COMMUNICATION

Protein-based contact electrification and its uses for mechanical energy harvesting and humidity detecting

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Abstract
In recent years, the use of triboelectric nanogenerators (TENGs) has become an effective technique to harvest mechanical energy based on contact electrification and the electrostatic effect. However, the electric output of TENGs decreases in environments with high relative humidity (RH), which restricts their application. The reason for this phenomenon is that charge transfer in most TENGs occurs through an electron pathway. By using gelatin/glycerol and polytetrafluoroethylene (PTFE) as triboelectric layers to construct a biocompatible TENG, we found that the electric output of the TENG can be maintained or is even enhanced at higher RH. The hydration of amino groups in gelatin resulted in additional charges (mobile ions) on the triboelectric layers during the contact electrification process, consequently increasing the electric output of the TENG. The electric output generated from the TENG increased 2-fold when the RH was increased from 20% to 60%. By using genipin to react with the amino groups in gelatin, the formation of mobile ions was blocked and the measured charge density on the triboelectric layers decreased as the RH gradually increased. We also demonstrated that the change of electric output generated from the TENG could be applied as a tool to detect RH, exhibiting the superior stability and durability of the TENG. This study also leads to a fundamental understanding of the mechanism of contact electrification when using protein as the triboelectric layer.
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Introduction

Triboelectric nanogenerators (TENGs), which provide an effective technique to harvest mechanical energy from different sources in the environment (human motions [1-3], wind [4,5], water [6-9], etc.), were developed in 2012 [10] and have attracted the attention of the world. Based on contact electrification and electrostatic effects, four different modes of TENGs show potential, which includes vertical-contact mode [11], lateral-sliding mode [12], single-electrode mode [13], and non-contact mode [14]. Not only can they be used as power sources for self-powered sensors and systems, but TENGs themselves can directly function as self-powered nanosensors when grown as functional nanomaterials or used to modify the surfaces of probe molecules. For example, self-powered nanosensors based on TENG structures have been successfully developed for mercury ions [15], catechin molecules [16], temperature [17], humidity [18], and light [19] detection.

Most TENGs are only able to function in environments with low relative humidity (RH) because surface triboelectrification is generally decreased by the presence of adsorbed water molecules, which will largely restrict the applications of TENGs. The decrease in the electric output from these TENGs at a higher RH is due to the charge transfer during contact electrification, which follows an electron pathway. To overcome this problem, it is necessary to maintain/increase the charge density on the triboelectric layers when the TENG is operated at a higher RH. Because previous studies have reported that the transferred charges during contact electrification could be either electrons or ions [20,21], one possible approach is to design the TENG to have mobile ions as additional charges on the triboelectric layers.

In addition, biocompatible TENGs are also in high demand for applications in harvesting mechanical energy from human motion and as a power source for implanted sensors [22]. An implantable TENG that uses polydimethylsiloxane (PDMS) and gold as triboelectric layers has been developed to harvest energy from the breathing mechanism of a living rat [23]. Ethyl cellulose and polylactic acid have also been used as triboelectric materials for building a cost-effective and lightweight TENG [24]. However, a TENG that uses proteins as a triboelectric layer does not yet exist and the mechanism of contact electrification has not yet been studied. Protein is a natural polyelectrolyte that can dissociate into a fixed charged polymer chain and attract mobile ions upon hydrating. For example, protonic conduction in hydrated lysozyme was reported and successfully analyzed by using percolation theory [25]. Additionally, bovine serum albumin (BSA) has been applied as the gate dielectric material for organic field-effect transistors. It was shown that the capacitance could increase by approximately 24 times as the relative humidity (RH) increased from 50% to 70% [26].

In this paper, we used gelatin as the model protein to study protein-based contact electrification. Gelatin is a protein with cost-effective, flexible, non-toxic, bioreversible, and biodegradable characteristics, and it has been extensively applied in the fields of food additives [27], tissue engineering [28], and drug delivery [29] for many years. By using acid-treated gelatin and polytetrafluoroethylene (PTFE) as the triboelectric layer, we integrated a biocompatible TENG and studied its electric performance at different RH levels. At high RH, the hydration of gelatin caused the formation of protonated amino groups, which attracted hydroxide ions on the side chain. The hydroxide ions can become mobile ions that increase the surface charge density of triboelectric layers in the presence of a water bridge, changing the charge transfer from an electron-dominated gateway to an ion-dominated one. The effects of adding glycerol and genipin were also studied in order to strengthen the TENG when harvesting mechanical energy and verify the mechanism we proposed.

Experimental Section

Preparation of gelatin-based films

Three different gelatin-based films including pure gelatin film, gelatin/glycerol film, and crosslinked gelatin/glycerol film were prepared and compared their triboelectric properties. First, 4 g gelatin powder (type A, Sigma) was dissolved in 25 ml deionized water. This is for the preparation of pure gelatin film. Regarding the gelatin/glycerol film, different amounts of glycerol were added to the gelatin solution. The final glycerol concentrations were determined to be 0.13 M, 0.25 M, 0.38 M, and 0.5 M. By adding genipin to react with the amino groups in gelatin, crosslinked gelatin/glycerol film was formed.

Fabrication of the gelatin-based TENGs

First, polyethylene terephthalate (PET) was selected as the substrates. Then aluminum (thickness around 100 nm) was deposited on the two PET substrates by e-beam evaporator. The dimensions of PET substrate used in this paper were 3 cm × 3 cm. Two conducting wires were connected to the two aluminum electrodes as leads for subsequently electric measurements. The PTFE film and gelatin-based films were directly coating on the aluminum electrodes as triboelectric layers. Finally, the triboelectric layers were attached on a linear motor system for the electric measurements.

Characterization

A Bruker Dimension Icon Atomic Force Microscope (AFM) was used to measure the surface morphology and roughness of PTFE and gelatin-based films. For the measurement of electric outputs of gelatin-based TENGs, a programmable electrometer (Keithley Model 6514) and a low-noise current preamplifier (Stanford Research System Model SR570) were used. A Linmot linear motor system was applied to provide stable external force making gelatin-based films to contact with and separate from the PTFE film. The relative humidity was controlled by nitrogen gas and monitored by a commercial humidity sensor. Before the measurement, the charges on the surface of PTFE film and gelatin-based films were removed by isopropanol.
Results and discussion

The basic structure of the gelatin-based TENG is illustrated in Figure 1a. We used polyethylene terephthalate (PET) as the substrate due to its thin, transparent, and flexible properties. Al thin films (100 nm) were deposited on PET by an e-beam evaporator to form the conductive electrodes. Then, biocompatible PTFE and gelatin-based films were directly coated on the surfaces to create the triboelectric layers. Three different gelatin-based films, including pure gelatin film, gelatin/glycerol film, and crosslinked gelatin/glycerol film, were prepared, and their triboelectric properties were compared. Figure 1b-e show AFM images of PTFE and gelatin-based films. The surface roughness (root mean square, rms) of the PTFE film, pure gelatin film, gelatin/glycerol film, and crosslinked gelatin/glycerol film are 48.1 nm, 2.8 nm, 3.0 nm and 4.6 nm, respectively. These results clearly show that the gelatin-based films have a similar surface roughness.

The working mechanism of the gelatin-based TENG follows a hybrid effect of contact electrification and electrostatic induction, which is similar to that of conventional TENGs. The only difference between the gelatin-based TENG and a conventional TENG is the pathway of charge transfer during contact electrification, which will contribute to their different electric outputs at high RH. Figure 2 illustrates the electricity generation process of the gelatin-based TENG at low and high RH. The PET substrate is not shown to simplify the representation. At low RH (Figure 2a), the charge transfer of the gelatin-based TENG during contact electrification is dominated by electron transfer. Before contact of the gelatin with PTFE (i), there is no charge transfer. When the gelatin film is pressed to make contact with the PTFE film, electrons transfer from the gelatin film to the PTFE film due to their different triboelectric properties (ii). At low RH, some areas of the gelatin and PTFE films adsorb water, which reduces the charge density on the surfaces of the films. The result is the same as that in conventional TENGs. Once the gelatin film is separated from the PTFE film, an electric potential difference is established (iii). This drives electrons to flow through the external load from Al electrode 1 to Al electrode 2 to reach equilibrium (iv). When the gelatin film begins to make contact with the PTFE film again, the decrease of the gap distance will cause another potential difference with the opposite value (v). This time, electrons will transfer from Al electrode 2 to Al electrode 1.

When RH is high in gelatin-based TENGs, as shown in Figure 2b, the charge transfer of the gelatin-based TENG during contact electrification is dependent on both electron transfer and ion transfer. At high RH, the hydration of gelatin results in the formation of protonated amino groups (–NH\textsubscript{3}\textsuperscript{+}) and the attraction of hydroxide ions (OH\textsuperscript{-}) on the side chain (vi) (Figure S1). Thus, when the gelatin film is forced to make contact with the PTFE film, electrons and other ions will transfer from the gelatin film to the PTFE film (vii). The hydroxide ions can become mobile and increase the charge densities on the gelatin and PTFE films. For conventional TENGs, the increase of RH only leads to a decrease in charge density on the triboelectric layers and electric output. [18,30] Once the gelatin film is separated from the PTFE film, an enhanced electric potential difference compared to that at low RH is established (viii), which causes more electrons to flow through the external load from Al electrode 1 to Al electrode 2 to eventually achieve equilibrium (ix). Pressing the gelatin film to make contact with the PTFE film will lead to another electric output with the opposite value (x). The key factor for the transfer of mobile ions is...
the presence of a water bridge, which will be discussed later with the measured data. With regard to hydrophobic PTFE materials, it is generally accepted that approximately 2 monolayers of water adsorb on the surface at 80% RH. [31]

To systematically study the electric output of the gelatin-based TENG, a linear motor was applied to control the contact and separation of the PTFE and gelatin-based films. By selecting the PTFE film as one triboelectric layer, we first studied the electric outputs generated from TENGs using the pure gelatin film and the gelatin/glycerol film as the other triboelectric layer. Glycerol was added as a plasticizer to help increase the mechanical strength of the gelatin film and build a more compact TENG. [32] Induced charge density ($\Delta \sigma_{\text{ind}}$), open-circuit voltage ($V_{\text{oc}}$), and short-circuit current density ($J_{\text{sc}}$) were measured to clearly present the characteristics of the gelatin-based TENG. Figure 3a shows the measured $\Delta \sigma_{\text{ind}}$ from TENGs composed of different glycerol concentrations. The measured $\Delta \sigma_{\text{ind}}$ first increases from 8.4 $\mu$C m$^{-2}$ to 27.1 $\mu$C m$^{-2}$ as the glycerol concentration changes from 0 to 0.25 M and then decreases to 11.5 $\mu$C m$^{-2}$ when the glycerol concentration increases to 0.5 M. This tendency explicitly indicates that the charge density on the triboelectric layers is influenced by the presence of glycerol. Similar results were observed in the generated $V_{\text{oc}}$ (Figure 3b). The generated $V_{\text{oc}}$ increases from 7.9 V to 58.2 V as the glycerol concentration changes from 0 M to 0.25 M and then decreases to 15.3 V when the glycerol concentration increases to 0.5 M. From our perspective, two main factors result in the enhanced electric outputs when using higher concentrations of glycerol (from 0 to 0.25 M). The first is that the hydroxyl groups in glycerol are good electron donors and can increase the amount of transferred electrons during

Figure 2 Working mechanism of the gelatin-based TENG at (a) low and (b) high RH. At low RH, the charge transfer of gelatin-based TENG during contact electrification is dominated by electron transfer. The presence of water decreases the surface triboelectrification and charge density. At high RH, the charge transfer of the gelatin-based TENG during contact electrification changes to an ion-transfer dominated pathway. The formation of the water bridge aids in mobile ion transfer and increase the surface charge density.
The output voltage generated from an airflow-induced triboelectric nanogenerator (using PTFE and fluorne-doped tin oxide (FTO) as triboelectric layers) was observed to decrease from 36 V to 18 V when the RH increased from 20% to 100% [18]. However, for the system dominated by ion transfer, the water layer can act as a water bridge for mobile ions to move and then increase the charge density on the triboelectric layers. Figure 4 presents the $\Delta \sigma_{\text{ind}}$ from gelatin-based TENGs at different RH levels (from 20% to 80%). By using the pure gelatin film (Figure 4a) as the triboelectric layer, the $\Delta \sigma_{\text{ind}}$ first decreased from 12.3 $\mu$C m$^{-2}$ to 7.6 $\mu$C m$^{-2}$ as the RH changed from 20% to 50%. The $\Delta \sigma_{\text{ind}}$ then increased to 14.2 $\mu$C m$^{-2}$ when the RH was altered to 80%. This result indicates that the contact electrification of gelatin and PTFE is not purely dominated by electron transfer at the tested RH range.

Gelatin is a mixture of peptides and proteins, meaning that it is a natural polyelectrolyte that contains various amino and carboxyl groups. Gelatin can enter either a positively or negatively charged form by varying the pH of the solution to be lower or higher than its isoelectric point (pI). Here, we first treated gelatin with acid to protonate its amino groups (Figure S1). The protonated amino groups in the gelatin would attract hydroxide ions to maintain electrical neutrality. The hydroxide ions can become mobile ions when the gelatin is hydrated, thus increasing the charges on the triboelectric layers. However, the transfer of mobile ions requires the presence of a water bridge. This can explain why the $\Delta \sigma$ decreases when the RH increases from 20% to 50%. In this RH range, the amount of adsorbed water on the PTFE surface is not enough to form a water bridge. As the RH continues to increase from 50% to 80%, a thin water layer is formed, and mobile ions are able to transfer to increase the charge density on the triboelectric layers.

Figure 4b shows the $\Delta \sigma_{\text{ind}}$ of the gelatin/glycerol film-based TENG measured at different RH levels. The presence of glycerol changes the behavior of the charge transfer between the gelatin and PTFE: the $\Delta \sigma_{\text{ind}}$ first increased from 17.5 $\mu$C m$^{-2}$ to 40.0 $\mu$C m$^{-2}$ as the RH changed from 20% to 60% and then decreased to 11.8 $\mu$C m$^{-2}$ when the RH was altered to 80%. As discussed earlier, the presence of glycerol can increase the amount of transferred electrons and the adsorption rate of water on the film surface. The hydroxyl groups in glycerol act as electron donors and result in higher electric outputs compared to those from the pure gelatin film-based TENG at different RH levels. In addition, the rapid adsorption rate of water on the gelatin/glycerol film surface causes a water bridge to form at low RH and gives rise to a larger $\Delta \sigma_{\text{ind}}$. However, when the RH is over
60%, the amount of adsorbed water causes a decrease in triboelectrification and the surface charges to leak away. To verify our concept, we then added genipin to react with the free amino groups in gelatin and obtained a crosslinked gelatin/glycerol film (Figure 4c) [36,37]. Among the three different gelatin-based films, the crosslinked gelatin/glycerol film provided the largest $\Delta \sigma_{\text{ind}}$ at 20% RH. Two factors could contribute to this result. One is when using genipin to react with the free amino groups in gelatin, the crosslinked gelatin/glycerol film will have more hydroxyl groups (Figure S3). And the hydroxyl groups are good electron donors and can increase the amount of transferred electrons during contact electrification. The other is the crosslinked gelatin/glycerol film is more rough than the gelatin/glycerol film (Figure 1), which can result in more contact area and transferred charges. Without the formation of protonated amino groups and mobile hydroxide ions, the contact electrification between the PTFE film and the crosslinked gelatin/glycerol film returned to the electron-transfer dominated system. Therefore, $\Delta \sigma_{\text{ind}}$ decreases as the RH gradually increases. The three different curves reveal that either electron transfer or ion transfer could be dominated during contact electrification when using gelatin as the triboelectric layer (Figure 4d). Figure S4 illustrates the situations of contact electrification of gelatin-based TENGs at different RH levels. The change of electric output generated from the crosslinked gelatin/glycerol film-based TENG can be applied as a tool to detect the RH (Figure 4e). We clearly observed that the $\Delta \sigma_{\text{ind}}$ changes repeatedly when the RH is varied between 20% and 62%; 62% RH was the environmental humidity on that day. The output $V_{oc}$ and $J_{sc}$ values of the pure gelatin film-based TENG, gelatin/glycerol film-based TENG, and crosslinked gelatin/glycerol film-based TENG were also measured (Figure S5), and they show a similar dependence on RH.

Figure 4  (a)-(c) Induced charge density generated from the TENG using pure gelatin film (a), gelatin-glycerol film (b), and crosslinked gelatin/glycerol film (c) as triboelectric layers. (d) A systematic comparison of the induced charge density generated from the gelatin-based TENGs at different RH levels. (e) Five-cycle measurements of induced charge density generated from the crosslinked gelatin/glycerol film-based TENG at 62% RH. This result demonstrates that the TENG can be applied as a self-powered humidity sensor.
To investigate the output power density, we measured the output voltage and output current of the gelatin/glycerol film-based TENG when connected to an external load resistor at approximately 40% RH (Figure 5a). The resistance was varied from 1 kΩ to 1 GΩ. When the resistance was below 1 MΩ, the output voltage was close to 0, and the output current only had slight changes. When the resistance was varied from 1 MΩ to 1 GΩ, the output voltage gradually increased, but the output current through the load declined. As a result, the instantaneous power density generated from the gelatin/glycerol film-based TENG remained small, with a resistance below 1 MΩ and a maximum of 116 mW m⁻² at a resistance of 100 MΩ (Figure 5b). To precisely understand the electric output of the gelatin/glycerol film-based TENG, we also measured the output power density at different RH levels when the TENG was connected to an external load resistor of 100 MΩ (Figure 5c). A maximum power density of 150 mW m⁻² was generated at 60% RH. The electric output of the gelatin/glycerol film-based TENG showed good stability and durability under 3600 cyclic measurements (Figure 5d).

Conclusion

In summary, gelatin-based contact electrification has been studied and applied to harvest mechanical energy and detect relative humidity in the environment. Different from previous reports that indicated that the surface charge density of triboelectric layers would be decreased at high RH, the results here show that the use of a protein such as gelatin can provide additional charges during contact electrification. The hydration of protein results in the formation of protonated amino groups and the attraction of hydroxide ions on the side chain. Those hydroxide ions increase the surface charge density of triboelectric layers when the water bridge is formed. By reacting the amino groups in gelatin with genipin to block the generation of mobile ions, the gelatin-based TENG can become a self-powered humidity sensor with good stability and durability. Due to its advantageous biocompatibility, the gelatin-based TENG has great potential in the fields of flexible sensors and implantable devices. We believe that this work will also inspire the development of self-powered protein sensors in the near future based on the contact electrification and electrostatic effects.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.01.017.

References

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