest stay in a preferential equilibrium state. In our calculation, the Van der Waals force between water and dielectric layer is also considered to better reflect the true water molecule-solid interaction. In our simulation, initially six water molecules are placed uniformly on the flat dielectric surface. Since these randomly distributed water molecules are not in an energetically stable state, they gradually relax with charges moving backward and forward between the liquid/solid interfaces. To better probe the charge transfer between the interfaces, we calculate the variation of the charge density associated with the water and dielectric layer before and after relaxation, respectively. Briefly, the differential charge density

is expressed as $\Delta \rho = \Delta \rho_E - \Delta \rho_D - \Delta \rho_W$, where $\Delta \rho_D$ and $\Delta \rho_W$ are the densities of initial dielectric layer and the water molecules, respectively. $\Delta \rho_E$ donates the charge density after relaxation in the entire system (SiO₂ dielectric layer and water).



Figure S1. Charge transfer between water droplet and SiO2 dielectric layer.

Briefly, the interaction between water molecules and dielectric layer mainly occurs in two regions. The first region that is stained in yellow or red corresponds to the depletion zone, whereas the other region that is stained is in blue, is referred to as the accumulation zone where electrons are gained. The charge transfer mainly occurs between the depletion zone where the electrons are lost and the accumulation zone where the electrons are gained. Notably, even without the presence of additional negative charges on the dielectric layer, the water molecules immediately contacting the dielectric layer maintain positively charged and the top surface of the dielectric layer immediately adjacent to the water molecules is negatively charged because of the electrostatic effect. Thus, our DFT calculation convincingly substantiates the charge transfer in the EDL region.

2. Droplet size and liquid/dielectric/electrode contact area

When different size droplet overlaps on the same position, the area S is enlarged with volume increasing from Ω_1 to Ω_2 (Fig. S2a). Here, we assume that the two size droplets centers are at stripe 2. Take volume Ω_2 for example, the solid/liquid area *S* can be written as:

$$S = S_1 + S_2 = \pi R_2^2 \tag{S2-1}$$

where S_1 and S_2 represents the solid/liquid area on stripe 1 and $2.R_2$ is the radius of the solid/liquid interface. To obtain the solid/liquid area S_1 on stripe 1, the sector area S_{sector} is calculated as: $S_{\text{sector}} = S_1 + s = \frac{1}{2}\theta R_2^2$. Here, θ is the central angle of the sector $\theta = 2 \arccos(\frac{l}{R_2})$ (Fig. S2b). Thus, S_1 is calculated as:

$$S_1 = S_{\text{sector}} - s = R_2^2 \left(\arccos(\frac{l}{R_2}) - \frac{1}{2} \sin(2\arccos(\frac{l}{R_2})) \right)$$
 (S2-2)

Given that a solid fraction f_i , the overlapping area difference between the negative and positive electrodes surfaces is calculated as:

$$S_N - S_P = f_2 S_2 - f_1 S_1 \tag{S2-3}$$

l is the distance between droplet center and stripe 1. It can be deduced from equation S2 that the area difference $S_N - S_P$ enlarges with overlapping area expanding via increasing the droplet volume from Ω_1 to Ω_2 .



Figure S2. (a) Different size droplet on the same position. (b) Model of calculating the solid/liquid area on different stripes.

3. Overlapping area correction coefficients

The position of droplet overlapping more than three stripes is ignored since the selected droplet volume is only 25μ L. Besides, the overlapping area is invariable

when droplet move on a same stripe, which doesn't induce the output voltage. Therefore, we only need to analyze the position of droplet overlapping two stripes in calculating the overlapping area correction coefficients. Taking 3-stripe electrode surfaces as an example, the process of droplet self-propelled motion is divided into three positions to calculate the correction coefficients c_P , c_N (Fig. S3). Considering the above analysis, the change of overlapping area S_1 in the position P_2 in the time of Δt can be given by

$$dS_{1} = R_{2}^{2} \left(\arccos(\frac{l}{R_{2}}) - \frac{1}{2} \sin(2 \arccos(\frac{l}{R_{2}})) \right) - R_{2}^{2} \left(\arccos(\frac{l - v(t) \times \Delta t}{R_{2}}) - \frac{1}{2} \sin(2 \arccos(\frac{l - v(t) \times \Delta t}{R_{2}})) \right)$$
(S3)

With Taylor series expansion of dS_1 under $\Delta t \rightarrow 0$, the Equ. (S3) can be derived as

$$dS_{1} = v(t) \times \Delta t \times c_{p}$$

$$c_{p} = \sum_{n=0}^{\infty} \frac{k^{(n)}(0)}{n!} (v(t) \times \Delta t)^{(n-1)}$$
(S4)

If Taylor series expansion is to the third order, the coefficients $k^{(n)}(0)$ be derived as

$$k^{(0)}(0)=0$$

$$k^{(1)}(0)=\frac{R\left(-1+\cos(2\arccos(l/R))\right)}{\left(1-l^{2}/R^{2}\right)^{l/2}}$$

$$k^{(2)}(0)=R^{2}\left(\frac{l}{2\left(1-l^{2}/R^{2}\right)^{3/2}R^{3}}-\frac{0.5l\cos(2\arccos(l/R))}{2\left(1-l^{2}/R^{2}\right)^{3/2}R^{3}}-\frac{\sin(2\arccos(l/R))}{\left(1-l^{2}/R^{2}\right)^{R^{2}}}\right)$$

$$k^{(3)}(0)=R^{2}\left(-\frac{l^{2}}{3\left(1-l^{2}/R^{2}\right)^{5/2}R^{5}}-\frac{1}{6\left(1-l^{2}/R^{2}\right)^{5/2}R^{3}}+\frac{(l^{2}-0.5R^{2})\cos(2\arccos(l/R))+l\left(R^{2}-l^{2}\right)^{l/2}\sin(2\arccos(l/R))}{\left(R^{2}-l^{2}\right)^{5/2}}\right)$$

When droplet moves towards different positions P1~P3, the overlapping area dS_P , dS_N can be derived as

P1: Overlapping stripe 0~1 $\begin{cases} dS_p = f_1 dS \\ c_p = f_1 T \\ dS_N = 0 \\ c_N = 0 \end{cases}$ P2: Overlapping stripe 1~2 $\begin{cases} dS_p = -f_1 dS \\ c_p = -f_1 dS \\ c_P = -f_1 T \\ dS_N = f_2 dS \\ c_N = f_2 T \end{cases}$



Figure S3. 25 µL droplet moving toward different positions.

4. Output power

As a 1 M Ω load is applied, the instantaneous output power was calculated based on the output current induced by a 25 μ L droplet self-propelled on the 3-stripe electrode surface. And the peak output power is 2.4 nW.



Figure S4. Instantaneous output power induced by a 25 μ L droplet self-propelled at the matched load of 1 M Ω , which has a accumulated 1.7×10^{-12} J in one period of self-propelled motion.



Figure S5. The output power increases with the external load resistance and reaches an optimum value of 2.4 nW with the resistance adding to 1 M Ω .

5. Power conversion efficiency

To further obtain the interfacial energy, we calculate the solid tension coefficient of different stripes via the method after Owens-Wendt-Rabel-Kaelble (OWRK)² which extracts the low surface energy values with comparing well to reported literature. And ethylene glycol and deionized water are used as working liquid in measuring and calculating the different stripes solid/water interfacial tension coefficient such as: 72.78 mN/m (stripe 0), 49.73 mN/m (stripe 1), 34.19 mN/m (stripe 2), 21.34 mN/m (stripe 3).

With these tension coefficients, the solid/water interfacial energy E_{SL} is calculated as³

$$E_{SL} = \gamma_{SL} S_{SL} \tag{S5}$$

where S_{SL} and γ_{SL} represent the solid-water interfacial area and tension coefficient. The difference of the interfacial energy is decided by its final and initial states of solid-water interface. The droplet was firstly deposited on stripe 0, and finally moved towards between stripe 2 and 3. Thus, the difference of the interfacial energy ΔE_{SL} between the final and initial states is evaluated as 1.36×10^{-10} J based on formula S3 and S5. The accumulated output electricity energy is 1.7×10^{-12} J in one period of selfpropelled motion. Therefore, the energy conversion efficiency of the self-propelled droplet-based electricity generation is 1.25%, which is estimated by $\eta_{W} = W_{out}/W_{in} \times 100\%$. Here, W_{in} is the power originating from the solid-water interfacial energy and W_{out} is the electrical power measured experimentally.

6. The effect of pH and salt concentration on the electricity generation

The investigating result of the effect of pH of droplet on the electricity generation is shown in Fig. S6. The pH of the droplet was adjusted by adding HCl and NaOH solutions in water. The OH- in the adjusted solution increase gradually with the PH, which are easier to be absorbed at the solid/liquid interface owing to the large polarity of the carbon–fluorine bond in the hydrophobic dielectric layer. Thus, the output peak voltage increases with the PH. The effect of the salt concentration on the electricity generation has been investigated as shown in Fig. S7.



Figure S6. The variation of the measured peak voltages induced by droplets with different PH.



Figure S7. The variation of the measured peak voltages induced by droplets with different concentrations of NaCl solution.

7. Experiment process

An OCA15EC Drop Shape Analysis (Dataphysics, Germany) was used to measure static contact angle of deionized water droplet deposited on different gradient stripes. A NI 9239 Measuring and Testing Equipment (National Instruments, USA) was used for electric detection and analysis. A Photron FASTCAM SA4 high speed camera (Photron, Japan) was employed to record the instantaneous movement of water droplet, and the frame rate was set as 3600 fps.A low-noise current preamplifier (Stanford Research System Model SR570) was used to measure the output current.

References

- 1. S.-H. Kwon, J. Park, W. K. Kim, Y. Yang, E. Lee, C. J. Han, S. Y. Park, J. Lee and Y. S. Kim, *Energy Environ. Sci.*, 2014, 7, 3279-3283.
- D. Janssen, R. De Palma, S. Verlaak, P. Heremans and W. Dehaen, *Thin Solid Films*, 2006, 515, 1433-1438.
- B. Chandesris, U. Soupremanien and N. Dunoyer, *Colloids Surf. Physicochem. Eng. Aspects*, 2013, 434, 126-135.