Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Cumulative charging behavior of water droplets driven freestanding triboelectric nanogenerator toward hydrodynamic energy harvesting

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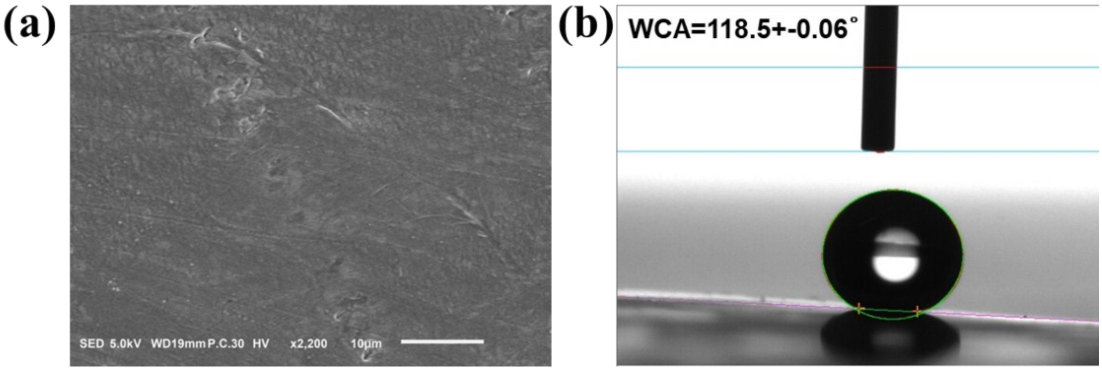


Figure S1. Surface morphology and wetting ability characterizations of (a) SEM image and (b) water contact angle of PTFE film.

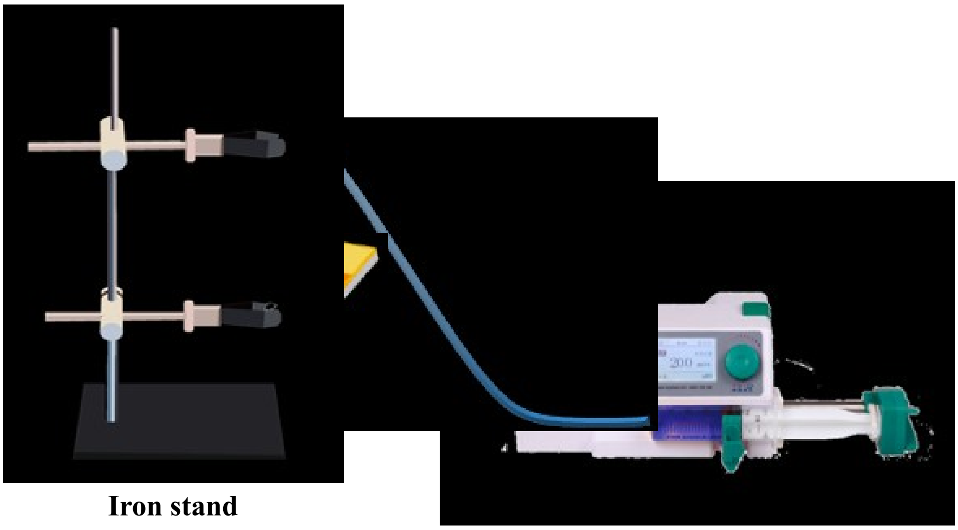
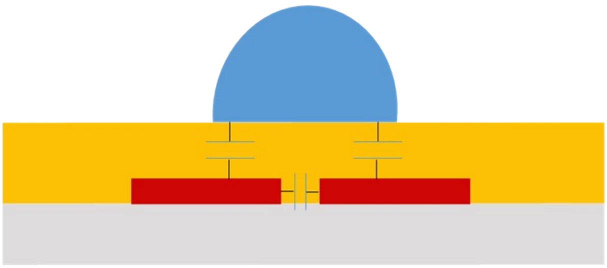


Figure S2. Setup of testing platform consisting of BF-TENG, iron stand and programmable syringe pump.



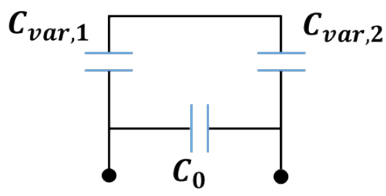


Figure S3. Influence of effective contact area (overlap area) between water droplet and electrodes of BF-TENG system and its equivalent circuit of capacitances.

Assuming the dimensions of the droplet-electrodes overlap area A_i (i=1 or 2) is much larger than the film thickness d, the droplet-electrode capacitance at time *t* can be given by:

$$C_{var,i} = \varepsilon A_i(t)/d \qquad \textit{Equation } 4$$

where ε is the permittivity of the insulating film. Since ε and *d* are constants, and $C_{var,i}$ is proportional to A_i. The total area of A_1 and A_2 is the area A of water droplets spread on PTFE, which equals to $A = A_1 + A_2$. The resultant variable electrode-electrode capacitance is:

$$C_{var} = C_{var,1} \cdot C_{var,2}/(C_{var,1} + C_{var,2}) \qquad \textit{Equation } 5$$

$$= \frac{\varepsilon}{d} A_1 \cdot A_2/(A_1 + A_2) \quad = \frac{\varepsilon}{dA}(-A_1{}^2 + AA_1)$$

Where the maximum electrode-electrode capacitance will be obtained when $C_{var,1} = C_{var,2}$ and then decreases when either of the capacitance reduced.

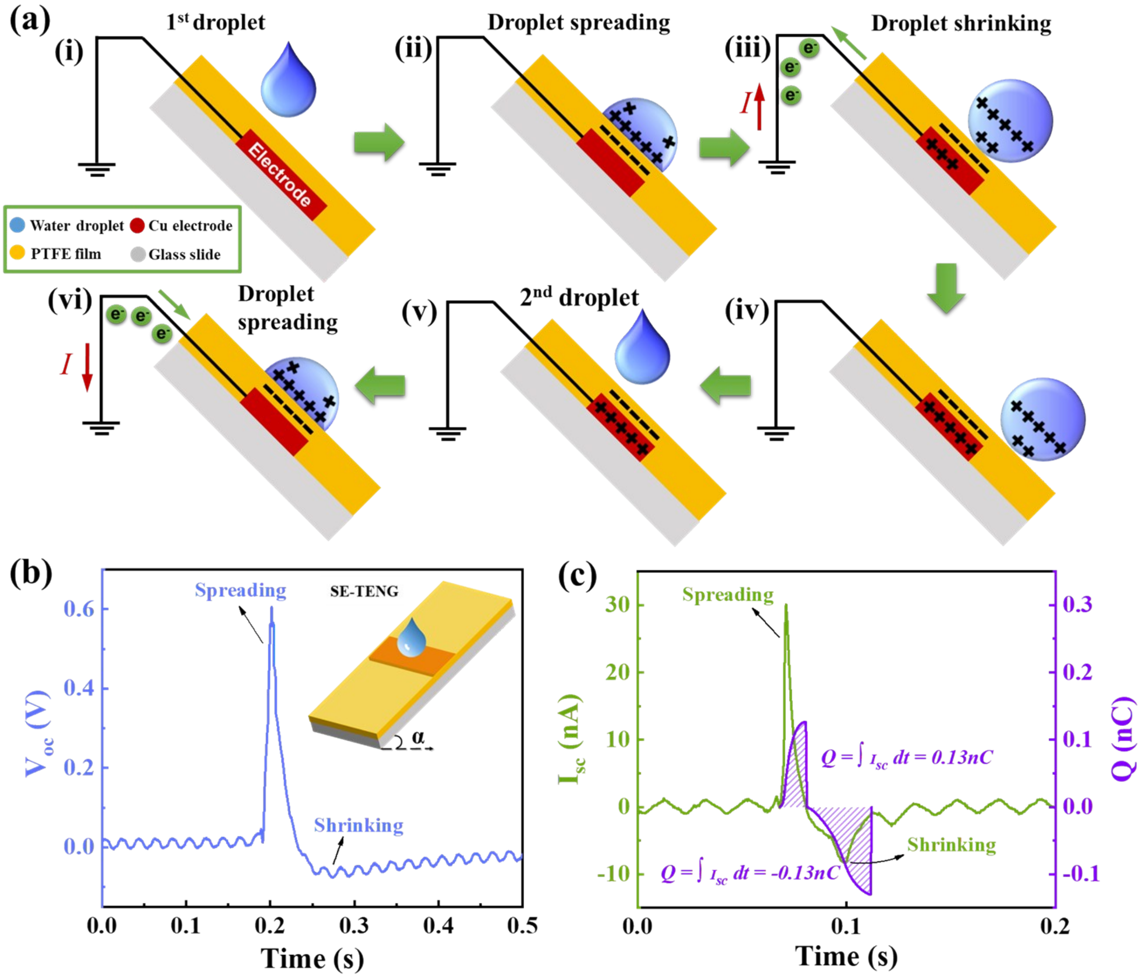


Figure S4. (a) Schematic diagram of the SE-TENG and working principle of water droplet charging process. Output signals of (b) V_{oc}, (c) I_{sc} and Q_{sc} generated by one water droplet during spreading and shrinking phase.

Figure S4a illustrates the SE-TENG structure and charge induction by one water droplet, meanwhile, the dynamic behavior of the water droplet was recorded by a high-speed camera as shown in Figure S4b. It is clearly observed that the water droplet gone through three successive stages: dropping at 0 ms, spreading at 3 ms and shrinking phase (8-28 ms). The working principle of charging SE-TENG can be described into four steps: (1) As the first water droplet dripping on (Figure S4a-i) and spreading out on the PTFE film, triboelectrification charges will be induced at the interface with water droplet positively charged and PTFE negatively charged according to the triboelectric series (Figure S4a-ii); (2) The water droplet immediately shrink to a semi-spherical shape due to the hydrophobic property of PTFE surface and rolling down the PTFE film , positive charges will be induced on the Cu electrode in order to achieve an electrostatic equilibrium, repelling the electrons from Cu electrode to the ground and producing a negative current signal (Figure S4a-iii) ; (3) Once the water droplet rolls off the PTFE film, electrostatic equilibrium state is established between PTFE film and Cu electrode with opposite charging polarity and equal amount of charges (Figure S4a-iv); (4) When the successive water droplets approach (Figure S4a-v) and break the equilibrium state, new equilibrium state is established between the water droplet and PTFE surface due to contact electrification, thus attracting electrons from the ground to neutralize the positive charges on Cu electrode and a positive current signal is generated (Figure S4a-vi). The output signals of V_{oc} and I_{sc} during spreading and shrinking phase are demonstrated in Figure S4b and Figure S4c, verifying that the generation of electricity is mainly attributed to the deformation of water droplet and a 0.13 nC short-circuit charge (Q_{sc}) is generated during this process.

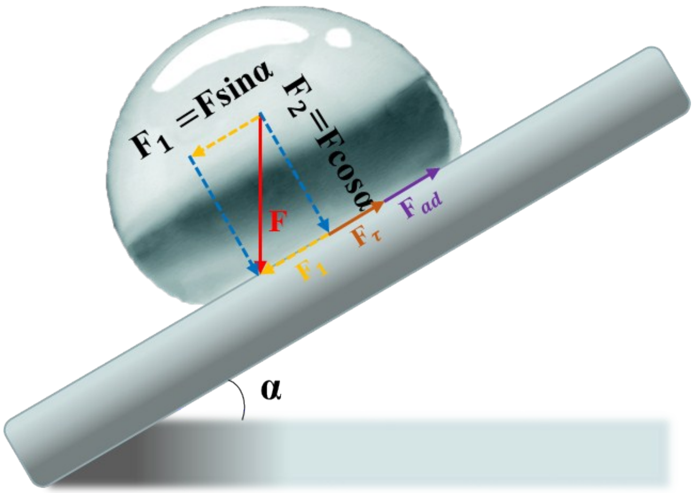


Figure S5. The schematic diagram of force balance for a steadily rolling droplet on PTFE surface.

The force balance for a steadily rolling droplet around the center of mass can be given by:

$$mgsin\alpha - F_{ad} - F_{\tau} - D_a = ma \qquad Equation\ S1$$

where *m* is the mass of water droplet, α is the inclination angle, F_{ad}, F_{τ} and D_a are the adhesion, shear and air drag forces, respectively. F_{ad} can be given as:

$$F_{ad} = \frac{24}{\pi^3}\gamma_{LV}Df\left(cos\theta_R - cos\theta_A\right) \qquad Equation\ S2$$

where γ_{LV} is the surface tension of the liquid on the solid surface, D is the droplet diameter prior to deformation (the same area as the ellipse), *f* is the solid surface fraction (solid/liquid contact fraction). θ_R is the receding (uphill) angle, and θ_A is the advancing (downhill) angle.

A shear force is generated when the droplet rolls on a surface because of the rate of fluid strain formed along the contact line between the water droplet and hydrophobic surface. The shear stress can be written as:

$$F_{\tau} = A_{w}\left(\mu\frac{dV}{dy}\right) \qquad Equation\ S3$$

where A_w is the contact area ($Aw = \pi r^2$ and r is the contact area radius), μ is the droplet fluid viscosity, V is the flow velocity, and y is the distance normal to the contact surface. The rate of fluid strain $\left(\frac{dV}{dy}\right)$ is obtained from the simulation data.

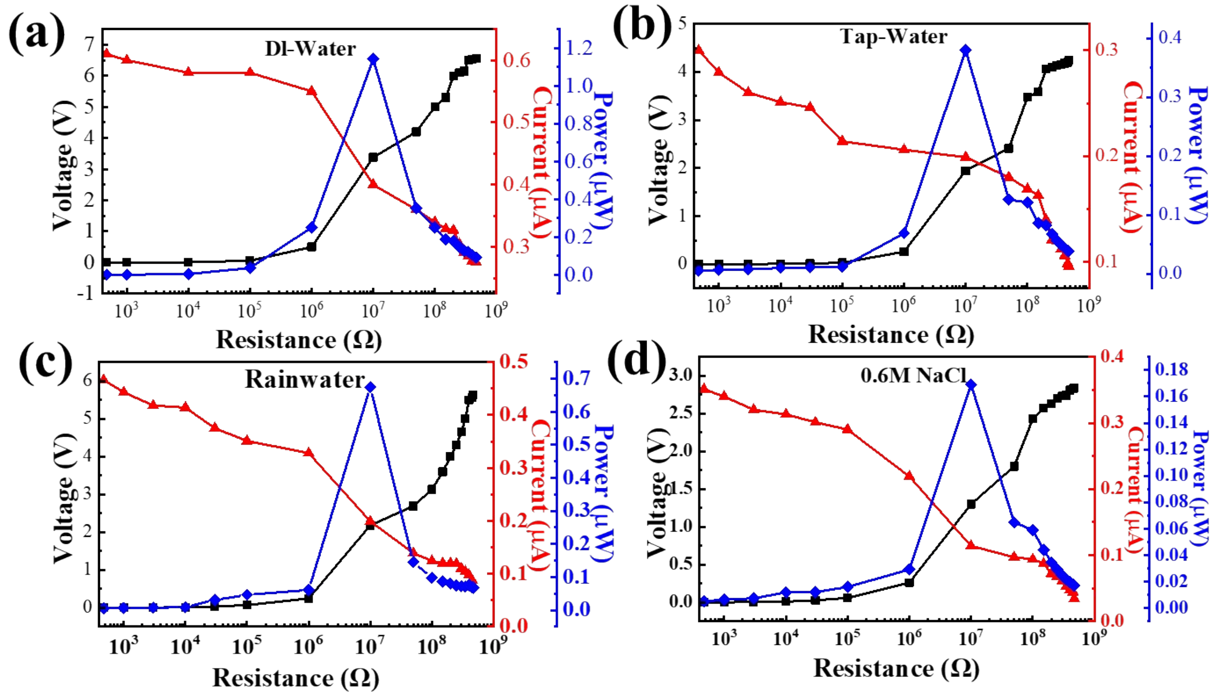


Figure S6. Comparison of voltage, current and power output performances generated from single droplet based on BF-TENG system of (a) DI-water, (b) Tap water, (c) Rain water and (d) 0.6M NaCl.

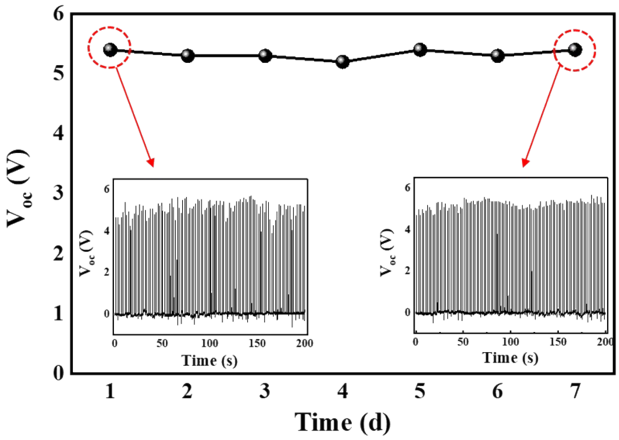


Figure S7. Stability measurement of voltage performance of BF-TENG at height of 20cm and inclination angle of 20° over 7 days.