Triboelectric nanogenerator as self-powered active sensors for detecting liquid/gaseous water/ethanol

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Abstract
Since the effectiveness of triboelectric charged surface being charged is strongly dependent on the surface adsorbed molecules, we show that the triboelectric nanogenerator, made of polyamide 6,6 (PA) film or polytetrafluoroethylene (PTFE) film, can serve as a self-powered active sensor for detecting water or ethanol in gas or liquid phase. The performance of the active sensors has been understood in reference to the levels of wettability of solid polymer surfaces. This new approach for sensing could be advantageous of simple fabrication, low-cost and easy application.

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Introduction
A control over humidity is necessary for improving quality of life and enhancing industrial processes. As a result, humidity sensors based on various working principles have been extensively adopted in environmental monitoring [1-3]. Ethanol, as a representative organic liquid/gas, is related with biomedicine, brewing, and other chemical processes, and its accurate analysis both in blood and breathing is of importance to the monitoring and control drink and drive [4-6]. Notably, a literature survey found two types of sensors used in the detection of humidity and ethanol. One is to detect the resistance change of metal oxide semiconductors, and the other one is the amperometric gas sensors by detecting the charge transfer in electrochemical redox process.

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A common characteristic of these sensors is, however, all of them require an electric power for operation [7-9]. Recently, the concept of self-powered active sensors by harvesting energy from environment is attracting a lot of attention. The core of such a self-powered device is the triboelectric nanogenerator (TENG), whose electric output signal depends on the surface adsorbed molecules that substantially affects the surface electrification result. TENG has been demonstrated for mercury ion detection, magnetic inspection and glucose biosensing without the use of an external power source [10-12]. Due to its convenient monitoring mechanism, simple fabrication and low cost, the self-powered sensors could be a most desirable and promising approach for environmental monitoring in the near future. Till now, the development of a fully integrated, stand-alone and self-powered sensor is a goal of many researchers.

Herein, in this paper, TENGs were designed as self-powered active sensors for detection of humidity or alcohol content. We demonstrated self-powered sensors based on the TENGs made of PA film and PTFE film (PA TENG, PTFE TENG), respectively, which not only can detect liquid waters and ethanol, but also can probe gaseous water and ethanol. It has been proved that the TENG-based sensors, with the desirable performance, can be used in liquid sensing, gas detection and other environmental monitoring areas.

Experimental section

Fabrication of TENGs

To obtain the nanopore-based Al foil with larger specific surface area, the electrochemical anodization was applied to etch Al foil [13-14]. Aqueous solution of oxalic acid (H$_2$C$_2$O$_4$), with a concentration of 3% (mass fraction), was used as electrolyte. The Al foil was anodized under a bias voltage of 30 V for 5 h, with a Pt electrode employed as the cathode. Subsequently, the etched Al foil was washed with deionized water and absolute ethanol several times, and then dried in air. After that, a thin Al layer was deposited on the etched Al foil via physical vapor deposition route (PVD75). For a comparison, the surface of etched Al foil, as an electrode, which is shown in Figure S1. Another different electrode layer, was prepared and adhered onto a PA film (5 cm × 5 cm) with a thickness of 25 μm. The prepared nanopore-based Al foil was used as the other electrode. To compare and confirm the performance of the TENGs to water and ethanol, the PA film was then substituted by PTFE film, Kapton film and PDMS film, respectively. To promote the usability of the TENG-based sensor, a self-powered device with 40 LEDs as indicator was fabricated. A spring was fixed on the bottom of a cylinder to hold reciprocating motion of the TENG above. The top of cylinder was poked with several holes left for dripping liquid. The corresponding schematic diagram was shown in Figure 3c.

Measurement of TENG-based active sensors

The TENG-based sensors were measured under different conditions such as liquid dripping and gas flowing. The voltage signals were measured by a low noise voltage preamplifier (Keithley 6514 System Electrometer), while the corresponding current signals were recorded by a low noise current amplifier (Stanford Research SR570). Both the voltage preamplifier and current amplifier were connected with a data acquisition card to record the output signals of TENGs.

Characterization of polymer surface

The levels of wettability of polymer surface were characterized by contact angle of water and ethanol. The contact angle measurements were performed with a Rame-Hart goniometer that had a CCD camera equipped for image capture.

Results and discussion

The TENG structurally consists of two plates with the basic structure sketched in Figure 1a. It is composed of a thin PA film adhered by a copper foil as a back electrode, and a nanopore modified Al foil after deposition as the contact electrode. In this designed TENG, PA film and Al foil are different in their ability to attract and retain electrons according to the triboelectric series, resulting in a preferable output performance [15]. Figure 1b shows a schematic diagram of the TENG working with a certain liquid dropped on the surface. The SEM image of the etched Al foil with anodization is shown in Figure 1c, indicating a uniform distribution of nanopores on the surface of the Al foil. According to the previous literature, the nanopores are composed of Al$_2$O$_3$. To make the surface of the etched foil conductive, a thin layer of Al was deposited on it by PVD method. Figure 1d shows the corresponding SEM image of the foil surface, revealing that the nanopore-based morphology remains after coating, which can improve the output performance of the TENG [16]. To confirm the TENG’s performance, control experiments were done by using Al foils without nanopores. The results indicate that the output voltage increases obviously by using etched Al foils as electrodes, which is shown in Figure S1. Another different TENG was fabricated with the same procedures besides taking PTFE film instead of PA film. The operating principle of the TENG relies on the coupling of triboelectrification and electrostatic induction. A potential drop is created by the triboelectric charges distributed on Al and PA/PTFE, which drives the electrons to flow in the external load in order to balance the potential drop [17]. A typical output performance of the two TENGs with different polymer (PA/PTFE) is shown in Figure S2. The PTFE TENG shows the reversed signals of voltage and current compared with the PA TENG under the same connection series. This is because the PTFE film tends to gain electrons from Al foil, resulting in being negative compared with Al, while the PA film tend to lose electrons to Al in the triboelectric process. To demonstrate that a TENG can be a self-powered active sensor for detecting certain liquid species, the performances of PA TENG and PTFE TENG were measured with different liquids dropped on the surface under the same conditions. Figure 2a shows the original output voltage of PA
TENG, which is more than 70 V. While a drop of water or ethanol was scattered on the bottom electrode of a size of 5 cm x 5 cm, the signal nearly decrease to zero, as shown in Figure 2b and c, respectively. This result implies that the TENG can be used as an active sensor for detecting liquid water or ethanol. As a comparison, PTFE TENG is also employed for measurement under the same condition, with the corresponding results shown in Figure 2d, e and f, respectively. Unlike PA TENG, there is no obvious response of PTFE TENG for a water drop. But, it reveals a drastic response with no output signals once an ethanol drop was dispersed, which is similar to the response of PA TENG to ethanol drop. The distinct performances of the PTFE TENG for water and ethanol drops suggest that the TENG can avoid the interference of water in the detection of ethanol. To investigate the response and recovery characteristics, the dynamic performances of the TENG-based sensors are shown in Figure S3, indicating that both sensors have the desirable response and recover time. To further study the response of TENG to ethanol drops, ethanol aqueous solutions with different concentrations were prepared and detected by the PTFE TENG. Figure 2g, h, i and j shows the output voltages of the TENG for ethanol solutions with a concentration of 20%, 40%, 60% and 80%, respectively. The relationship between the output voltage and the concentration of ethanol solution is depicted in Figure 2k. The fitting line shows the output signals decreased logarithmically with the ethanol concentrations, which is very similar to the gas response of semiconductor sensor versus different concentrations. To rule out disturbance from nanopores on the Al electrode, the TENGs fabricated by using Al foils without nanopores were performed in the same way, which presents consistent results as those using Al foils with nanopores (Figure S4).

Although the fundamental mechanism of the triboelectric effect still remains debating [18], possible reasons are proposed to explain the different responses of the TENGs for water and ethanol drops here. As we know that the triboelectric charges are for solid surface conditions [18-19], the levels of the wettability of solid polymer surface as characterized by a contact angle is measured for water and ethanol. The corresponding results are presented in the insets of Figure 2, exhibiting that the contact angles of PA film to water and ethanol is 47° and 0° with that of PTFE film to water and ethanol is 110° and 43°, respectively. Hence, it is proved that the PA film is hydrophilic to both water and ethanol, while the PTFE film is hydrophilic to ethanol and hydrophobic to water. The different responses of TENGs might be caused by the different levels of surface wettability of solid polymers to water and ethanol. Due to the significant difference of wettability, much more water was absorbed on surface of PA

Figure 1  (a) A basic scheme of the designed TENG. (b) The schematic diagram of the TENG working with a certain liquid dripping. (c) SEM image of the nanopores on etched Al foil with anodization. (d) SEM image of surface morphology of etched Al foil after deposition with Al film.
film to form an isolated layer between PA film and Al electrode. The isolated layer can screen/deplete the triboelectric charges generated on the surfaces. Meanwhile, the triboelectric charged area of the device got a sharp decrease due to the absorbed water. This conjecture is in accord with previous report in general [19-20]. As to ethanol on the polymer films, a possible principle is similar to that of water. As for PTFE film, the contact angle decreases as the concentration of ethanol solution increases gradually, which is consistent with the variation trend of PTFE TENG's

Figure 2  (a–c) The output performance of PA TENG without solution, with water dripping and with ethanol dripping. (d–f) The output performance of TNEG-PTFE under original condition, with water dripping and with ethanol dripping. (g–j) The performance of PTFE TENG with ethanol solution dripping at different concentrations (20%, 40%, 60%, 80%). (k) The relationship between the output voltage and the concentration of ethanol solution. Inset of b, c, e, f, g, h, i, j is the corresponding contact angle. Inset of k is the dependence of contact angle on concentration of ethanol solution.
Figure 3  (a and b) The output voltage and current performance of TENG-based device. (c) A schematic diagram of the fabricated device. (d) 40 LEDs lighted up by the TENG device before dripping ethanol.

Figure 4 (a–e) The performances of the PA TENG under different relative humidity. (f) The plot of the output voltage versus RH.
responses to ethanol solution with different concentrations. The ethanol solution with higher concentration is more inclined to be absorbed on the surface of PTFE film, to form a liquid layer with a larger spreaded area. The liquid ethanol solution layer can shield the triboelectric charges and reduce the triboelectrically charged area.

To confirm the proposed model, a Kapton film and PDMS film were selected and tested. The performances of the TENGs made with Kapton and PDMS film (Kapton TENG, PDMS TENG) are shown in Figure S5 with the corresponding contact angles indicated in insets. The Kapton TENG shows obvious responses to both water and ethanol drops with the Kapton film hydrophilic to both water and ethanol. On the contrary, the performance of PDMS TENG only drastically changed for ethanol dripping and the PDMS film is hydrophilic for ethanol with hydrophobicity for water. A similar response of TENGs to water or ethanol drops and the corresponding contact angles further verified the explanation proposed above, which is that the responses of TENGs for water and ethanol drops are owning to the wettability of solid polymer surface to the corresponding liquids.

To enhance the TENG-based sensor availability, a self-powered device was fabricated with PTFE film. Figure 3a

![Diagram](image-url)

**Figure 5** (a) 3D graph of PTFE TENG sensor response to the changing external RH and ethanol concentrations. (b) Output voltage response of the sensor to the ethanol gas with different concentrations. (c) Output voltage response of the sensor under different RH. (d-i) Output voltage response of the sensor to the ethanol gas with different concentrations (0, 20%, 40%, 60%, 80%, 100%) under 40% RH.
and b shows the output voltage and current signals, respectively, revealing that the voltage can be up to 57 V with the current more than 6 μA. A schematic diagram of the device is displayed in Figure 3c. The spring fixed on the bottom of the cylinder was employed as a rebounder to keep the TENG above reciprocating vibration when the device is shackled. In addition, 40 LEDs as indicators were connected to the device. All of the LEDs were lighted when shaking the device, as is shown in Figure 3d. However, with dripping ethanol through the holes on the top of the cylinder, the device could no longer light the LEDs no matter how to shake it. This suggested the device can be used for detecting ethanol due to its sensitive and quick response.

In the routine environmental monitoring and industrial production, the gas detection is as important as liquid detection. It is, therefore, necessary to explore the response of the self-powered TENG-based sensors to the target gas. A schematic plot of the measuring system is shown in Figure 5b. The performances of the PA TENG under different relative humidity (RH) are shown in Figure 4a, b, c, d, and e, respectively. The output voltage dropped with the RH increasing from 40% to 80%. The plot of the output voltage versus RH is drawn in Figure 4f. The fitting line indicates the output signals logarithmically decrease with the increase of RH. The response and recovery characteristic of the PA TENG sensor is shown in Figure 5a, indicating that the sensor has a desirable response and recover time.

In addition, the response of the PTFE TENG for the ethanol gas is investigated and displayed in Figure 5. By systematically investigating the TENG-based sensor response to the changing RH and ethanol concentration, the results were extracted and plotted in a 3-dimensional (3D) graph, as shown in Figure 5a. An overall trend of how output voltages vary with the change of ethanol concentrations and RH can be simultaneously derived from this 3D graph. It is straightforward to see that the output signal decreases as the concentration increases, but, has negligible change with the variation of the RH. Two 2D graphs are shown in Figure 5b and c for more details, which were extracted from Figure 5a by projecting on the voltage-concentration surface and the voltage-RH surface, respectively. Figure 5b shows the voltage response of the TENG-based sensor to different concentrations of ethanol gas when RH was fixed at 40%, 50%, 60%, 70% and 80%, respectively, indicating that the output signal decreases with the increase of the ethanol gas concentration. Figure 5c presents the output signal under different RH, with the concentration fixed in each curve, ranging from 0 to 100%, respectively. This 2D graph presents eleven curves with eleven different concentrations of ethanol gas, revealing that RH has the negligible influence to the performance of the PTFE TENG sensor, namely, the PTFE TENG sensor can prevent the interference from ambient humidity. The performances of PTFE TENG to different ethanol gas concentrations (0, 20%, 40%, 60%, 80% and 100% wt) under the 40% RH are shown in Figure 5d, e, f, g, h and i, respectively, with that to other concentrations (10%, 30%, 50%, 70% and 90% wt) are shown in Figure 5f, indicating that the TENG-based sensor has an excellent responses to variation in ethanol gas concentrations. The dynamic response of the TENG-based sensors to 100% ethanol gas under 40% RH is shown in Figure 5b, indicating that this sensor can recover within less than 20 s, which is acceptable in most conditions.

Conclusions

In summary, TENG-based devices, made with different polymer films, have been demonstrated as self-powered active sensors for detecting liquid/gaseous water and ethanol without the use of external power sources. The working principle of the active sensors has been illustrated, which is due to the degrees of wettability of the solid polymer surface, identified by contact angle, to water and ethanol. Our study suggests that these TENG devices can be applied as self-powered active sensors for environmental monitoring and industrial manufacture with advantages of being low cost, simple fabrication, and good performance.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2013.08.004.

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