Research on high instantaneous power droplet generator by using super-hydrophobic electrode

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Abstract. In 2020, a droplet-based electricity generator (DEG) was proposed. Compared with the traditional water drop generator structure, the voltage and current generated by the DEG structure are much higher. In our work, an aluminum electrode with a superhydrophobic surface was prepared by electrodepositing an aluminum substrate in an organic electrolyte. This electrode is applied to the DEG friction generator to optimize the coupling process between the surface water droplets and the DEG structure, which reduces the residual water droplets while maintaining the same level of electrical output characteristics. And the model of the solid-liquid coupling is also discussed.

Keywords: superhydrophobic; droplet-based electricity generator; lanthanum; TENG; DEG.

1. Introduction
Triboelectric nanogenerator (TENG) is an energy harvesting device, invented in 2012 by Academician Wang Zhonglin and his research team. This technology has received widespread attention and has been rapidly developed in recent years. The use of nano generators can harvest energy from water in the form of raindrops, river and ocean waves, tides and others. In the accelerating Internet of Things era, it can provide electricity for micro sensors and small electronic products [1].

However, the traditional friction module uses the friction of water droplets and electret FEP to generate electricity. Due to the limitation of the interface effect, the energy conversion efficiency of this kind of generator system corresponding to a drop of water is 2.1×10⁻⁵%, the peak voltage still very small. In 2020, Xu et al. proposed a droplet-based electricity generator (DEG), which realizes the charge transfer of the high-density electric charge induced by the friction material on the electrode, and increases the instantaneous power by multiple orders of magnitude [2], breaking the bottleneck in this field. This work has aroused widespread concern.

Regarding the mechanism of charge generation, Wang et al. verified the "two-step" model of the formation of electric double layers through experiments in 2020 [3]. The exploration of related mechanisms has not stopped.
On the other hand, the surface wettability of solid materials is one of the most important characteristics. With the gradual development of superhydrophobic science, artificial micro/nano particle structures are gradually being explored and applied [4]. Chen et al. published a superhydrophobic preparation method based on electrodeposition in 2012 [5], which can be applied to various conductor materials on a large scale.

In the improvement of the DEG structure of the triboelectric nanogenerator, the hydrophobic surface can reduce the residue of liquid droplets on the electrode, so that when the liquid leaves the surface, it does not leave a layer of charged liquid film [6]. The triboelectric nanogenerator based on the solid/liquid interface has been widely used to collect the kinetic energy in the low-frequency water flow. In the current reported literature, the charge density and peak power density generated by this method have been greatly improved, but how to improve the triboelectricity of the solid-liquid interface. The hydrophobic properties of nanogenerator electrodes are currently an important issue.

2. Experimental Section

In this study, a new type of droplet-based electricity generator was produced. This new energy harvesting device is made of three main parts, including: aluminum electrodes coated with superhydrophobic surfaces, fluoroethylene propylene copolymer (FEP) films. Its surface contains fluorine, which is an important electret material. and indium tin oxide (ITO) electrodes. Figure 1a is a structural diagram, Figure 1b is a physical diagram, and Figure 1c is a nano friction generator with ordinary aluminum electrodes. Observed from the picture, compared with the ordinary aluminum electrode, the electrode has excellent hydrophobic properties.

The FEP film used in this experiment has a thickness of 0.05mm, is colorless, and has an area of about 24cm². The electrode thickness is 0.06mm and the width is 3mm. The preservation and processing of materials reduce the contact with air to maintain its output efficiency. Test the output characteristics of the water drop generator, and use different external impedances to test the electrical output characteristics.

3. Device performance

For the droplet-based electricity generator in this experiment, the voltage data measured using the resistance box of and as the external impedance is shown in Figure 2. In addition, we tested the output characteristic curve when the external resistance was connected. The result is shown in Figure 3(b). Experiments have proved that as the external impedance increases, the output voltage increases and the output current decreases. When the external impedance is a certain value, the output power has a maximum value, and this power can light up 100 LED lights.
The results show that when the external resistance is connected, the open-circuit voltage value is not equal. Compared with the traditional water-droplet/solid based triboelectric nanogenerator (TENG), this generator increases the output power by several orders of magnitude. Observation shows that the current rises sharply when the dropped droplet just touches the aluminum electrode, and when the droplet separates from the aluminum electrode, the current returns to zero. The action of the water drop and the output current show synchronization in time.

![Figure 2](image)

**Figure 2.** When the external impedance is 0.9MΩ. (a) The voltage output characteristic curve of the DEG structure of the aluminum electrode with super-hydrophobic treatment; (b) The voltage output characteristic curve of DEG structure with ordinary aluminum electrode; (c) After being placed for a period of time, the voltage output characteristic curve of the DEG structure of the aluminum electrode with super-hydrophobic treatment; (d) After being placed for a period of time, the voltage output characteristic curve of the DEG structure using ordinary aluminum electrodes.

The value of the interface energy between a non-hydrophobic surface (WCA ≤ 90°) and water is usually greater than the value of the interface energy between a hydrophobic surface (WCA ≥ 90°), surface ionization is not easy to occur in hydrophobic surface [3], and the contact between solid and liquid is electrified The electron transfer is the main focus, so it can also achieve the effect of generating high voltage.

Fluorinated ethylene propylene (FEP) fluoride polymer has excellent UV-visible light transmittance, laser-induced damage threshold and mechanical properties. In addition, this device also has the advantages of good flexibility, good environmental protection, and light weight.

In this experiment, the method of electrodepositing aluminum substrate in the electrolyte was used to prepare a superhydrophobic surface with excellent performance. The contact angle of the hydrophobic surface can reach above 150°. Compared with other methods, this droplet-based electricity generator has the advantages of simplicity and speed, and has potential in large-scale general-purpose conductor materials.
4. Capacitor model of external circuit
The external circuit transport of the Triboelectric nanogenerator (TENG) can be derived from the capacitance model. When a voltage is applied to the two plates of the capacitor, the change of the capacitance over time causes the change of the amount of charge on the plate, thereby generating an external current:

\[ I = \frac{dQ}{dt} = C \frac{dV}{dt} + \nu \frac{dC}{dt} \]

For this type of triboelectric nanogenerator (TENG), the current of the external circuit can be simplified to:

\[ I = A \left( \frac{d\sigma_t(z,t)}{dt} \right) \]

The relationship between the transport and the open circuit voltage in the external circuit is:

\[ V_{oc} = RA \frac{d\sigma_t(z,t)}{dt} + A \left( \frac{\sigma_t(z,t)}{C} \right) \]

It can be proved that the expression derived from the displacement current inside the material is equivalent to the expression derived from the capacitance model. The displacement current is the internal mechanism of current generation, and the capacitance model of the external circuit is the external output of the displacement current [7].

5. Electric double layer model of solid-liquid contact
In the 19th century, experiments found that under an external electric field, the solid and liquid phases can move relative to each other; conversely, if the solid and liquid phases are forced to move relative to each other, a potential difference can occur. In 1879, Helmholtz first proposed the concept of forming an electric double layer at the interface between the solid and liquid phases; in 1910, Goay and Chapman proposed the diffusion electric double layer theory considering the thermal movement of ions; Turner proposed a modified diffusion double layer model [7]. As people have a more in-depth understanding of the structure of the electric double layer, the regulation of ion semiconductors and the micelle structure of the sol have also been understood.

![Figure 3](image)

**Figure 3.** When the external impedance is 11MΩ, the output voltage generated when a single droplet hits near the aluminum electrode. The peak voltage is generated at the moment when the water droplet falls.

In fact, during liquid-solid contact, both ion transfer and electron transfer affect the process. Previously, people could not distinguish the specific effects of these two transfers. 2020. Through experiments, the researchers used Kelvin probe force microscopy (KPFM) to measure the charge density on the solid surface after the liquid-solid contact. Based on the temperature effect on the charged surface, the surface charge decay experiment at different temperatures distinguished the liquid- Electron transfer and ion transfer in solid contact [3].

For liquids, the results show that the ion density transferred by the deionized water of PH 7 is relatively high, and the charge density transferred is relatively low compared to the solutions of PH 7
and pH 7. For solids, the effect of the size of the solid/liquid contact angle (WCA) on the E/I value was experimentally studied. The interfacial energy between a non-hydrophilic surface (WCA ≤ 90°) and water is usually greater than that of a hydrophobic surface (WCA ≥ 90°) and the interface energy between water. The results show that the solid surface with smaller WCA is more prone to surface ionization reaction and generate ions, while the surface ionization reaction between the hydrophobic solid surface and water is less, and the contact electrification between the solid and the aqueous solution is mainly electron transfer.

![Figure 4. Detailed explanation drawing of the process of forming the electric double layer.](image)

According to the theoretical model, the principle of the high instantaneous power nanogenerator in this paper is explained as follows: In the first step, the liquid contacts the solid surface, and the molecules and ions in the liquid hit the solid surface by thermal motion and pressure (a) (b). During this process, the water droplets and the FEP film on the fluorine-containing surface will overlap the electron cloud of atoms. The electrons are transferred from solid atoms to liquid atoms, or from liquid atoms to solid atoms (depending on the pH value of the solution and the type of material and solid material related). If the conditions of the ionization reaction are met, the ionization reaction will also occur. Both electrons and ions are generated on the surface. In the second step, the positively charged ions in the liquid are attracted by the electrons and ions on the surface through electrostatic interaction, and move to the surface to form an electric double-layer, finally as shown in (d). After the liquid leaves, the electrons are absorbed and transferred by the electrode, and a voltage is generated macroscopically.

It is worth noting that the TPFE film commonly used in nano friction generators and the FEP film used in the design of this article are all fluorine-containing materials. In this field, some researchers use natural materials to make electrets, including tree roots and leaves. All of them contain fluorine elements. Its essential function is to make it easier to realize the a-step in the electric double layer model, that is, the process of transferring electrons from solid atoms to liquid atoms, or from liquid atoms to solid atoms.

6. Conclusion
We used a electrochemical method to prepare aluminum electrodes with large hydrophobic angle films. The super-hydrophobic surface has excellent durability and corrosion resistance, also ensures the contact between the solid and the liquid in the electrified electrons. The high voltage output of the DEG structure is maintained under suitable impedance, which has increased the output power by several orders of magnitude compared with the traditional solid-liquid coupling-based nano friction generator. This structure reduces the residue of liquid droplets on the electrode, so that when the liquid leaves the surface, it does not leave a layer of charged liquid film. Electric double layer model of the solid-liquid coupling is also discussed in this work, it has meaning to explain the electrical output characteristics.
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