Research on Controlling Contact Electrification by Modification of Cellulose Molecule Surface with Amino Group

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Abstract

As a green material, cellulose is widely used in friction triboelectric nanogenerators (TENGs). However, the weak polarity of the cellulose surface leads to its weak contact electrification performance, which is not conducive to its utilization in TENGs. In this study, epoxy chloropropane and ethylenediamine were grafted onto cellulose to form paper and were assembled with an FEP film. The output voltage, current, and surface charge density were 34.9%, 26.7%, and 16.7% higher than those of ordinary paper, respectively. When 20% nano TiO$_2$ filler was added to the paper made from amino-modified cellulose, the output voltage, current, and surface charge density of the TENG increased by 70.9%, 226.7%, and 122.2%, respectively, compared with ordinary paper. As the air humidity of the TENG increased from 60% to 90%, the output voltage, current, and surface charge density were maintained at 53.7%, 38.9%, and 61.0%, respectively. When a $5 \times 10^7$ $\Omega$ resistor was connected to the working circuit, its output power reached 13.78 $\mu$W·cm$^2$. This showed that cellulose as a green material has wide application prospects in the field of TENG.

Introduction

A triboelectric nanogenerator (TENG) is an effective method for obtaining environmental mechanical energy. In 2012, Wang first proposed the concept of a TENG and realized the effective harnessing and conversion of triboelectric power. To date, TENGs have been widely studied (Niu et al., 2013; Wang & Wu, 2012; Zhu et al., 2013b). The cathode materials commonly used in TENG friction layers mainly include metals, metal oxides, and polyamides (Yang et al., 2013; Yilin et al., 2019; Zhao et al., 2016). However, metal materials are easily oxidized or corroded under harsh environmental conditions, and this affects the operational stability of TENG systems. Furthermore, most synthetic polymers are nonrenewable and nonbiodegradable. The long-term use of such triboelectric materials can easily cause environmental problems, such as white pollution (Ma et al., 2018; Niu & Wang, 2015; Wu et al., 2019). Therefore, the introduction of new environmentally friendly materials is a new trend for TENGs in the future. The development of green friction electrode materials is challenging to optimize their performance. In recent years, natural fiber materials, paper-based materials, and materials derived from lignocellulose fibers have been increasingly used to prepare TENGs (Cao et al., 2020; Lai et al., 2019; Wu et al., 2016). Zhang coated a layer of indium tin oxide (ITO) on commercial printing paper to make ITO paper and FET film, which were used to assemble TENG. The short-circuit current density reportedly reached 2.0 mA/m$^2$ (Zhang et al., 2014). Xia used paper as an electrode substrate and polytetrafluoroethylene (PTFE) tape to prepare a paper-based TENG, working in sliding mode through origami technology. The corresponding maximum open circuit voltage was observed to have reached nearly 1000 V (Xia et al., 2018).

The output performance of the TENG was related to the surface charge density of the friction materials, and the surface charge density was, in turn, related to the difficulty of gaining and losing electrons from friction materials. The easier it is for the materials to gain and lose electrons, the greater the surface
charge density (He et al., 2015). Cellulose has an almost neutral relative polarity based on its chemical molecular formula and is in a positive position in the triboelectric material series (Zhu et al., 2016; Zi et al., 2016). The weak polarization of natural cellulose leads to its limited ability to generate surface charge, and this makes its performance much lower than that of synthetic polymers. At present, research on improving the properties of lignocellulose-based TENGs has mainly focused on improving the surface charge density by changing the material composition and increasing the effective contact area.

Based on the good chemical modification of lignocellulose fibers (Roy et al., 2009), the friction polarity was enhanced by changing the functional groups on the surface of lignocellulose fiber materials, such as introducing different functional groups (such as nitro, amino, and methyl) to improve its charge capture ability (Mi et al., 2018a; Yao et al., 2017). Mi prepared polyethyleneimine-modified cellulose nanofiber (CNF) to prepare aerogels, which not only enhanced the mechanical properties of CNF/PEI aerogels, but also increased the power density by 14.4 times due to the increase in friction polarity (Mi et al., 2018a). Nie used triethoxy-1H, 1H, 2H, 2H-tetradecfluoro-N-octylsilane (PFOTES) to modify the surface of CNF, so that the output current of the PFOTES-CN Fib-based TENG was approximately twice that of the CNF-based TENG (Nie et al., 2021). Adding filler in the papermaking process could increase the contact area between the paper and another electrode owing to the existence of the filler, thus improving the performance of the TENG (Cuncun et al., 2019; Mi et al., 2018b). Ding used a porous polydimethylsiloxane (PDMS) film doped with carbon nanotubes (CNTs) and aluminum sheets as electrodes to assemble TENG. The output voltage was reported to be 16 times that of TENG using a PDMS film (Xiaoheng et al., 2018).

In this study, ethylenediamine (EDA) was used to modify the molecular surface of cellulose, and an amino group with electron-donating ability was introduced into the cellulose to improve the charge density on the surface of cellulose. The modification of cellulose could be characterized by techniques such as Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). To test the contact electrification performance of cellulose, the modified cellulose was made into paper (nano TiO2 particles were added as papermaking filler), and TENG was then assembled with FEP film and measured using an electrometer.

**Experimental**

1. **Raw materials and reagents**

The raw cellulose used was eucalyptus cellulose (Nanning, China). Chemical reagents such as sodium hydroxide, epichlorohydrin (EPI), EDA, and sodium bicarbonate were all analytically pure and purchased from Tianjin Zhiyuan Chemical Reagent. TiO2 nanoparticles were purchased from Beijing Deke Daojin Technology Co., Ltd. (Beijing, China). An acrylic board was purchased from Yafan Plastic Trading Co., Ltd. (Foshan, China), conductive double-sided tape was purchased from Jufu Technology Co., Ltd. (Shenzhen, China), and FEP film was purchased from Jiahe Plastic Technology Co., Ltd. (Taizhou, China).

2. **Amino modification of cellulose**
First, 1 g of cellulose was weighed and transferred into a 100 mL conical flask. Then, 50 mL of 0.1 mol/l NaOH solution and 5 mL epichlorohydrin were added and stirred in a constant temperature water bath (50 °C) at 160 r/min for 6 h. After the reaction, the product obtained was epoxidized cellulose (EPI cellulose). Subsequently, 1 g of EPI-cellulose was weighed and transferred to a 500 mL conical flask. Next, 200 mL of ethylenediamine solution, with a volume concentration of 25%, and 3 g NaHCO₃ were added, and the reaction was oscillated in a constant temperature water bath at 75 °C for 7 h. After the reaction, the product obtained by suction filtration was an amino cellulose (EDA-cellulose).

3. Preparation of paper and EDA paper

A quantity of 0.6 g of cellulose and 0.6 g of EDA-cellulose (nano TiO₂ particles with a mass fraction of 0–30% as papermaking filler) were weighed and placed in a 500 mL conical flask. Then, distilled water was added, the suspension was sonicated for 20 min, and then stirred at room temperature for 6 h. The vacuum suction filtration method was used for paper-making. The suspension with evenly dispersed cellulose was poured into a G5 sand core funnel with a microporous filter membrane (Zhang et al., 2019b). After suction filtration, the paper was dried in an automatic molding dryer (ESTANITHAAGE BBS-2, Germany) at 75 °C for 15 min to obtain dry paper and EDA paper.

4. Structure of TENG

The TENG device was assembled based on a traditional vertical contact separation mode. A transparent acrylic plate was used as the supporting material for the device. The overall height of the acrylic plate was 5.8 mm, and the size was 7 cm × 7 cm. A raised structure in the middle of the plate measured 0.8 mm in height and 4 cm × 4 cm in size. Paper and EDA-paper were used as the anode electrode materials and FEP film was used as the cathode electrode material. The electrode material was cut to a size of 4 cm × 4 cm, fixed on the acrylic plate with double-sided conductive tape, and a part of the conductive double-sided tape, on one side, was used to fix the copper conductor.

5. Characterization

Scanning electron microscopy (SEM) (Hitachi su8020, Japan) was used to observe the morphology and surface elemental distribution of cellulose before and after amino modification. The samples were sprayed with gold prior to the observation. Atomic force microscopy (AFM) (Hitachi 5100n Japan) was used to observe the roughness of the fiber surface. FTIR (Vertes 70, Germany) was used to analyze the changes in the molecular structure of cellulose before and after amino modification. The scanning range of the test wave number was 4000–400 cm⁻¹. XPS (Kratos Axis Ultra DLD, UK) was used to analyze the types and contents of the surface elements before and after cellulose modification. XRD (Smartlab 3KW, Japan) was used to determine the change in the crystallinity of cellulose before and after amino
modification. The crystallinity (CRI) was calculated according to Segal method (C.J. Segal, 1959), and equation (1) was an empirical method for calculating cellulose crystallinity:

\[
CRI(\%) = \frac{(I_{200} - I_{am})}{I_{200}} \times 100\% \tag{1}
\]

Where \(I_{200}\) is the intensity of the diffraction peak at \(2\theta = 22^\circ\), \(I_{am}\) is the intensity of the diffraction peak at \(2\theta = 18^\circ\).

Through a vibration exciter (jzk-10, China) and tubular linear motor (Linmot h10-70×240/210, US), the TENG was periodically subjected to a certain frequency and pressure. The generated electrical signal was captured using an electrometer (Keithley 6514, US) and an acquisition card (Ni usb-6259, USA).

**Results And Discussion**

1. **Characterization of cellulose**

FTIR could provide quantitative and semi-quantitative information, indicating the existence and absence of functional groups of lignocellulose before and after treatment. In addition, the change in peak strength could also indicate the change in functional group content. Figs. 3a and b show the FTIR spectra at 4000–500 cm\(^{-1}\) and 1200–800 cm\(^{-1}\) before and after cellulose modification. As shown in Fig. 3a, EPI- and EDA-cellulose retained the absorption peak of cellulose. After the cellulose was treated with epichlorohydrin, a new functional group absorption peak appeared in the infrared spectrum of EPI-cellulose. As shown in Fig. 3b, the absorption peak at 1124 cm\(^{-1}\) corresponds to the antisymmetric stretching vibration of C-O-C, and the absorption peak at 1067 cm\(^{-1}\) is the symmetrical absorption peak of C-O-C (Muhammad et al., 2017). The epoxy group originated from epichlorohydrin, indicating that the epoxy group was introduced into the cellulose. After the EPI-cellulose was further treated with ethylenediamine, some new absorption peaks appeared in the infrared spectrum, of which the absorption peak at 1119 cm\(^{-1}\) is the stretching vibration peak of C-N, and the absorption peak at 830 cm\(^{-1}\) corresponds to the bending vibration peak of N-H. As shown in Fig. 3a, the absorption peak at 3168 cm\(^{-1}\) is the stretching vibration peak of N-H (Bo et al., 2009; Hattori et al., 2004; Musyoka et al., 2011), and these absorption peaks originate from the -NH\(_2\) of ethylenediamine. This shows that amino groups were introduced into the cellulose.

XRD can be used to determine the changes in the cellulose structure, crystal form, and crystallization degree. As shown in Fig. 4, the peaks at \(2\theta = 18^\circ\) and \(22^\circ\) are diffraction absorption peaks of cellulose in cellulose type I (French, 2014). The intensities of the diffraction peaks at \(2\theta = 18^\circ\) and \(22^\circ\) in EPI-cellulose weakened, and the crystallinity decreased from 84.36% to 82.20%. The decrease in crystallinity was due to the introduction of epichlorohydrin into cellulose and the reduction of the crystallization area. Furthermore, the intensity of \(2\theta = 18^\circ\) and \(22^\circ\) diffraction peaks further weakened, and the crystallinity decreased to 70.14%. These can be attributed to the epoxy group on the surface of cellulose being
replaced by ethylenediamine, and the crystalline region of cellulose being further destroyed, thus resulting in a decrease in crystallinity.

XPS can be used for quantitative and semi-quantitative analysis of the surface elements of the samples. As shown in Fig. 5a, the peaks of cellulose and EPI-cellulose appeared at 532.4 eV and 286.5 eV, corresponding to O1s and C1s, respectively, and a new peak of EDA-cellulose appeared at 399.6 eV, corresponding to N1s. The proportion of elements on the sample surface analyzed by XPS is shown in Table 1. Compared with cellulose, the C1s content of EDA-cellulose increased, and the O1s and O/C contents decreased. This was because epichlorohydrin was introduced into cellulose, but epichlorohydrin introduced both C and O elements; hence, the proportion of elements on the sample surface changed slightly. N was detected on the surface of the EDA-cellulose. At the same time, the content of C1s continued to increase, and the contents of O1s and O/C continued to decrease. This was because ethylenediamine destroyed the epoxy group of epichlorohydrin, grafted to the sample surface, and introduced a large amount of C (Junka et al., 2014; Nie et al., 2020).

| Sample       | C1s (%) | O1s (%) | N1s (%) | O/C (%) |
|--------------|---------|---------|---------|---------|
| Cellulose    | 55.72   | 44.28   | 0       | 79.47   |
| EPI-Cellulose| 56.18   | 43.82   | 0       | 77.96   |
| EDA-Cellulose| 60.85   | 37.19   | 1.96    | 61.09   |

2. Surface topography

The SEM image of the cellulose is shown in Fig. 7. Before modification, the cellulose surface was smooth, without significant folds and a compact structure. After modification with epichlorohydrin and ethylenediamine, the cellulose surface became rough, wrinkled, and loose. Simultaneously, the cellulose began to break, and the specific surface area increased. This showed that after modification, the main chain of the cellulose was destroyed, the chain length became shorter, and the amorphous region was degraded. At the same time, when the nano TiO$_2$ particle filler (with 5% mass fraction of EDA-cellulose in papermaking) was added, the distribution of nano-TiO2 particles could be seen between the cellulose fibers. As shown in Fig. 6, the RMS value of paper after modification increased from 52.24 nm to 76.83 nm. After adding the nano-TiO$_2$ particle filler, the RMS value of EDA-paper/5% TiO$_2$ further increased to 97.63 nm.

3. Output performance of TENG

The working principle of the vertical contact separation TENG is shown in Figs. 8a–d. In the initial state, electrodes I and II were in contact with each other. Because of the contact electrification effect, the
electrons of electrode I were transferred to the surface of electrode II, such that the surface of electrode II was negatively charged and the surface of electrode I was positively charged. When the two electrodes were separated, a potential difference was generated, and electrons flowed from electrode II to electrode I, thus generating a positive instantaneous current. When the electrode contacted again, the potential of electrode II would be higher than that of electrode I, and the electrons would move from electrode II to electrode I to produce a reverse instantaneous current. When the two electrodes circulate for contact-separation movement, the TENG can carry out continuous electrical energy output (Gong et al.).

To explore the effect of amino modification on the contact electrification performance of cellulose, paper-based TENG and EDA-paper-based TENG were used as experimental objects. In addition, periodic contact-separation movement was carried out for the two electrodes of TENG, with an acceleration of 0.5 m/s², by a linear motor. As shown in Fig. 9, the open-circuit voltage of the paper-based TENG was 86 V and the short circuit current was 1.5 μA. The charge density was 1.8 nC·cm⁻², the open circuit voltage of EDA-paper based TENG increased from 86 V to 116 V, by 34.9%, and the short circuit current increased from 1.5 μA to 1.9 μA, by 26.7%. The charge density increased from 1.8 nC·cm⁻² to 2.1 nC·cm⁻²—an increase of 16.7%. This was because the amino group functioned as an electron source, which could improve the friction positive polarity of cellulose and improve the electrical output performance of the TENG (2015; Nie et al., 2021).

To explore the influence of the working frequency and contact pressure on the contact electrification performance of cellulose, the EDA-paper-based TENG was used as the experimental object, and the working frequency of the TENG was controlled by a linear motor. As shown in Figs. 10a–c, when the acceleration of relative contact-separation movement between two electrodes increased from 0.5 m/s² to 0.9 m/s², the open circuit voltage increased from 112 V to 123 V (a 9.8% increase), and the closed-circuit current increased from 1.6 μA to 2.1 μA (a 31.3% increase). The charge density increased from 2.5 nC·cm⁻² to 3.1 nC·cm⁻², which translated to an increase of 24.0%. This was because, under the same contact pressure, a higher contact frequency could make the external electrons reach flow balance in a shorter time, shorten the duration of the current peak, and increase the short-circuit current (Shen et al., 2017). An exciter was used to control the contact pressure of the TENG. As shown in Figs. 10d–f, when the contact pressure between the two electrodes increased from 10 N to 50 N, the open circuit voltage increased from 58 V to 70 V, which is an increase of 20.7%. In addition, the closed-circuit current increased from 0.50 μA to 0.96 μA (an increase of 92.0%), and the charge density also increased from 1.5 nC·cm⁻² to 2.0 nC·cm⁻² (a 33.3% increase). This can be attributed to the surface of the EDA-paper being rougher. When the contact pressure was small, the rough surface prevented close contact with the FEP film. With the increase in contact pressure, EDA-paper deforms slightly and fills the gap with the FEP film, thereby increasing the contact area, and thus improving the output performance of the TENG (Zhang et al., 2019a; Zhu et al., 2013a).

The movement acceleration between the two electrodes of the TENG was fixed at 0.5 m/s², and the influence of humidity on the contact electrification performance of cellulose was studied by changing the
ambient air humidity. As shown in Fig. 11a and b, with an increase in air humidity, the output performance of the TENG decreased to varying degrees regardless of whether the cellulose was modified. When the air humidity increased from 60% to 90%, the open circuit voltage of EDA-paper-based TENG decreased from 109 V to 52 V, and the closed-circuit current decreased from 1.55 μA to 0.52 μA; they maintained levels of 47.7% and 33.6%, respectively. The output performance loss of the paper-based TENG was large. With the increase in air humidity, the open-circuit voltage decreased from 86 V to 28 V, and the closed-circuit current decreased from 1.26 μA to 0.18 μA. They maintained levels of 32.6% and 14.3%, respectively. After introducing amino groups into cellulose, the surface energy of EDA-paper was reduced, the hydrophobic performance was enhanced, the negative friction polarity of the friction nanogenerator was improved, and the influence of water vapor in air on the output performance of TENG was reduced.

Providing energy for external loads is the most common practical application of TENGs (Li et al., 2015; Mule et al., 2019). To explore the output performance of the EDA-paper-based TENG in the circuit, the TENG was connected to a variable resistance box, and its output performance in the range of $10^3$–$10^8$ Ω was tested under the condition that the motion acceleration between the two electrodes was 0.5 m/s². As can be observed from Figs. 11c and d, with the gradual increase in external resistance, the output voltage of TENG gradually increased, reaching a maximum value of 105 V at a resistance of $10^8$ Ω. Furthermore, the output current gradually decreased, and reached the minimum value of 0.28 μA at a resistance of $10^8$ Ω. The output power increased first and then decreased at a resistance of $8 \times 10^7$ Ω, reaching a maximum value of 0.63 μW·cm². With excellent output power, the EDA-paper-based TENG can be used to power small electronic devices. The output stability of the TENG is an important index for evaluating its practical application. The EDA-paper-based TENG was tested under the condition that the motion acceleration between the two electrodes was 0.5 m/s². The open-circuit voltage was tested after 10000 continuous cycles. As shown in Fig. 11e, the open-circuit voltage in the beginning and end stages of the test was stable at approximately 115 V, thus indicating that the EDA-paper-based TENG was stable and reliable in providing long-term power for electronic devices.

Different mass fractions of nano TiO$_2$ particles were added to the paper to test their output performances. As shown in Figs. 12a–c, the output performance was the best when the doping of TiO$_2$ was 20%. The corresponding open circuit voltage, closed-circuit current, and charge density were 147 V, 4.9 μA, and 4.0 nC·cm$^2$, respectively, which translate to increments of 26.7%, 157.9%, and 90.5%, respectively, compared to that before doping. The main reason was that after adding nano TiO$_2$ particles, some of them adhered to the surface of the paper. Under a certain pressure, the FEP surface would slightly deform to fill the space formed by nano TiO$_2$ particles, increase its contact area with the paper surface, and generate more surface charged during friction, thus improving the output performance of TENG. As shown in Fig. 10, the open circuit voltage, closed-circuit current, and charge density of EDA-paper/20% TiO$_2$-based TENG increased by 70.9%, 226.7%, and 122.2%, respectively, compared with paper-based TENG after amino modification and adding nano TiO$_2$ particles.
As shown in Fig. 12d, as the air humidity increased from 60% to 90%, the open circuit voltage of EDA-paper/20% TiO$_2$-based TENG decreased from 145 V to 78 V, the closed-circuit current decreased from 3.6 μA to 1.4 μA, and the charge density decreased from 4.1 nC·cm$^{-2}$ to 2.5 nC·cm$^{-2}$, and maintained the levels of 53.7%, 38.9%, and 61.0%, respectively. This was because the roughness of the paper surface increased, and the moisture resistance was enhanced. As shown in Figs. 13e and f, the TENG is connected to the resistance box. When the resistance increased from $10^3$ Ω to $10^8$ Ω, the output voltage of TENG continued to increase, reaching the maximum value of 161 V at $10^8$ Ω. In addition, the output current continued to decrease, and reached the minimum value of 0.26 μA at $10^8$ Ω. The output power first increased and then decreased at a resistance of $5 \times 10^7$ Ω, reaching a maximum of 13.78 μW·cm$^{-2}$.

**Conclusions**

The cellulose was treated with epichlorohydrin and ethylenediamine, and the amino group was introduced into the cellulose. This not only changed the surface polarity of the cellulose, but also made the fiber surface rougher, thereby improving the contact electrification performance of the cellulose. When making paper, nano TiO$_2$ particles were added as filler to slightly deform the FEP film under a certain pressure. This increased the friction area between the paper and FEP film. The open-circuit voltage, closed-circuit current, and charge density of the EDA-paper/20% TiO$_2$-based TENG reached 147 V and the closed-circuit current reaches 4.9 μA. The charge density reached 4.0 nC·cm$^{-2}$. When the resistance connected in the working circuit was $5 \times 10^7$ Ω, the output power reached 13.78 μW·cm$^{-2}$. This shows that cellulose has wide application prospects in the field of polymer replacement for TENG electrodes.

**Declarations**

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**Conflicts of Interest:** The authors declare no conflict of interest.

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Figures
Figure 1

Preparation of paper
Figure 2

(a) Schematic diagram of triboelectric nanogenerator (TENG) electrode; (b) Physical drawing of TENG electrode; (c) Scanning electron microscopy (SEM) image of EDA-paper; (d) TENG structure.
Figure 3

Fourier-transform infrared spectroscopy (FTIR) spectra of cellulose before and after modification: (a) 4000–500 cm\(^{-1}\); (b) 1200–800 cm\(^{-1}\)
Figure 4

X-ray diffraction (XRD) spectrum of cellulose before and after modification

| Samples          | CrI (%) |
|------------------|---------|
| Cellulose        | 84.36   |
| EPI-cellulose    | 82.20   |
| EDA-cellulose    | 70.14   |
Figure 5

(a) Full spectrum of XPS before and after cellulose modification; (b) C1s peak on cellulose surface; (c) C1s peaks on EPI-cellulose surface; (e) C1s peaks on EDA-cellulose surface; (f) N1s peak splitting on EDA-cellulose surface.

Figure 6

AFM image: (a) paper; (b) EDA-paper; (c) EDA-paper/5% TiO2
Figure 7

SEM images at different magnification: (a–b) cellulose; (c–d) EPI-cellulose; (e–f) EDA-cellulose; (g–h) EDA-paper/5% TiO₂

Figure 8

Structure and working principle of TENG
Figure 9

Output performance of paper-based TENG before and after cellulose modification (a) open circuit voltage; (b) closed-circuit current; (c) charge density.

Figure 10

Effect of frequency and pressure on TENG output performance
(a–b) Changes of open circuit voltage and closed-circuit current of EDA-paper-based TENG with air humidity; (c) Change of output voltage and current of TENG under external resistance; (d) Power output curve of TENG under external resistance; (e) Continuous electrical output performance of TENG under 10,000 cycle contact-separation

Figure 11
Figure 12

(a–b): Open circuit voltage, closed-circuit current, and charge density of paper-based TENG doped with different mass fractions of TiO2; (d–f): Change of electrical output performance of EDA-paper/20% TiO2-based TENG with air humidity, change of voltage and current under external resistance and power curve.