ABSTRACT: Triboelectric nanogenerators (TENGs) have obtained soaring interest due to their capability for environmental energy harvesting. However, as a harvester for green energy, the frequent adoption of the hardly degradable plastic films is not desirable. Here, we report a fully biodegradable TENG (FBD-TENG) that all elements are made from natural substances, and the utilization of plastic materials is avoided. The leaf cuticle and the inside conductive tissue are utilized as the tribo-material and electrode for one part in the FBD-TENG, and water droplets are employed as the counterpart. By using water droplets to bridge the originally disconnected components into a closed-loop electrical system, we successfully collect energy from the droplet impact onto a plant leaf. The electricity generation phenomenon and the working mechanism of the FBD-TENG have been investigated. Five kinds of plants, as well as rain water droplets, are employed to demonstrate the wide availability of the proposed approach. This study provides a strategy to utilize the pervasively presented electrostatic charges in nature in an eco-friendly way.

KEYWORDS: triboelectric nanogenerator, water droplet energy harvester, biodegradable triboelectric nanogenerator, electronic plants, plant leaves

1. INTRODUCTION

Despite the natural ability to convert food energy into energy that we need for sustaining metabolism and driving muscles, humankind has been seeking ways to harvest and utilize the energy from nature. Nowadays, as electricity is a major energy currency, converting various energy sources into electricity without polluting the environment becomes an important issue. Environmental mechanical energy is renewable and ubiquitously available on the Earth. Although massive and high-frequency mechanical energy can be harvested by using the traditional electricity generator based on the electromagnetic mechanism, the “random” energies with low frequency distributed in the environment are hard to be collected and utilized, such as wind, rain, waves, and motions of the human bodies. As the power of each individual random motion is usually small, their energies were always ignored previously. However, with the rapid development of the “Internet of things (IoT)”, numerous smart devices raise a huge demand for the distributed sensors and energy sources, which can be supported by harvesting the random environmental energies. As a promising technology for environmental energy harvesting, triboelectric nanogenerators (TENG) have attracted increasing attention. By coupling the contact electrification and electrostatic induction, TENGs can collect and convert mechanical energy even at the nanojoule level into electricity.

The output performance of TENGs relies on the tribo-charges, and therefore, the tribo-materials are essential. Various kinds of plastics, such as polytetrafluoroethylene (PTFE, also named as “Teflon” commercially), polypropylene (PP), fluorinated ethylene propylene (FEP), polyvinylidene fluoride (PVDF), and polyimide (Kapton), are often used as the tribo-layers in TENGs. However, these plastic materials are either non-biodegradable or hard to degrade, which need decades or even thousands of years. Research has been done by burying the plastics into the soil for over 32 years with no evidence of biodegradation found. Moreover, microplastics can be ingested by various marine animals, and the plastic debris may penetrate and accumulate in the food chain, exerting further hazards. A recent report estimated that there are 17–47 million tons of plastic litter in Atlantic waters and sediments. As a harvester for green energy, the non-biodegradable plastics utilized in TENG devices are obviously not satisfactory. To solve this problem, extensive effort has
been invested to explore the biodegradable and environmentally friendly tribo-materials.38–31

Natural materials, including waste teases, plant leaves, fish scales, and rice papers, are one of the desirable biodegradable candidates for TENGs because they are low-cost (or even no cost) and easy to achieve.30,32,33 One of the tribo-layers in TENGs could be fabricated by secondary processed fish scales or dry leaves, and thus, the TENG device could be partially biodegradable.30,33 However, the other tribo-layer, as well as the electrodes in such devices, still have to be plastics and metal sheets. With the concept of electronic plants being proposed,34 it was realized that the plant itself could be utilized as a part of the electric circuit.34–36 The conductive tissue liquids in the plant leaves can serve as a natural electrode, and the cuticles are natural dielectric materials. Moreover, the lipid layers on the surface of the leaves could be charged by triboelectrification and employed in TENG devices.37 Several types of TENGs that are based on living plants are thus proposed for wind energy harvesting.38–40 However, for all these applications, the natural materials (such as plant leaves) only serve as one part of the tribo-pair in TENGs, and there is a lack of TENG devices fabricated thoroughly by using biodegradable materials from nature.

According to the currently proposed nanogenerators based on water droplets,41–43 water droplets have been proven to serve as both triboelectric and conductive materials. Consequently, the droplet impact behavior not only generates surface charges on the dielectric surface but also bridges the originally disconnected components into a closed-loop electrical system, thereby generating electricity. In this work, by utilizing the water droplets and the living plant as the two parts of the tribo-pair, for the first time, we developed the fully biodegradable TENG (FBD-TENG) device that all elements are made of materials from nature. A leaf of Mytilaria laosensis Lec. is chosen as an example object for this FBD-TENG study. Voltage and current over 1 V and 4 μA are achieved from a water impact onto a leaf. The inferences were observed between the leaves before and after the drop impact, as shown in Figure S2. The wettability of the leaf surface is demonstrated by placing a 150 μl water droplet on the leaf surface, and the water contact angle is above 100°. Raman spectroscopy of the leaf surface (Figure 1b and Figure S1), which may increase the effective contact area during the triboelectrification.38 Raman spectroscopy is employed to characterize the chemical structure of the leaf sample. As shown in Figure 1c, a typical Raman spectrum of plant leaves has been detected with two distinct bands at 1151 and 1520 cm$^{-1}$.44,45 The band at 1151 cm$^{-1}$ is associated with C−O−C vibrations in carbohydrates and C−C vibrations in carotenoids. The band at around 1520 cm$^{-1}$ can be assigned to the C=C vibrations of carotenoids.44–47 Raman spectroscopy of the leaf surface was also detected for the water droplet impact, and no obvious difference was observed between the leaves before and after the drop impact, as shown in Figure S2. The wettability of the leaf surface is demonstrated by placing a 150 μl water droplet on the leaf surface, and the water contact angle is above 100° based on the observation (inset of Figure 1b and Figure S3). This hydrophobic property of the leaf surface allows the water droplets to be able to detach from the surface after its impact.

Figure 1d illustrates the cross section of the blade of a leaf and the external circuit connection of the FBD-TENG. A leaf blade typically consists of four distinct tissue layers: the upper epidermis, the palisade layer, the spongy layer, and the lower epidermis. Since there are full of electrolytes in these tissue layers of a living plant, charges can be transported within the entire plant including the leaves by ionic conduction.34,38,48 On the contrary, the plant cuticle that covers the epidermis is a natural hydrophobic and dielectric material.48,49 With two major components of the polymer cutin and cuticular waxes, the plant cuticle protects the leaves against desiccation and external environmental stresses.49 The ion-conductive tissue is employed as the bottom electrode, and the leaf cuticle is utilized as the dielectric capacitor and tribo-materials in the FBD-TENG. For the external circuit, one end of the circuit is placed inside the petiole (labeled in Figure 1a) and touches the conducting liquid in the leaf, and the other end is a conductive wire placed on the surface of the leaf blade. By employing the tissue electrode and the cuticle capacitor, together with the external circuit, a plant-based open circuit is thus formed.

2. EXPERIMENTAL SECTION

2.1. Materials. Natural leaves (Mytilaria laosensis Lec., etc.) were collected from the plants in Hong Kong. All tests were done within several hours after the leaf was taken off from the plants. A silver wire with a diameter of 0.1 mm and a silver-coated Cu wire with a diameter of 0.25 mm were used as a conductive wire placed on the leaf surface connecting the water droplet with the external circuit. Rain water was also collected in Hong Kong.

2.2. Characterization. Raman spectra were characterized by a customized Raman spectrometer (Horiba Scientific LabRAM HR Evolution) with an objective lens of 100X. The wavelength of the excitation laser is 532 nm, and the laser spot is around 1μm. The electric current was measured by using a low-noise current preamplifier (Model SR570, Stanford Research System) with computer measurement software written in LabVIEW. The voltage was measured with a Digital Storage Oscilloscope (DSOX2014A, KYNSIGHT). High-speed imaging for water impact dynamics detection was performed at up to 960 fps. Unless specified otherwise, all tests in this work were conducted within 6 h after the leaves were taken off from the plants.

3. RESULTS AND DISCUSSION

The leaf of Mytilaria laosensis Lec. used in this work is shown in Figure 1a. As a typical leaf, there are microstructures on its surface (Figure 1b and Figure S1), which may increase the effective contact area during the triboelectrification.38 Raman spectroscopy is employed to characterize the chemical structure of the leaf sample. As shown in Figure 1c, a typical Raman spectrum of plant leaves has been detected with two distinct bands at 1151 and 1520 cm$^{-1}$.44,45 The band at 1151 cm$^{-1}$ is associated with C−O−C vibrations in carbohydrates and C−C vibrations in carotenoids. The band at around 1520 cm$^{-1}$ can be assigned to the C=C vibrations of carotenoids.44–47 Raman spectroscopy of the leaf surface was also detected for the water droplet impact, and no obvious difference was observed between the leaves before and after the drop impact, as shown in Figure S2. The wettability of the leaf surface is demonstrated by placing a 150 μl water droplet on the leaf surface, and the water contact angle is above 100° based on the observation (inset of Figure 1b and Figure S3). This hydrophobic property of the leaf surface allows the water droplets to be able to detach from the surface after its impact.

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![Figure 1](https://dx.doi.org/10.1021/acsami.0c17601)
equivalent circuit with the switch at its open state is shown in Figure 1e. $C_{cuticle}$, $R_{cut}$, and $R_L$ are the cuticle capacitor, leaf resistance, and the load resistance, respectively. Once a conductive water droplet impacts onto the plant cuticle and touches the conductive wire, the water will serve as the top electrode and connect the external circuit with the FBD-TENG, leading to a close circuit loop for the electricity generation (Figure S4).

The experimental setup of a water droplet impacting onto the leaf surface and the generation of electrical current is shown in Figure 2a and Video S1 in the Supporting Information. A train of water droplets was released from 5 cm height above the leaf surface by using a syringe pump. Given that the cuticle of the plants is hydrophobic and can be charged by contact electrification, it can be regarded as a natural tribo-material for TENGs. The contact electrification of the leaf cuticle was reported to be caused by the layer of lipid crystals on top of it. We indeed find that after several tenths of the water droplet impact, the surface of the leaf has been gradually charged and finally reaches saturation (Figure S5). After that, uniform electric signals can be generated from the following water droplet impacts. As shown in Figure 2b and c, open-circuit voltage around 1.3 V and a short-current of 4.1 $\mu$A were generated from when droplets (33 $\mu$L; 100 mM NaCl solution) impact onto the leaf surface. This process is similar to the previously reported results when water droplets impact onto a Teflon surface, and the difference is that the Teflon surface is always negatively charged while the currently used leaf surface is positively charged in most of the cases.

Once the surface is saturated with tribo-charges and continually generates electricity, the mechanism of current generation can be understood as shown in Figure 2e. To clearly illustrate the mechanism, we divide the process into 4 stages: (1) A droplet impacts on the charged leaf surface and becomes polarized. At this stage, induced by the surface charges, an electric double layer was formed at the leaf/water interface. (2) At the moment when the droplet spreads to the maximum area and touches the conductive wire, the droplet acts as an electrode and bridges the leaf surface with the external circuit. The water as the top electrode and the leaf tissue as the bottom electrode are thus connected with the external circuit loop. To balance the electric potential difference between the top and bottom electrodes, the electrons in the external circuit move from the end of leaf tissues to the end of water droplets, and an electric current in the inverse direction is thereby formed. Given that this process is comparable with a capacitor discharge process, the generated current shows an exponentially declining behavior. At stage (3), the water droplet contracts, and the water/leaf contact area decreases. Along with the area reduction of the electric double layer, the electrons move backward to the plant tissue end so that the current reverses its direction. When the droplet leaves the surface at stage (4), the current falls to zero. The snapshots and video that reveal the droplet dynamics during these four stages are shown in Figure 2d and Video S2 in the Supporting Information.

Although the output of the FBD-TENG is lower than the water droplet-based electricity generator with a similar circuit design by using Teflon, it has already been much higher compared to the conventional single electrode TENG for water droplet energy harvesting. As shown in Figure 3 and Figure S6, no electric signal can be detected from the water droplet-based electricity generator with a similar circuit design by using Teflon, it has already been much higher compared to the conventional single electrode TENG for water droplet energy harvesting. As shown in Figure S6, no electric signal can be detected from the water droplet impact onto a leaf-based TENG with the conventional single electrode design. The output of only nA level current and around 0.1 V voltage can be generated from the water droplet impact onto a conventional Teflon-based TENG. These results are consistent with the previous report. Consequently, the energy of the water droplet impact onto a leaf surface is hardly to be harvested by using the conventional TENG.

Figure 2. (a) Photograph of the FBD-TENG. (b) Open-circuit voltage and (c) short-circuit current generated by the water droplet impact onto the Mytilaria laosensis leaf (droplet volume, 33 $\mu$L; 100 mM NaCl solution). (d) Water droplet impacts onto the leaf surface at four stages. The positions of the water droplets are labeled by red circles. (e) Schematic of the working mechanism of the FBD-TENG.

Figure 3. Schematic of (a) FBD-TENG proposed in this work, (b) leaf-based TENG with the conventional single electrode design, and (c) conventional single electrode Teflon-based TENG. (d) Current generated from the droplet impact onto the FED-TENG, leaf-based TENG, and Teflon-based TENG.
The variation of the leaf/water interface area so that the negative current curves are generally broad and with low values.

The instantaneous current, voltage, and power depending on the load resistance \( R_L \) are shown in Figure 4c. As the \( R_L \) increases, the charge transfer in the circuit will be slowed down by the increasing resistance; therefore, the current value drops. The current peak value \( I_p \) can be calculated as \( I_p = \sigma/R_c \) where \( R \) is the resistance in the circuit, \( \sigma \) is the surface charge density, and \( c \) is the dielectric capacitance per area.\(^{42,43} \) When \( \sigma \) and \( c \) are constant, the current should be inversely proportional to the resistance. Our testing result with a natural leaf as the bottom electrode and dielectric layer shows this trend generally, but some testing points appear with quantitative deviation. This may be due to the non-homogeneous surface of the natural leaf, and the local capacitance and surface charge density could vary depending on the location. We also find that the voltage across the \( R_L \) increases with the increase in \( R_L \) instead of being a constant value. This is because the ion-conductive tissue is not an ideal conductor and the resistance \( R_{leaf} \) exists inside the leaves, in series of the capacitor part in the TENG (as shown in Figure 1e). So, with the higher value of the \( R_L \) compared with the \( R_{leaf} \), the higher voltage falls onto the load resistor. The maximum power is around 1 \( \mu W \) with an \( R_L \) of 200 k\( \Omega \). Considering the maximum drop impact area of cm\(^2\) magnitude, the power density is in the magnitude of tens of mW/m\(^2\). Maximum harvested energy and the energy conversion efficiency are around 3.1 nJ and 0.2\% respectively, as shown in Figure S7. Further enhancement of the energy harvesting efficiency of the FBD-TENG may be achieved by exploring plant leaves with high surface charge density.

Figure 4d shows the amount of transferred charges \( Q \) depending on the \( R_L \), being calculated by \( Q = \int I(t)\,dt \), where \( I(t) \) is the current at the time of \( t \) (see Figure S8). The amount of positive charges transferred from the droplet electrode to the leaf tissue electrode, \( Q_{tp} \), is dominated by the charge relaxation process of the cuticle dielectric capacitor. When the relaxation time, \( \tau = RC \), is longer compared to the drop contract time, there is not enough time for all the charge transfer in the circuit before the drop starts to contract. As a result, \( Q_{tp} \) falls to small values with a high \( R_L \). However, the trend of the charge transfer amount at the inverse direction (\( Q_{tn} \)) shows a fluctuation. This may be due to the effect of the non-uniform droplet dynamics during their interaction with the conductive wire. At stage (3), the negative current is mainly dominated by the water/leaf contact area. The generated current was proven to be proportional to the variation ratio of the area in contact, namely, \( I = e\sigma dA/dt \), where \( \sigma, A, \) and \( t \) are the surface charge density, water/solid interface area, and the time, respectively.\(^{42,43} \) Given that the leaf itself is a soft material and the surface structure as well as its wettability is not as uniform as the synthetic materials, the hydrodynamics of the droplet impact is usually not identical each time (Figure S9). Moreover, the conductive wire placed on the leaf surface may disturb the movement of the droplet. The droplet could oscillate before its detaching from the conductive wire, and another current curve may be generated by such droplet oscillation, as shown in Figure S10. As a result, the \( Q_{tn} \) is in a random manner.

The current generated from droplets with different volumes is shown in Figure 5a. A higher current peak can be generated by droplets with larger volume. Given the current peak value \( I_p = \sigma/R_c \), the high \( I_p \) indicates a high surface charge density, \( \sigma \). It has been reported that the charge density generated from the droplet impact is positively related with the Weber number of the droplet,\(^{50} \) \( W_e = \rho Dv^2/\gamma \), where \( \rho \), \( D \), \( v \), and \( \gamma \) are respectively the liquid density, diameter, impact velocity, and surface tension of the droplet. So, the large droplet with a high \( W_e \) will reasonably lead to a high \( \sigma \) and \( I_p \). We also observed that the influence of the water drop rates on the generated electric current is very little, as shown in Figure S11. Rain water collected in Hong Kong has also been utilized as the droplet liquid, and the current generation results are shown in Figure 5c and d. Because the conductivity of rain water is lower than that of the 100 mM NaCl solution,\(^{42} \) the rain water droplet will act as another resistance \( R_{drop} \) of the circuit, as shown in the inset of Figure 5b so that the current is lowered.
The leaves we used in this work were plucked from the plants, and they became dry after several days. As a result, the generated current signal decreased as time passed (Figure S12), and no signal could be detected when the leaf is totally dry. However, if the FBD-TENGs are integrated into a living plant, we suppose that the device will work for a much longer time.

Like a droplet impacting onto a charged Teflon surface, the generated current also depends on the impact position of the droplet. When the droplet impacts at the vicinity of the conductive wire and touches the wire at its maximum spreading area (Figure 6a), the electricity generation mechanism is as the four stages described above. A high and sharp current peak is generated at the moment when the droplet impacts the conductive wire. The black lines in (a,b) label the position of the conductive wire.

In summary, we demonstrated an FBD-TENG that was based on natural plant leaves and water droplets. In this proposed FBD-TENG, we utilized the leaf cuticle as the dielectric and triboelectric material, the conductive leaf tissue as the bottom electrode, and the water droplet as both tribo-materials and the surface. Static electricity is pervasively presented in nature, such as on animals, skin, hairs, pollens, and flowers.37,31,32 it is possible that the nature-driven fully biodegradable energy harvesting strategy proposed in this work can also be applied with other natural elements that contain static charges.

4. CONCLUSIONS

In summary, we demonstrated an FBD-TENG that was based on natural plant leaves and water droplets. In this proposed FBD-TENG, we utilized the leaf cuticle as the dielectric and triboelectric material, the conductive leaf tissue as the bottom electrode, and the water droplet as both tribo-materials and the
top electrode. By using such an FBD-TENG, the voltage and current of over 1 V and 4 μA were achieved from a water impact onto a Mytilaria laosensis leaf, respectively. We have investigated the influencing factors of the electricity generation, including the load resistance, the droplet impact location, and the leaf surface wettability. Both the charge density and the hydrophobic property of the leaf surface are essential for energy harvesting by using the FBD-TENG. We demonstrated the wide applicability of the proposed strategy with five different kinds of plant leaves and also by using rain water as the droplet liquid. The energy harvesting efficiency could be enhanced by searching plant leaves with higher surface triboelectric charges. Considering the huge amount of plant leaves and abundant water droplets in nature, our strategies could be applied together with urban greening, in home garden, forest, and islands for energy harvesting and plant-related sensing. Moreover, as the static charges ubiquitously exist in nature, this concept of the nature-driven FBD-TENGs may also be expanded to other natural materials.

- ASSOCIATED CONTENT

- Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsa.0c17601.

- Experimental details; schematic and equivalent circuit of the droplet impact onto the leaves; surface topography, Raman spectra, and wettability of the leaves’ surfaces; generated current depending on the drop number; snapshot of dynamic behavior of the water droplet impact onto the wire; harvested energy depending on resistance; current/voltage generation using conventional TENGs; transferred charge measurement; full current curves depending on load resistance; generated current and details of transferred charge by using five kinds of leaves; description of the videos (PDF)

- (Video S1) Electric current generation from the water droplet impact onto a Mytilaria laosensis Lec. leaf surface (MP4)

- (Video S2) Slow motion video of the droplet impact next to the wire on a Mytilaria laosensis Lec. leaf surface (speed: 64 times slower) (MP4)

- (Video S3) Slow motion video of the droplet impact onto the wire on a Mytilaria laosensis Lec. leaf surface (speed: 64 times slower) (MP4)

- (Video S4) Electric current generation from the water droplet impact onto a Bryophyllum pinnatum (Lam.) Oken. leaf surface (MP4)

- (Video S5) Slow motion video of the droplet impact next to the wire on a Bryophyllum pinnatum (Lam.) Oken. leaf surface (speed: 64 times slower) (MP4)

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Author Contributions

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Notes

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