Green-in-green biohybrids as transient biotriboelectric nanogenerators

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Highlights
The construction of transient bio-TENG using green-in-green bionanocomposites
The CNC/PHB has a higher degradation rate and a higher dielectric constant
The enhanced dielectric constant improves the triboelectricity of CNC/PHB-based TENG
The bio-TENG-based arch sensor attains real-time monitoring of human motions

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SUMMARY

Green self-powered devices based on biodegradable materials have attracted widespread attention. Here, we propose the construction of the transient biotriboelectric nanogenerator (TENG) using green-in-green bionanocomposites. The green-in-green nanocomposites, cellulose nanocrystal (CNC)/polyhydroxybutyrate (PHB), are prepared with a high-pressure molding method. The CNC promotes the degradation and enhances the dielectric constant of CNC/PHB. It further allows for the significant improvement of the triboelectric output of CNC/PHB-based TENG. The voltage output and current output of CNC/PHB-based TENG are 5.7 and 12.5 times higher than those of pristine PHB-based TENG, respectively. Also, the bio-TENG exhibits admirable signal stability in over 20000 cycles. Despite the high hardness of CNC/PHB, a soft but simple-structured arch sensor is successfully assembled using CNC/PHB-based TENG. It can attain the precise real-time monitoring of various human motions. This study may provide new insights into the design/fabrication of green functional materials, and initiate the next wave of innovations in eco-friendly self-powered devices.

INTRODUCTION

With the increasing consumption of energy and the gradual depletion of traditional fossil resources, the development of sustainable energy harvesting/supply technology has been attached much attention. The self-powered system can convert all kinds of ambient energy into electrical energy to maintain the operation of the device. The technology mainly depends on the special coupling effects that include triboelectric effect, piezoelectric effect, electromagnetic effect, thermoelectric effect and pyroelectric effect, and so forth. He et al. conceived a flexible piezoelectric-enhanced triboelectric nanogenerator (TENG), which could harvest ambient energy to drive commercial electronic devices. Ouyang et al. fabricated a bioresorbable pressure sensor based on the triboelectric effect for cardiovascular postoperative care. Natural biodegradable materials have biocompatibility and renewability, which makes these materials be used in TENG for implantable healthcare function devices, transient medical equipment, and wearable sensors. Consequently, there is tremendous potency and value for using the biomaterials in self-powered electronics and systems. However, most bio-materials generally have structural or functional drawbacks which limit their applications. Therefore, it is very necessary to employ versatile chemical or physical methods for solving these problems.

Polyhydroxybutyrate (PHB) is a thermoplastic, chiral polyester. It is synthesized by microorganisms as a carbon source and energy storage in the case of the imbalance of carbon and nitrogen nutrition. PHB has good environment compatibility and biodegradability, and its decomposition products can be safely absorbed by the environment. In addition, the microbial polyester has some special functions, including piezoelectric property and pyroelectric property. So far, there are some reports and applications about these properties. Chernozem et al. utilized the electrospinning technology to prepare PHB/rGO (graphene oxide) 3D composite biological scaffolds used in various tissue engineering. Zviagin et al. fabricated fibrous scaffolds with ZnO/PHB, which improved scaffolds’ piezoelectric responses. However, these employments merely involve the bio-engineering. To our knowledge, there are few reports involving the PHB in green self-powered devices.

Cellulose is a productive and widely sourced biopolymer on the earth. One dimensional cellulose nanocrystal (CNC), with high crystallinity and diameter smaller than 100 nm, can be prepared by chemical,
physical or biological treatment. The natural CNC has highly ordered crystalline structure, large specific surface area, unique morphological structure, good environmental compatibility, and strong hydrophilicity. As far, CNC has been applied in much advanced applications, such as supercapacitors, batteries, sensors, and so forth. It is recognized as an attractive component for fabricating functional materials. Consequently, it is conceivable that the combination of CNC and PHB can induce new performances or improve existing performances.

As depicted in Figure 1, we prepare a green-in-green CNC/PHB-based TENG for the first time. Simultaneously, a flexible biological TENG sensor comprising the high hardness bioderived CNC/PHB composite is further manufactured. The structure and performance of CNC/PHB suggest the green nanofiller CNC has considerable effects on the degradation and dielectric property of green PHB. Meanwhile, the CNC/PHB with higher dielectric constant can induce more charges on the back electrode, which greatly enhances the performances of the bio-TENG. Additionally, the TENG exhibits remarkable stability of the electrical signal in over 20000 cycles. Based on the triboelectric effect of CNC/PHB bionanocomposites, a simple but flexible bio-TENG sensor is conceived and assembled to collect information about human motions. This further demonstrates the considerable value of CNC/PHB bio-composites in environment-friendly self-powered sensors.

RESULTS AND DISCUSSION

The dispersion and morphology of CNC in water and in the 5CNC/PHB casting membrane were directly revealed using TEM, as shown in Figure 2. Clearly, the CNC had good dispersion in water (Figure 2A). The length and the diameter of CNC were about 200 nm and 10 nm, respectively. The morphology and structure of CNC did not change in the as-fabricated CNC/PHB composite sample. Most importantly, the green dopant achieved a relatively good dispersion in the PHB matrix (Figure 2B).

Additionally, FTIR spectra of PHB-based composites were obtained to investigate CNC in bio-nanocomposites (Figure 2C). The band at 1428 cm⁻¹ and 3342 cm⁻¹ were assigned to -CH₂- bending and stretching vibration of O-H respectively. The intensity of these two bands increased with the increment of CNC content. This further confirms that the CNC was doped into the composite system successfully.

To study the effects of CNC on the PHB crystalline structure, further characterizations were carried out. Figures 2D and 2E show the DSC and WAXD results of CNC/PHB nanocomposites, exhibiting melting behaviors and information about the crystalline region, respectively. For the pristine PHB sample, its crystalline degree is 76.0% (Figure S1). When the 1% CNC is added, the green-in-green composite has a higher crystalline degree of 78.0%. However, with the further increase of CNC content, the crystallinity of the CNC/PHB nanocomposites decreases from 78.0% to 75.4% (Figure 2D). It is generally believed that the
crystallization of polymer can be divided into two stages: nucleation and growth. This result reveals that the moderate content of CNC, as a nucleating agent, is beneficial for the formation of anisotropic structures. But the excess CNC may impede the polymer molecular chain from getting into the lattice, which finally dwindles the proportion of PHB crystals. Similar phenomenon also occurred in the crystallization of PDLA/PLLA/CQD composites. 50 WAXD was further employed to examine the microstructure of the PHB crystals in CNC/PHB (Figure 2E). It is obvious that the three CNC/PHB samples had similar X-ray diffraction spectra due to high-pressure treatment, which suggests there may be similar crystalline structures. 51 The direct morphological observation of the crystalline structure of 3CNC/PHB samples was acquired through SEM (Figures 2F–2H). Apparently, a wrinkled spherulite structure was obtained in the 3CNC/PHB sample. Also, it occurred in other PHB-based nanocomposites (Figure S2).

Besides these structural characterizations, the degradation of the bio-materials was discussed. As shown in Figure 2I, obviously, there is almost no mass loss for the pristine PHB specimens in the alkali aqueous solution. Moreover, no obvious change in appearance was exhibited (Figure 2J). Contrary to the PHB sample, the residual weight fraction of the 5CNC/PHB composite decreased with time, which indicated the hydrolysis of bio-composite occurred (Figure 2I). When the degradation time reached 29 days, the sample edge whitened and cracks appeared on the sample surface (Figure 2J). With the time extended, the white area expanded continually and the sample was disintegrated into pieces in 116 d. After another 60 days, the residual mass fraction of the 5CNC/PHB sample reached about 84%.

The reason for almost no degradation of pure PHB in comparison with 5CNC/PHB may be ascribed to the following three points. First, the tight structure in the crystalline region is known to make the solution penetration difficult. The pure PHB sample has higher crystallinity that is more detrimental to hydrolytic degradation (Figure S1). Second, the CNC, a hydrophilic nanomaterial, improves the hydrophilicity of CNC/PHB nanocomposites. This further facilitates the solution diffusion and the hydrolysis in CNC/PHB. Last but not least, lower experiment temperature inhibits the hydrolysis reaction for both PHB and CNC/PHB. In a word, this result confirms the enormous possibility and value of green-in-green nanocomposites in the field of degradable electronic devices.

The CNC/PHB composite with different CNC contents was assembled into TENGs respectively. Because the surface potential of CNC/PHB is different from that of polydimethylsiloxane (PDMS), a triboelectric potential is established when the two materials contact and then separate. It can drive the reciprocating flow of electrons between the back electrode and the ground (Figure S3). Also, the pristine PHB-based TENG was prepared as a reference using the same method. Subsequently, kinetic energy collection performance of generators was evaluated (Figure 3A). Figures 3B and 3C show the electrical outputs of the bio-TENGs under the external excitation of 4 N and 1 Hz. It is obvious that the generated energy output of CNC/PHB-based TENG was improved with the increase in the CNC content. Among them, the open-circuit voltage and short-circuit current of the 5CNC/PHB-based TENG could reach 248.8 V/cm³ and 2.5 μA/cm³, respectively, which were about 6.7 times and 13.5 times than those of the pure PHB-based TENG, respectively. Because these composites have similar exterior appearances and internal structures, this result suggests that the addition of CNC might affect the intrinsic property of the nanocomposites, thus improving the performances of the bio-TENG.

In order to better explain this phenomenon, a characterization of these materials was carried out. The dielectric constant ($\varepsilon_r$) of CNC/PHB nanocomposites at different frequencies was obtained (Figure 3D). The dielectric constant reflects the ability of materials in responding to the external electric field. In other words, the material with a higher dielectric constant has greater polarization intensity in the same electric field. At the range of $10^0$ ~ $10^3$ Hz, material polarization mainly depends on interfacial polarization. With the increase of frequency of alternating electric field, the relaxation of interfacial polarization occurs. So, the polarization of these CNC/PHB composites is very low at higher frequencies, and the dielectric constants
had similar value. However, $\varepsilon_r$ of the nanocomposite demonstrated a positive correlation with the content of CNC at lower frequencies. Previous reports have proved that materials with a higher dielectric constant can enhance electrification induction and favor higher triboelectric performances.52,53 As shown in Figure 3 E, the open-circuit voltage and short-circuit charges of the single-electrode bio-TENGs can be approximately regarded as 54:

$$V_{oc} = \frac{S\sigma_1}{2C} \quad \text{(Equation 1)}$$

$$Q_{sc} = \frac{S\sigma_1}{2} \quad \text{(Equation 2)}$$

Figure 3. Working mechanisms of the CNC/PHB-based TENG
(A) Impact-measurement system for simultaneously collecting the electrical potential and current outputs.
(B and C) Open-circuit voltage (B) and short-circuit current (C) outputs of pure PHB and CNC/PHB, generated at the same stimulating frequency of 1 Hz, and an applied force of 4 N. Sample size: 8.0 mm in diameter and 0.6 mm in thickness.
(D) Dielectric constant profiles of CNC/PHB nanocomposites.
(E) Schematic drawing of the working mechanism for the single-electrode bio-TENGs.
where $V_{oc}$ is the open-circuit voltage, $Q_{sc}$ is the short-circuit transferred charges, $\sigma_1$ is the surface charge density over the back electrode, $S$ is the surface area of the electrode, and $C$ is the capacitance between the back electrode and the grounding terminal. When test conditions remain the same, $S$ and $C$ are usually constant. Thus, $V_{oc}$ and $Q_{sc}$ are related to $\sigma_1$ only. For CNC/PHB with higher dielectric constant, it can induce more charges over the back electrode and thereby improve both $V_{oc}$ and $Q_{sc}$. Consequentially, because the short-circuit current ($I_{sc}$) is defined as the ratio of $Q_{sc}$ to time, $I_{sc}$ also increases with the increment of the CNC amount.

Furthermore, the 5CNC/PHB-based TENG was investigated in detail to determine the effect of stimulating frequency and force amplitude over triboelectric outputs. As presented in Figures 4A and 4B, the electrical outputs of the 5CNC/PHB-based TENG were collected, under the stimulation of a given frequency of 1 Hz with the various applied forces from 4 N, 8 N, and 16 N. It is evident that the open-circuit voltage and short-circuit current outputs increased gradually with the increase of impact force. The voltage and current output density increased from 248.8 V/cm$^3$ and 2.5 $\mu$A/cm$^3$ to 331.4 V/cm$^3$ and 4.9 $\mu$A/cm$^3$, respectively. These results indicate the 5CNC/PHB-based TENG is relatively sensitive to the change of the external applied force, thereby proving the green generator can convert diverse environmental mechanical energy into electrical energy.

Figures 4C and 4D show the electrical outputs of 5CNC/PHB-based TENG stimulated by an impact force of 16 N, with the frequency varied from 1 Hz, 2 Hz to 3 Hz. Similarly, with the increase of stimulation frequency, the bio-TENG can generate higher electrical outputs, and the voltage density could achieve 365.2 V/cm$^3$ and 5.5 $\mu$A/cm$^3$. However, the increment obtained was relatively small and a similar phenomenon also occurred in previous reports. In conclusion, this bio-material nanogenerator could respond to the variation of stress and frequency. This indicates that the triboelectric electromechanical conversion device can adapt to various mechanic movements in ambiance.

More investigations were implemented on electrical output performance (Figure 5). In order to determine the maximum electric power output, the voltage and current of 5CNC/PHB-based TENG under different exterior resistance were collected. As depicted in Figure 5A, the current and voltage present positive
and negative correlations with external load resistance respectively, because of ohmic loss. When the resistance varies from 1 MΩ to 5 GΩ, there is a dramatic change in output electric signals. Additionally, the dependence of instantaneous power density on external load resistance is calculated and plotted in Figure 5B. Evidently, the instantaneous peak power is the maximum when the external resistance reaches around 166 MΩ. The corresponding electric power density is about 58.4 mW/cm³. Figure 5C shows that a series of capacitors are charged by using a 5CNC/PHB-based TENG. The capacitors of 0.1 μF and 0.2 μF are charged to 3 V within about 50 s and 100 s, respectively. As we all know, stable energy output is one of the important criteria to evaluate the performance of electronic devices. Consequently, the short-circuit current of 5CNC/PHB-based TENG under incessant stimulation is selected as the main criterion. Amazingly, as shown in Figure 5D, the current generated by the apparatus has hardly changed in more than 20000 cycles, demonstrating the great possibility of this device in self-powered sensors.

The previous tests have proved that the 5CNC/PHB-based TENG has considerable energy output performance. However, it is well acknowledged that PHB materials generally have high brittleness that discourages the value of the bio-polyester. Consequently, because of the small size, a flexible sensor with a simple structure was conceived (Figure 6). It could accurately perceive the human movement according to the electrical signals from this sensor. As depicted in Figure 6A, PI is used as supporting materials to carry the 5CNC/PHB sample and PDMS film, and conductive carbon cloth is used to transfer electric charges. Figure 6B exhibits a digital picture of the sensor which has the proper size and could be attached to joints of the limbs. The charges on the friction surface can create a triboelectric potential between the 5CNC/PHB sample and the ground. To balance the generated electric potential drop, the electrons are driven...
Figure 6. Working principles and performances of the flexible sensor
(A and B) Schematically illustration (A) and a digital picture (B) of a 5CNC/PHB-based sensor for behavior monitoring.
(C) A diagram of the working mechanism of the sensor.
(D and E) Output currents of bio-TENG sensor attached to a volunteer’s knuckles (D) and elbow (E) with different bending angles.
(F) Output currents of bio-TENG sensor fixed in the shoes of a volunteer with different speeds.
to flow back and forth between the back electrode and the earth (Figure 6C). Then, the rotating angle of the joints can affect the stress applied to the arch structure, which makes the sensor generate different electric signals. Consequently, we can analyze and perceive the motion of volunteers. When the sensor is attached to the finger joints or elbow, the sensor can generate characteristic signals in response to joint motions (Figures 6D and 6E). The signal induced by a flexion-extension movement has been highlighted with the blue dotted oval frame. Apparently, a positive correlation is unraveled between the signal by this sensor and the rotation angle of the joints. In addition, the sensor was also placed into the shoes to demonstrate the versatility of the sensor. Figure 6F exhibits the output signals generated by the sensor over a volunteer at different walking speeds. The magnitude of signals will expand with the increase of the velocity of the volunteer. In a word, the sensor based on the bio-TENG can precisely reflect the movement of volunteers. This fact further demonstrates its potential in the field of behavior perception, athletic monitoring, and human-machine interfacing.

Conclusions
Here, a green-in-green CNC/PHB bionanocomposite was prepared by high-pressure molding. It was used for the first time to fabricate biotriboelectric nanogenerators. Contrary to the pure PHB sample, the degradation of the CNC/PHB nanocomposite could occur at room temperature with the existence of hydrophilic CNC. Also, the CNC changed the dielectric properties of CNC/PHB, which could induce more charges over the electrode of the bio-nanogenerator. Consequently, the electrical output of CNC/PHB-based single-electrode TENG increased with the increase of CNC contents. The output voltage and output current of 5CNC/PHB-based TENG were approximately 5.7 times and 12.5 times higher than those of pristine PHB-based TENG, respectively. Besides, the CNC/PHB-based TENG demonstrated considerable high performance in instantaneous output power output and charging various external capacitors. Importantly, in more than 20000 continuous cycles, it exhibited a remarkable stability/durability of the output electric signals. Further, despite high hardness of CNC/PHB composite, a flexible but simple arch sensor was assembled using the CNC/PHB-based bio-TENG. It showed significant practical value in athletic monitoring. In a word, we believe this work confirms a simple but effective method to improve the electrical outputs of a bio-polyester-based TENG. It also provides a great template for preparing more green-in-green materials used in environmental-friendly self-powered devices.

Limitations of the study
The uniform dispersion of nanofillers in the polymer matrix is very critical to the final properties of the polymer matrix nanocomposites. It is known nanofillers essentially tend to agglomerate in the polymer matrix. Currently, it remains a great challenge to prepare a uniformly dispersed polymer matrix nanocomposite with a very high nanofiller content. In this study, we prepared a series of PHB-based composites with different amounts of CNC. The positive effect of CNC on the electrical output of CNC/PHB-based TENG was discovered. This phenomenon is ascribed to the improvement of the dielectric constant of bio-composite systems, which is induced by CNC. It is notable that the dispersion of nanofiller in the matrix has immense effects on the dielectric property of the biocomposite system. However, serious aggregation of CNC will occur if the amount of CNC is increased further to more than 5%. Therefore, at the present stage, we conclude that the 5% CNC content is the optimal CNC content for the best output performance of the CNC/PHB-based TENG. Future research efforts will mainly focus on the design and manufacture of green-in-green bionanocomposites with extremely high content of uniformly dispersed CNC. We anticipate that this will further boost the generated energy output of green-in-green bionanocomposites.

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Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.105494.

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AUTHOR CONTRIBUTIONS

J.L. and C.W. conceived the idea. J.L. initiated the study. C.W., L.L., W.L., D.S., and C.Z. carried out the sample preparation and characterization. J.L. and W.Y. organized the entire research. C.W., J.L., and W.Y. analyzed and interpreted the data, and wrote the article with the assistance of all other co-authors. All authors discussed the results and commented on the article.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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STAR★METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Chemicals, peptides, and recombinant proteins | TianAn | Product# ENMAT Y3000P |
| Polyhydroxybutyrate | Hengqi | Polydimethylsiloxane Product# Dow Corning Sylgard 184 |
| Cellulose nanocrystal | ScienceK | Product# ScienceK2022 |

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Jun Lu (unluprc@hotmail.com).

Materials availability
This work is an experimental study of construction of bio-nanocomposites and nanogenerators and there is no new code generated.

Data and code availability
All data reported in this paper will be shared by the lead contact upon reasonable request.

No new code was generated during the course of this study.

Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon reasonable request.

EXPERIMENTAL MODEL AND SUBJECT DETAILS

In the monitoring of human behaviors
The experimental protocol complied with the regulations of Animal and Human Experimentation Committee of Southwest Jiaotong University. A 26-year-old healthy male volunteer was recruited from Southwest Jiaotong University and gave informed consent prior to testing. In the test, the flexible sensor was fixed on the subject’s knuckles and elbow with adhesive tape. Simultaneously, one end of the sensor was connected to a Keithley 6514 system electrometer. After, the subject was asked to exercise continuously for about 15 s. During the period, the sensor measured the bending angle and collected the data on the computer through the electrometer. When the sensor was placed inside the shoe and fixed with adhesive tape, the walk speed of the subject was recorded in the same way.

METHOD DETAILS

Preparation of CNC/PHB composites
The flow chart of CNC/PHB fabrication is shown in Figure S4. Dimethyl formamide (DMF) could be freely mixed with water and most organic solvents, such as chloroform. It could dissolve PHB powder at high temperature and also be used as a dispersant for CNC. A homogeneous solution of PHB in DMF was prepared by stirring at 131 °C for 40 min. After that, the corresponding amounts (1%, 3%, and 5%, w/w) of CNC, dispersed in DMF and sonicated in an ice bath for 10 min previously, were added into the PHB solution. The mixture was further stirred for 20 min at the 131 °C, and then sonicated again for 10 min to obtain a uniformly mixed solution. Afterward, the solution was poured into glass dishes and placed in an oven at 80 °C for 12 h to remove the solvent by evaporation. Then, the blend film was cut into shreds, and subjected to a self-made piston-cylinder apparatus for high pressure treatment. The temperature of mold was increased to 180 °C, allowing them to melt completely. Subsequently, the temperature was then quickly lowered to 130 °C, and a high pressure (300 MPa) was loaded. Under the above condition for 30 min, then the whole apparatus was cooled down to room temperature. Finally, the samples were taken out from the mold. The high pressure treated specimens are denoted as 1CNC/PHB, 3CNC/PHB, and...
SCNC/PHB, respectively, according to the content of biological nanoscale additive CNC. The specimens were \( \approx 8.0 \text{ mm} \) in diameter and \( \approx 0.6 \text{ mm} \) in thickness.

**Characterization of materials**

Transmission electron microscope (TEM) observation was conducted with a JEM-2100F apparatus. Fourier transform infrared spectroscopy (FTIR) was employed to identify the CNC in composites by a Nicolet iS500 instrument. Wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) tests were performed at atmospheric pressure by using an Empyrean instrument and a DSC-404F1 instrument, respectively. The melting behavior of PHB-based samples was studied by heating scanning in N\(_2\) atmosphere at a heating rate of 10 °C/min. The crystallinity \( (X_c) \) of the nanocomposite was calculated with the following equations:

\[
X_c = \frac{\Delta H_m}{\Delta H_{m0} \times \omega_{(PHB)}} \times 100\% \quad \text{(Equation 3)}
\]

where \( \Delta H_m \) is the endothermic enthalpy of the melting peak in DSC curves, and \( \omega_{(PHB)} \) is the weight ratio of PHB in the composites. \( \Delta H_{m0} \) is regarded as 146 J/g, and assumed as the equilibrium melting enthalpy of PHB crystal.\(^{56-58}\) The methylamine aqueous solvent, used as etching agent, was adopted to expose the crystalline structure of PHB. The etched PHB-based samples were then covered with gold for scanning electron microscopy (SEM) observations using a JSM-6330F apparatus. The dielectric properties of specimens were evaluated through a broad frequency dielectric spectrometer, Concept 80 (Novocontrol, Germany). The sample was placed between two metallic plates. Under the premise of constant electric field strength, the dielectric constant at corresponsive frequency was obtained by changing the frequency of electric field applied on the plates.

**Degradation of the nanocomposite**

For the better illustration of degradation performances of the bio-nanocomposite, a hydrolysis experiment was carried out. The pure PHB and the CNC/PHB samples were shaped with similar appearance and similar weights. Firstly, these samples were placed in glass tubes to perform hydrolytic degradation. Secondly, in each tube, the sodium hydroxide solution with pH 12 was poured into the tube. Thirdly, the sample was taken from the solution at the appointed time. They were washed 2-3 times in deionized water and once in ethanol. Lastly, the samples were placed in oven at 40 °C for 24 h to remove the solution residue. It is worth noting that the entire hydrolysis process took place at room temperature (25 °C). The weights of samples were recorded, and the residual weight fraction \( (\Phi) \) was calculated as follows:

\[
\Phi = \frac{W_t}{W_0} \times 100\% \quad \text{(Equation 4)}
\]

where \( W_0 \) is the initial mass of the sample before the hydrolysis, and \( W_t \) is the residual mass.

**Measurement of triboelectric outputs**

A periodic impacting test was designed for evaluating the energy output performances of PHB-based TENG. A NTIAG HS01-37 \( \times 166 \) linear motor provided stable and controllable external stimulus. The generated open-circuit voltage and short-circuit current were collected simultaneously on a Keithley 6514 system electrometer.

**Fabrication of the TENG sensor**

For fabricating the sensor, two pieces of polyimide (PI) film were prepared as substrates of the friction functional layers. On one substrate, a PDMS film was coated to form a triboelectric layer by a blade coater, and then placed in a vacuum oven at 80 °C for curing. On the other piece of PI film, a CNC/PHB sample was placed with carbon cloth served as the back electrode. Subsequently, the ends of the two flexible substrates were pasted and fixed by adhesive tape face to face. At the same time, an arch structure was constructed to create a gap between friction layers. Finally, the sensor was connected with the signal collection and analysis systems for subsequent tests.

**QUANTIFICATION AND STATISTICAL ANALYSIS**

The TENG data were collected with a Keithley 6514 system electrometer. Figures were produced by Origin from the raw data.