Low-cost, environmentally friendly and high-performance cellulose-based triboelectric nanogenerator for self-powered human motion monitoring

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Abstract Cellulose-based triboelectric nanogenerators (TENGs) can provide power for various monitoring devices and are environmentally friendly and sustainable. Chemical functional modification is a common method to improve the electrical output performance of cellulose-based TENGs. In this work, an environmentally friendly high-performance triboelectric nanogenerator based on a polydopamine/cellulose nanofibril (PDA/CNF) composite membrane and fluorinated ethylene propylene was developed. Dopamine generates polydopamine nanoparticles through oxidative self-polymerization and adheres to the surface of nanofibers. The synergistic effect of amino group introduction and membrane surface microstructure effectively enhanced the output performance of TENGs to a certain extent. The effects of PDA content, CNF composite film thickness and different working conditions on the electrical output were systematically investigated. The optimized PDA/CNF-TENGs exhibited an enhanced electrical output performance with voltage, current, and power density values of ≈205 V, ≈20 µA, and ≈48.75 μW·cm⁻², respectively. The PDA/CNF-TENGs exhibited stable and identifiable signals when used as a self-powered sensor for human motion monitoring, showing the potential prospects of cellulose materials for TENGs and other electronic applications.

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Introduction

With the increase in demand for sustainable and renewable energy, triboelectric nanogenerators (TENGs) (Mi et al. 2018) have recently attracted attention as a new type of energy collection device. TENGs convert low-frequency irregular mechanical energy into electrical energy through frictional electrification and electrostatic induction (Niu et al. 2013; Wu et al. 2019). At the same time, TENGs have the advantages of low cost, simple structure, outstanding output stability, and high energy conversion efficiency. Triboelectric materials are core components of TENGs. Choosing the appropriate triboelectric materials is key to preparing high-performance TENGs. We found that most of the triboelectric materials of TENGs with excellent performance are nonrenewable synthetic polymers (Dong et al. 2017; Guo et al. 2021; Han et al. 2020). With the development concept of sustainable industrial ecology and the requirements for new materials, advocating the use of green and environmentally friendly materials has become the mainstream of current research (Zhang et al. 2022). Therefore, it is urgent and necessary to find green and low-cost materials to replace the nondegradable polymers in TENGs.

Bio-TENGs are becoming an environmentally friendly alternative to conventional TENGs. Natural biomass-based materials are increasingly being used as triboelectric layers in TENGs, including cellulose nanofibrils (CNFs) (Shi et al. 2019; Zhang et al. 2020a, b), biohydrogels (Wang et al. 2018; Yiming et al. 2021), and gelatin (Han et al. 2020). CNFs are the most abundant natural renewable resource in nature; they are flexible, biodegradable, and easy to be functionally modified (Niu et al. 2021; Zhang et al. 2022).
2021). CNFs are triboelectric materials with great application prospects (Lin et al. 2018). However, compared with synthetic polymers, CNFs exhibit a weaker triboelectric polarity (Qian et al. 2019). At present, research on enhancing the performance of CNF-based TENGs is mainly focused on expanding the potential difference between triboelectric layers and improving the structural design. Different functional groups (such as nitro-, amino-, and fluorine-containing groups) have been introduced to improve the charge capture ability (Yao et al. 2017), high dielectric particles were doped to improve the dielectric constant (Sriphan et al. 2020), and surface microstructures were introduced to increase the effective contact area (Kim et al. 2021).

In recent years, inspired by the viscous protein components in mussels, catechol-based 3,4-dihydroxy-l-phenylalanine (dopamine) has been shown to self-polymerize and act as a binder (PDA) that adheres to the substrate through covalent or noncovalent bonding. PDA has attracted extensive research attention in composite design because of its remarkable adhesion, conductivity, and oxidation resistance. Liu et al. (2018) modified natural cellulose by coating a PDA layer, showing a very high adsorption capacity for Pb²⁺ and methyl orange. Yang et al. (2020) achieved dye adsorption and photocatalytic degradation by preparing a 3D bacterial cellulose/PDA/TiO₂ nanocomposite membrane, and Su et al. (2017) prepared conductive cellulose-based rice paper with long-term durability through PDA modification. For TENGs, Yang et al. (2021) used PDA-modified carbon nanotubes (CNTs) to prepare self-curing PDA-CNT/PVA hydrogels with high electrical conductivity and photothermal properties. Sun et al. (2021) used PDA-modified fish gelatin to prepare degradable and high-performance cathode triboelectric materials. PDA contains a large number of amino groups with strong electron-donating ability. After chemical modification by PDA, the triboelectricity of paper fibers is greatly improved. The electrical conductivity of PDA can also play a synergistic role in friction materials to accelerate electron transfer. Additionally, PDA is nontoxic, biodegradable, and has a high level of biocompatibility, and the modified material still possesses the qualities of an eco-friendly material. As a positive triboelectric material, PDA-modified CNFs are considered a reasonable means to achieve ideal high output performance of CNF-based TENGs.

In this study, we used PDA-functionalized modified CNFs to fabricate cellulose-based positive friction materials with high performance and biocompatibility by vacuum filtration and systematically investigated the factors affecting the triboelectric performance. The PDA/CNF-TENG exhibited excellent performance, with an open-circuit voltage and short-circuit current of 205 V and 20 μA, respectively, which were significantly higher than those of the pure CNF TENG (65 V and 2.85 μA), mainly benefiting from the introduction of amino groups and the formation of micro/nanostructures on the membrane surface. In addition, we demonstrated that a 4 cm × 4 cm PDA/CNF-TENGs can instantly light 158 light-emitting diodes (LEDs), when this TENG was used for motion detection as a self-powered sensor. The TENG sensor can be attached to different body parts and output stable and recognizable electrical signals to monitor human motion, which shows the great potential of this cellulose-based TENG in wearable sensing.

Materials and methods

Materials

Bagasse cellulose fibers was supplied by Nanning, China. Dopamine hydrochloride (DA·HCl) was purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). A polymethyl methacrylate (PMMA) plate was purchased from Deyao Building Materials Co., Ltd. (Guangzhou, China), conductive tape was purchased from Sitejie office store (Shenzhen, China), and a fluorinated ethylene propylene (FEP) film was purchased from Aofa Plastics Co., Ltd. (Suzhou, China).

Construction of CNF and PDA/CNF films

We dissolved 38.0 mg of dopamine hydrochloride in 100 ml of 0.1 mmol/L Tris(hydroxymethyl)aminomethane solution (Tris–HCl, pH = 8.5) to form a 2 mmol/L PDA solution. The modification of CNFs was carried out in PDA solution. First, 0.5 g of CNFs (dry weight) was completely dispersed in the PDA solution and stirred at room temperature (25 °C) for 12 h in the dark. Images of different stages of the reaction process are shown in Fig. S1. After the reaction was completed, the samples were washed with...
distilled water, and the PDA/CNFs suspension was poured into a G5 sand core funnel equipped with a microporous filter membrane. After vacuum filtration, the wet PDA/CNFs film was removed and dried at 70 °C for 15 min with a molding machine; then, the film was placed in an oven and dried at 70 °C for 2 h.

CNF film without modification: Deionized water was added to the CNF suspension (0.5 g dry weight) to dilute the sample to <0.2 wt.%, and CNF films were prepared by vacuum filtration. When preparing PDA/CNFs films of different thicknesses, the thickness was controlled by changing the CNF quantification, and the film thickness was measured with a Paper Thickness Tester.

Fabrication and characterization of TENGs

Acrylic plates (PMMA) were used as the upper- and lower-pole support plates of the TENG. Conductive copper foil was pasted on the upper and lower electrode plates. The FEP and PDA/CNFs films were cut to a certain size and pasted onto the upper and lower electrode surfaces with conductive double-sided tapes as the positive and negative triboelectric materials of the device, and the positive and negative copper wires were connected to the triboelectric materials and electrodes, respectively. Positive and negative wires were connected to the electrometer to test the output performance of the TENG.

Through a vibration exciter (JZK-10, China) and tubular linear motor (LINMOT H10-70×240/210, US), the TENG was driven periodically at a certain frequency and pressure, and the generated electrical signal was captured by an electrometer (Keithley 6514, US) and an acquisition card (Ni USB-6259, USA) and output by a computer.

Characterization of PDA/CNF films

Transmission electron microscopy (TEM, JEM-1200, Japan) and field-emission scanning electron microscopy (FESEM, Hitachi SU8220, Japan) were used to...
observe the morphology of the CNFs before and after PDA modification. The samples were sprayed with gold prior to SEM observation. The surface roughness of the CNF films was measured using atomic force microscopy (AFM, 5100 N, Japan). Fourier transform infrared spectroscopy (FTIR, VERTES 70, Germany) was used to detect the changes in the functional groups in the CNFs before and after PDA modification, and the range of measurement was 4000–400 cm\(^{-1}\). X-ray photoelectron spectroscopy (XPS, KRATOS Axis Ultra DLD, UK) was used to determine the type and content of surface elements before and after PDA modification. X-ray diffraction (XRD, Smart Lab 3 kW, Japan) was used to determine the change in crystallinity of CNFs before and after modification. The scanning range was 20°=5–50°, and the scanning speed was 5°/min.

**Results and discussion**

Microstructural characterization of hybrid PDA/CNF films

Figure 1a schematically illustrates the preparation of PDA/CNFs composite membranes by PDA self-polymerization. Dopamine (DA) polymerizes and self-assembles under weakly alkaline conditions and can be adsorbed on the material surface by the synergistic action of covalent and noncovalent forces. The FTIR and XRD spectra of CNFs before and after modifications and the XPS spectra of the CNF and PDA/CNF films are shown in Figure 2. The AFM images of the CNF and PDA/CNF films are also presented in Figure 2. The RMS roughness values of the CNF and PDA/CNF films are 73.92 and 109.1, respectively.
bonds (Cheng et al. 2019). Based on this principle, we used PDA to modify CNFs to prepare composite membrane materials. First, a 2 mmol/L DA Tris solution was prepared at pH = 8.5. The PDA/CNFs precursor solution was prepared by mixing the CNF and DA solutions under magnetic stirring. Afterward, the obtained PDA/CNFs solution was washed, and suction filtered to form a membrane, which was dried for further use. Figures 1b–d show the TEM images of CNFs before and after modifications. Dopamine self-polymerizes and assembles into polydopamine nanoparticles under alkaline conditions, and the particle size is approximately 100–200 nm. After mixing with CNF, PDA nanoparticles aggregated on nanocellulose fibrils, PDA nanoparticles can still be seen on the surface of the PDA/CNFs film, as shown in the SEM image of the modified CNF composite membrane in Fig. 1e.

To verify the effect of PDA on the CNFs, FT-IR, XRD, and XPS were used for functional group characterization and element mapping of the films. As shown in Fig. 2a, the PDA/CNFs retained the characteristic absorption peak of CNF. The wide absorption peak at 3388 cm\(^{-1}\) is attributed to the O–H stretching vibration in CNFs, the absorption peak at 2896 cm\(^{-1}\) belongs to the C–H stretching vibration of –CH\(_2\)–, and the 890 cm\(^{-1}\) β-characteristic absorption peak corresponds to the glycosidic bond (Kaynak et al. 2018). As shown in Figs. 2a and S2, compared with the CNF film, the PDA/CNFs film showed new absorption peaks at 1543 cm\(^{-1}\) and 1524 cm\(^{-1}\), corresponding to the C=C double bond of the PDA aromatic ring stretching vibration (Cheng et al. 2018; Xu et al. 2016) and N–H bending vibration peaks (Qin et al. 2019). With increasing PDA content, the absorption peak of the PDA/CNFs film at 3388 cm\(^{-1}\) broadened due to the loading of PDA (the surface of PDA contains a large amount of –OH, and its characteristic peak is located at 3200–3600 cm\(^{-1}\)) (Zhao et al. 2019), confirming that CNFs were successfully modified by PDA, and an amination reaction also occurred between the amino groups and hydroxyl groups of CNFs in PDA.

Figure 2b shows the XRD diffractograms of the CNFs before and after PDA modification. The peaks of cellulose (JCPDS 03-0289) around at 2θ = 16° and 22.3° indicated that the CNF before and after modification still retained the typical pattern of cellulose I. The crystallinity (\(CrI\)) was calculated according to Segal method (Segal et al. 1959), and Eq. (1) was an empirical method for calculating cellulose crystallinity:

\[
CrI(\%) = \frac{(I_{200} - I_{am})}{I_{200}} \times 100\%
\]

where \(I_{200}\) is the intensity of the diffraction peak at 2θ = 22°, \(I_{am}\) is the intensity of the diffraction intensity minimum at about 2θ = 18°. The crystallinity of CNF is 70.67%. With increasing PDA content, and the diffraction peak becomes wider, as shown in Fig. 2b. The crystallinity of 5% PDA/CNFs is 65.20%, which is not much different from that before modification, indicating that the modification of a small amount of PDA has little effect on the crystallinity of CNF. PDA is an amorphous polymer that contains a large number of hydroxyl groups. Some hydroxyl groups on the surface of CNFs are replaced by PDA, which affects the total crystallinity.

XPS was used to analyze the composition and chemical structures of the samples. The peaks of the unmodified CNFs, shown in Fig. 2c and Table 1, appear at 531.20 and 285.62 eV, corresponding to O\(_{1s}\) and C\(_{1s}\) in the sample, respectively (Wang et al. 2016a, b). After modification, the CNFs show a new peak at 399.85 eV, corresponding to N\(_{1s}\) (Nie et al. 2020). These results were further confirmed by the high-resolution carbon spectra of carbon (C\(_{1s}\)) and nitrogen (N\(_{1s}\)) and the distribution of chemical bonds. Figure 2d and e show four carbon bonds of the CNF films, namely, C–C/C–H (C1, 284.42 eV), C–O/C–O–OH (C2, 285.80 eV), O–C–O (C3, 286.45 eV), and O=\(O\)–C–O (C4, 287.83 eV). Compared to that in the CNF film, the proportion of carbon bonds in the PDA/CNFs film changed, and the proportion of O–C–O bonds increased from 25.90 to 37.52%, which is attributed to the dehydration condensation of hydroxyl groups of CNFs and the phenolic hydroxyl group of PDA connected by O–C–O bonds. Consistent with the conclusions reported in the literature, catechol in PDA tends to react with hydroxyl groups to cause dehydration and generate charge transfer. The increase in the number of O–C–O bonds suggested successful chemical grafting between the CNFs and PDA. In addition, as shown in the high-resolution nitrogen spectrum of N\(_{1s}\) (Fig. 2f), new peaks appeared at 398.58 and 399.50 eV, corresponding to primary and secondary amines,
respectively. These results strongly confirm the successful modification of the CNFs.

Figure 2g–i and Fig. S3 show the surface roughness of the CNF films before and after modifications. The roughness of the PDA/CNFs films increased significantly, corresponding to the structure of the composite film in Fig. 1e, and the introduction of micro/nanostructures increased the effective contact area of the films. Fan et al. (2012) confirmed the enhancement of the nano/microstructure on the electrical output performance of TENGs. They concluded that the enhancement of structured films is due to the larger effective friction area of the surface with complex structures, which can generate more surface charges during friction.

Electrical characterization of hybrid PDA/CNF film-based TENGs

As a typical contact-separation TENG, the working principle of the PDA/CNF-TENGs is the coupling of electrification and electrostatic induction. In TENG operation, the potential difference between the material surfaces determines the triboelectric charge density of the materials (Diaz 2004). Because the potential of organic substances mainly depends on the electronic affinity of their functional groups, chemical functionalization is an important way to adjust the potential of the material surface. The amino group, as a strong electron-donating functional group, has proven to be an effective and direct method to improve the triboelectric properties of materials (Nie
et al. 2020; Wang et al. 2016a, b; Zhang et al. 2019). As shown in Fig. 3b, when the two triboelectric layers of the PDA/CNFs and FEP films were not in contact, there was no charge on the electrode surface. When the two triboelectric layers were in contact with each other, the surface of the PDA/CNFs film induced a positive electrostatic charge, whereas the FEP film induced a negative electrostatic charge. Because FEP has a strong electron capture ability and the NH functional group has a strong positive induction, the PDA/CNFs film provides electrons to FEP during contact, as shown in Fig. 3a. Once the two triboelectric layers are separated, a potential difference appears between them. Electrons are driven from the upper electrode to the lower electrode to balance the potential difference. When the two layers reach a certain distance, the electrons stop flowing and reach an equilibrium. Subsequently, the PDA/CNFs and FEP films squeeze each other, resulting in electrons returning from the lower electrode to the upper electrode, thus balancing the electric field. The aforementioned steps constitute the motion cycle.

The triboelectric output performance of TENGs mainly depends on the friction material. To determine the best concentration and thickness of the PDA/CNFs film to obtain the best output performance, a series of PDA/CNFs films with different concentrations (wt.% = 1.0–5.0%) and thicknesses (50–80 μm) were prepared. Using FEP as the negative triboelectric layer, the PDA/CNFs films (4.0 cm × 4.0 cm, 60 μm) were tested at an operating frequency of 2 Hz and a working pressure of 30 kPa. Figures 3c–d, the output values for the open-circuit voltage and short-circuit current of the pure CNF-TENGs were 64 V and 2.5 μA, respectively. The triboelectric properties of the PDA/CNF-TENGs were significantly improved, and the maximum output values for \( V_{oc} \) and \( I_{sc} \) of 4.0% PDA/CNFs reached 185 V (a 189% increase) and 15.7 μA (a 528% increase), respectively. When the thickness increases, the surface charge of the PDA/CNFs film increases, and the output performance increased with increasing film thickness. With a further increase in film thickness, the performance decreases, which may be the result of the weakening
of electrostatic induction between the friction layer and the conductive electrode (Han et al. 2020).

As a promising power source for electronic devices, it is necessary to evaluate the triboelectric properties of PDA/CNF-TENGs (4 cm × 4 cm, 4% PDA, 60 μm) under different working conditions. The working conditions include changes in the operating frequency, pressure and relative humidity. As shown in Fig. 4a, when the working pressure between the two electrodes increases from 1 to 50 kPa, $V_{oc}$ increases from 10 to 152 V. Figure 4b shows the functional relationship between pressure and output voltage, indicating that the material has good pressure response characteristics.

In the working mechanism of vertical contact separation mode, the open circuit voltage can be expressed as the following formula (Niu et al. 2013):

$$ V_{oc} = \frac{\sigma_0 d_0}{\varepsilon_0} \tag{4} $$

where $d_0$ is the distance between the two triboelectric layers of the TENG, $\sigma_0$ is the surface charge density of the triboelectric layer, and $\varepsilon_0$ is the vacuum permittivity. Sensitivity, as an important parameter for evaluating sensor performance, is defined as follows (Chen et al. 2020; Lei et al. 2021):

$$ S = \frac{\partial V}{\partial P} \tag{5} $$
where $\Delta V_{oc}$ is the change in open circuit voltage with pressure change $\Delta P$. According to Hooke’s law, the sensitivity can also be expressed as follows:

$$S = \frac{\Delta V_{oc}}{\Delta P}$$

(6)

Among them, $Y$ is the Young’s modulus between the triboelectric layers. It can be seen from the above formula that the sensitivity $S$ is positively related to $d_0/Y$. In the experiment, $d_0$ is set as a constant, and a lower Young’s modulus can obtain higher sensitivity (Lei et al. 2022).

TENG’s output voltage increases with applied pressure, as shown in Fig. 4b, with pressure sensitivity of 3.47 mV Pa$^{-1}$ (in the pressure range of 0–30 kPa) and 0.605 mV Pa$^{-1}$ (in the pressure range of 30–100 kPa) (Lei et al. 2022).

Table 1

| Sample     | C1s (%) | O1s (%) | N1s (%) | O/C (%) |
|------------|---------|---------|---------|---------|
| CNFs       | 64.79   | 35.21   | 0       | 54.34   |
| PDA-CNFS   | 62.18   | 33.60   | 4.22    | 54.37   |

Fig. 5 Output current and voltage (a) and output power density (b) under different load resistances. c Comparison of output performance between the PDA/CNF-TENGs and CNF-based TENGs. d PDA/CNF-TENGs charge time of commercial capacitors. e Circuit schematic and images of the LEDs manually powered using a PDA/CNF-TENGs. f Performance stability of the PDA/CNF-TENGs in 2000 press-release cycles.
range of 30–50 kPa). This is because PDA endows the CNFs with rough nanostructures on the surface. When the working pressure is small, the rough surface prevents close contact with the FEP film. With an increase in the working pressure, the PDA/CNFs film deforms slightly and fills the gap with the FEP film, increasing the contact area and thus improving the output performance of the TENG (He et al. 2018; Mi et al. 2018). The good pressure response properties indicate that the material has great potential for pressure sensing.

As shown in Fig. 4c–e, when the working frequency of the relative contact separation movement between the two electrodes increased from 1 to 2.5 Hz, $V_{oc}$ increased from 166 to 205 V, $I_{sc}$ increased from 7.6 to 20.0 μA, and $Q_{sc}$ increased from 4.1 to 5.2 nC cm$^{-2}$. The output performance of the TENG was positively correlated with the operating frequency. This is because at different operating frequencies, the charge transfer rate increases at higher frequencies, which makes the external electrons reach the flow balance faster, shortens the duration of the current peak, and leads to an increase in the short-circuit current. As shown in Fig. 4f–h, with increasing relative humidity, the output performance of the PDA/CNF-TENGs decreased to varying degrees. When the relative humidity increases from 60 to 90%, the $V_{oc}$ of the TENG decreases from 180 to 50 V, and the variation trends of $I_{sc}$ and $Q_{sc}$ are similar to that of voltage. PDA/CNFs contain hydrophilic OH groups. Thus, with the increase in relative humidity, water molecules will be physically adsorbed on hydroxyl groups through single hydrogen bonds, forming a barrier layer on the surface of the material that hinders the formation of induced charges (Bi et al. 2013), which leads to a sharp decline in the output performance of the PDA/CNF-TENGs at high humidity.

To investigate the relationship between the output performance and load resistance, impedance matching was performed at a load resistance of 1000 Ω to 80 GΩ. When the PDA/CNF-TENGs was connected to an external load, the open-circuit voltage increased with increasing load resistance, and the short-circuit current decreased with increasing load resistance (Fig. 5a). The output power density of the equipment is calculated using the following formula:

$$P = \frac{U^2}{RA}$$ (7)

where $P$ is the power, $U$ is the output voltage, $A$ is the contact area and $R$ is the external load resistance.

We then plotted the dependence of the power density on the external load (Fig. 5b). The maximum power density (48.75 μW cm$^{-2}$) was achieved with a load resistance of 10 MΩ, which is sufficient to power many portable or wearable electronic devices. Compared with other CNF-based TENGs, the PDA/CNF-TENGs exhibited a good output performance. A comparison of the output performance

| Positive materials | Negative materials | Current (μA/cm²) | Power density (μW/cm²) | Applications | References |
|--------------------|--------------------|-----------------|------------------------|--------------|------------|
| CNF-phosphorene    | PET                | 1.8             | 1.06                   | Energy harvesting | Cui et al. (2017) |
| PA                 | PFOTES-CNF         | 0.58            | 1.35                   | Energy harvesting | Nie et al. (2021) |
| Alc-S$_2$-CNF      | PVDF               | 1.28            | 18.2                   | Energy harvesting | Roy et al. (2020) |
| AEAPDMS-CNF        | FEP                | 0.84            | 22                     | Self-powered sensing | Nie et al. (2020) |
| CNF-PEI/Ag         | FEP                | 0.25            | 43                     | Self-powered sensing | Zhang et al. (2019) |
| CMF-CNf            | FEP                | 0.73            | 7.68                   | Self-powered sensing | He et al. (2018) |
| EDA-paper          | FEP                | 0.12            | 13.78                  | Energy harvesting | Sheng et al. (2022) |
| CA-PEI             | LTV                | 6.3             | 0.221                  | Monitoring human motion | Bai et al. (2020) |
| Regenerated cellulose | PVDF              | 0.3             | 12.7                   | Monitoring human motion | Zhang et al. (2020a, b) |
| CNF                | PDMS               | 0.09            | 2.9                    | Self-powered sensing | Qian et al. (2019) |
| Paper              | PCL/GO             | 0.25            | 7.25                   | Eco-friendly power sources | Parandeh et al. (2019) |
| PDA-CNF            | FEP                | 1.25            | 48.75                  | Monitoring human motion | This study |
of the CNF-based TENG is presented in Table 2 and Fig. 5c. We used capacitors of different capacities to store electrical energy, as shown in Fig. 5d. Small capacitors (1 μF (50 V), 2.2 μF (50 V), and 4.7 μF (50 V)) can be charged to 2.5 V in 100 s, while the charging speed decreases with increasing capacitor size (22 μF (25 V), 47 μF (25 V), and 100 μF (50 V)). TENGs can collect energy from various types of mechanical movement. As a demonstration, our equipment was used to supply power to LEDs, and 158 LED bulbs were successfully lit (Fig. 5e). As shown in Fig. 5f, the equipment showed good cycling stability and maintained approximately 99% of its initial value after 10,000 consecutive cycles.

Application for human motion detection

Cellulose has a lot of potential for use in flexible sensing devices because it is an inexpensive, sustainable, degradable, and renewable material (Han et al. 2020). PDA/CNF-TENGs can generate different electrical signals under different external forces, so PDA/CNF-TENGs have great application potential in pressure sensing. In addition, compared with sensors based on capacitive or piezoresistive principles (Duan et al. 2021), PDA/CNF-TENGs do not require an external power supply to provide energy and conduct sensing in a self-powered manner (Tai et al. 2020). Various human motions are detected by attaching a PDA/CNF-TENGs to different body parts for biomechanical motion energy harvesting in a self-powered manner. The fabrication of PDA/CNF-TENGs as a wearable sensing device is depicted in Fig. 6a–b. When the sensor is compressed, it generates a pulse signal, which disappears when it is relaxed, forming a cycle, and the pulse signal is consistent with the frequency of the actual movement, as shown in Fig. 6c. The electrical signals of connecting the TENG to the hand to monitor clapping (contact area 4 cm × 4 cm) and finger clicking (contact area 1 cm × 1 cm) are shown in Fig. 6d–e, and their output voltages were approximately 100 V and 15 V, respectively. The
output voltage versus time for skipping and walking when the TENG was attached to the sole of the foot is shown in Fig. 6f–g. The output voltage shows a regular rhythm when walking and jumping. Because when the foot touches the ground and lifts the foot, the two friction layers are contacted and separated, forming a regular output voltage signal. Voltage sinks during running are stable with repetitive signals. It is worth noting that the voltage response is synchronized with low frequency and high frequency. Specifically, the output voltage also exhibits stable, repeatable, and recoverable signals when monitoring various human motions, indicating great potential in wearable electronics.

Conclusions

CNFs were modified with PDA, and a new CNF-based triboelectric layer was successfully prepared. When it was used as a triboelectric pair with an FEP layer, it exhibited excellent triboelectric output performance. The results showed that the 4% PDA/CNF-TENGs generated a significant output power density (48.75 μW cm$^{-2}$), open-circuit voltage as high as 205 V, and short-circuit current of 20 μA. The main reasons for the improvement in the triboelectric output performance are as follows: (1) PDA contains many amino and imine groups, which can increase the surface polarity and surface charge density of the CNF films; (2) the surface of the PDA/CNFs film has a micro/nanostructure, which can provide a larger contact area and more energy collection points. For a size of 4 cm x 4 cm, the 4.0% PDA/CNF-TENGs can manually light 158 LEDs. We also successfully simulated the human motion state when the self-powered biomechanical sensor of the PDA/CNF-TENGs was installed and collected its environmental energy, showing the potential prospects of cellulose materials for TENGs and other electronic applications.

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Declarations

Conflict of interest  The authors declare that they have no conflict of interest.

References

Bai Z, Zhang Z, Li J, Guo J (2019) Textile-based triboelectric nanogenerators with high-performance via optimized functional elastomer composites tribomaterials as wearable power source. Nano Energy 65:104012
Bai Z, Xu Y, Zhang Z, Zhu J, Gao C, Zhang Y, Jia H, Guo J (2020) Highly flexible, porous electroactive biocomposite as attractive tribopositive material for advancing high-performance triboelectric nanogenerator. Nano Energy 75:104884
Bi H, Yin K, Xie X, Ji J, Wan S, Sun L, Terrones M, Dresselhaus MS (2013) Ultra-high humidity sensitivity of graphene oxide. Rep 3:2714
Chen S, Wu N, Lin S, Duan J, Xu Z, Pan Y, Zhang H, Xu Z, Huang L, Hu B, Zhou J (2020) Hierarchical elastomer tuned self-powered pressure sensor for wearable multifunctional cardiovascular electronics. Nano Energy 70:104460
Cheng D, He M, Ran J, Cai G, Wu J, Wang X (2018) In situ reduction of TiO2 nanoparticles on cotton fabrics through polydopamine templates for photocatalysis and UV protection. Cellulose 25(2):1413–1424
Cheng W, Zeng X, Chen H, Li Z, Zeng W, Mei L, Zhao Y (2019) Versatile polydopamine platforms: synthesis and promising applications for surface modification and advanced nanomedicine. ACS Nano 13(8):8537–8565
Cui P, Parida K, Lin M, Xiong J, Cai G, Lee PS (2017) Transparent, flexible cellulose nanofibril-phosphorene hybrid paper as triboelectric nanogenerator. Adv Mater Interfaces 4(22):1700651
Diaz AF, Felix-Navarro RM (2004) A semi-quantitative tribo-electric series for polymeric materials: the influence of chemical structure and properties. J Electrostat 62(4):277–290
Dong K, Deng J, Yi Z, Wang Y, Xu C, Zou H, Ding W, Dai Y, Gu B, Sun B, Wang ZL (2017) 3D orthogonal woven triboelectric nanogenerator for effective biomechanical energy harvesting and as self-powered active motion sensors. Adv Mater 29(38):1702648
Duan Z, Jiang Y, Huang Q, Wang S, Zhao Q, Zhang Y, Liu B, Yuan Z, Wang Y, Tai H (2021) Facilely constructed two-sided microstructure interfaces between electrodes and cellulose paper active layer: eco-friendly, low-cost and high-performance piezoresistive sensor. Cellulose 28(10):6389–6402
Fan F, Lin L, Zhu G, Wu W, Zhang R, Wang ZL (2012) Transparent triboelectric nanogenerators and self-powered pressure sensors based on micropatterned plastic films. Nano Lett 12(6):3109–3114
Guo H, Chen J, Wang L, Wang AC, Li Y, An C, He J, Hu C, Hsiao VKS, Wang ZL (2021) A highly efficient triboelectric negative air ion generator. Nat Sustain 4(2):147–153
Han Y, Han Y, Zhang X, Li L, Zhang C, Liu J, Lu G, Yu H, Huang W (2020) Fish Gelatin based triboelectric nanogenerator for harvesting biomechanical energy and self-powered sensing of human physiological signals. ACS Appl Mater Inter 12(14):16442–16450

He X, Zou H, Geng Z, Wang X, Ding W, Hu F, Zi Y, Xu C, Zhang SL, Yu H, Xu M, Zhang W, Lu C, Wang ZL (2018) A hierarchically nanostructured cellulose fiber-based triboelectric nanogenerator for self-powered healthcare products. Adv Funct Mater 28(45):1805540

Kaynak B, Sporek M, Shirole A, Ziegler W, Sapkota J (2018) Polypropylene/cellulose composites for material extrusion additive manufacturing. Macromol Mater Eng 303(5):1800037

Kim W, Yasmeen S, Nguyen CT, Lee H, Choi D (2021) Toward enhanced humidity stability of triboelectric mechanical sensors via atomic layer deposition. J Nanomater 11(7):1795

Lei H, Chen Y, Gao Z, Wen Z, Sun X (2021) Advances in self-powered triboelectric pressure sensors. J Mater Chem A 9(36):21–213

Lei H, Cao K, Chen Y, Liang Z, Wen Z, Jiang L, Sun X (2022) 3D-printed endoplasmic reticulum rGO microstructure based self-powered triboelectric pressure sensor. Chem Eng J 445:136821

Li L, Wang X, Zhu P, Li H, Wang F, Wu J (2020) The electron transfer mechanism between metal and amorphous polymers in humidity environment for triboelectric nanogenerator. Nano Energy 70:104476

Lin X, Wu Z, Zhang C, Liu S, Nie S (2018) Enzymatic pulping of lignocellulosic biomass. Ind Crop Prod 120:16–24

Liu R, Dai L, Si C (2018) Mussel-inspired cellulose-based nanocomposite fibers for adsorption and photocatalytic degradation. ACS Sustain Chem Eng 6(11):15756–15763

Mi H, Jing X, Zheng Q, Fang L, Huang H, Tung L, Gong S (2018) High-performance flexible triboelectric nanogenerator based on porous aerogels and electrospun nanofibers for energy harvesting and sensitive self-powered sensing. Nano Energy 48:327–336

Nie S, Cai C, Lin X, Zhang C, Lu Y, Mo J, Wang S (2020) Chemically functionalized cellulose nanofibrils for improving triboelectric charge density of a triboelectric nanogenerator. ACS Sustain Chem Eng 8(50):18678–18685

Nie S, Fu Q, Lin X, Zhang C, Lu Y, Wang S (2021) Enhanced performance of a cellulose nanofibrils-based triboelectric nanogenerator by tuning the surface polarizability and hydrophobicity. Chem Eng J 404:126512

Niu S, Wang S, Lin L, Liu Y, Zhou YS, Hu Y, Wang ZL (2013) Theoretical study of contact-mode triboelectric nanogenerators as an effective power source. Energ Environ Sci 6(12):3576

Niu Z, Cheng W, Cao M, Wang D, Wang Q, Han J, Long Y, Han G (2021) Recent advances in cellulose-based flexible triboelectric nanogenerators. Nano Energy 87:106175

Parandeh S, Kharazisha M, Karimzadeh F (2019) An eco-friendly triboelectric hybrid nanogenerators based on graphene oxide incorporated polycaprolactone fibers and cellulose paper. Nano Energy 59:412–421

Qian C, Li L, Gao M, Yang H, Cai Z, Chen B, Xiang Z, Zhang Z, Song Y (2019) All-printed 3D hierarchically structured cellulose aerogel based triboelectric nanogenerator for multi-functional sensors. Nano Energy 63:103885

Qin Z, Liu W, Chen H, Chen J, Wang H, Song Z (2019) Preparing photocatalytic paper with improved catalytic activity by in situ loading poly-dopamine on cellulose fibre. B Mater Sci 42(2):1–6

Roy S, Ko H, Mapi JK, Van Hai L, Kim J (2020) Large amplification of triboelectric property by allylic to develop high performance cellulose triboelectric nanogenerator. Chem Eng J 385:123723

Segal L, Creely J, Martin AE, Conrad CM (1959) An empirical method for estimating the degree of crystallinity of native cellulose using the x-ray diffractometer. Text Res J 29(10):786–794

Sheng Z, Quxiao Z, Tingting W, Xuchong W, Xiaoping S, Yuhe W, Lianxin L (2022) Contact electrification property controlled by amino modification of cellulose fibers. Cellulose 29(6):3195–3208

Shi X, Chen S, Zhang H, Jiang J, Ma Z, Gong S (2019) Portable self-charging power system via integration of a flexible paper-based triboelectric nanogenerator and supercapacitor. ACS Sustain Chem Eng 7(22):18657–18666

Sriphan S, Charoosuk T, Maluagnont T, Pakawanit P, Rojviriya C, Vittayakorn N (2020) Multifunctional nanomaterials modification of cellulose paper for efficient triboelectric nanogenerators. Adv Mater Technol 5(5):2000001

Su Y, Zhao Y, Zhang H, Feng X, Shi L, Fang J (2017) Polydopamine functionalized transparent conductive cellulose nanopaper with long-term durability. J Mater Chem C 5(3):573–581

Sun Q, Wang L, Yue X, Zhang L, Ren G, Li D, Wang H, Han Y, Xiao L, Lu G, Yu H, Huang W (2021) Fully sustainable and high-performance fish gelatin-based triboelectric nanogenerator for wearable movement sensing and human-machine interaction. Nano Energy 89:106329

Tai H, Duan Z, Wang Y, Wang S, Jiang Y (2020) Paper-based sensors for gas, humidity, and strain detections: a review. ACS Appl Mater Inter 12(28):31037–31053

Wang J, Li S, Yi F, Zi Y, Lin J, Wang X, Xu Y, Wang ZL (2016a) Sustainably powering wearable electronics solely by biomechanical energy. Nat Commun 7:12744

Wang S, Zi Y, Zhou YS, Li S, Fan F, Lin L, Wang ZL (2016b) Molecular surface functionalization to enhance the power output of triboelectric nanogenerators. J Mater Chem A 4(10):3728–3734

Wang R, Gao S, Yang Z, Li Y, Chen W, Wu B, Wu W (2018) Engineered and laser-processed chitosan biopolymers for sustainable and biodegradable triboelectric power generation. Adv Mater 30(11):1706267

Wu C, Wang AC, Ding W, Guo H, Wang ZL (2019) Triboelectric nanogenerator: a foundation of the energy for the New Era. Adv Energy Mater 9(1):1802906

Xu Z, Miyazaki K, Hori T (2016) Fabrication of polydopamine-coated superhydrophobic fabrics for oil/water separation and self-cleaning. Appl Surf Sci 370:243–251

Yan L, Song Y, Zhou Y, Song B, Li Y (2015) Effect of PEI cathode interlayer on work function and interface resistance of ITO electrode in the inverted polymer solar cells. Org Electron 17:94–101
Yang L, Chen C, Hu Y, Wei F, Cui J, Zhao Y, Xu X, Chen X, Sun D (2020) Three-dimensional bacterial cellulose/polydopamine/TiO2 nanocomposite membrane with enhanced adsorption and photocatalytic degradation for dyes under ultraviolet-visible irradiation. J Colloid Interface Sci 562:21–28
Yang D, Ni Y, Kong X, Li S, Chen X, Zhang L, Wang ZL (2021) Self-healing and elastic triboelectric nanogenerators for muscle motion monitoring and photothermal treatment. ACS Nano 15(9):14653–14661
Yao C, Yin X, Yu Y, Cai Z, Wang X (2017) Chemically functionalized natural cellulose materials for effective triboelectric nanogenerator development. Adv Funct Mater 27(30):1700794
Yiming B, Han Y, Han Z, Zhang X, Li Y, Lian W, Zhang M, Yin J, Sun T, Wu Z, Li T, Fu J, Jia Z, Qu S (2021) A mechanically robust and versatile liquid-free ionic conductive elastomer. Adv Mater 33(11):2006111
Zhang C, Lin X, Zhang N, Lu Y, Wu Z, Liu G, Nie S (2019) Chemically functionalized cellulose nanofibrils-based gear-like triboelectric nanogenerator for energy harvesting and sensing. Nano Energy 66:104126
Zhang L, Liao Y, Wang YC, Zhang S, Yang W, Pan X, Wang ZL (2020a) Cellulose II aerogel-based triboelectric nanogenerator. Adv Funct Mater 30(28):2001763
Zhang R, Dahlström C, Zou H, Jonzon J, Hummelgård M, Örtegren J, Blomquist N, Yang Y, Andersson H, Olsen M, Norgren M, Olin H, Wang ZL (2020b) Cellulose-based fully green triboelectric nanogenerators with output power density of 300 W m^-2. Adv Mater 32(38):2002824
Zhang C, Mo J, Fu Q, Liu Y, Wang S, Nie S (2021) Wood-cellulose-fiber-based functional materials for triboelectric nanogenerators. Nano Energy 81:105637
Zhang Z, Liu W, Lv B, Ju T, Ji J (2022) Gas-driven shearing nanonization of lignin particles for efficient reduction of graphene oxide. Ind Crop Prod 180:114665
Zhao P, Qin N, Ren CL, Wen JZ (2019) Surface modification of polyamide meshes and nonwoven fabrics by plasma etching and a PDA/cellulose coating for oil/water separation. Appl Surf Sci 481:883–891

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