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Research Update: Recent progress in the development of effective dielectrics for high-output triboelectric nanogenerator

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A new energy generating device, triboelectric nanogenerator (TENG), was discovered in 2012 and thereafter, many applications such as portable power sources and self-powered, appropriate for portable electronic devices. So far, rapid development of device fabrication technologies and mechanical system designs significantly increased the instantaneous output power up to several tens of mW/cm². This article provides a comprehensive review of effective dielectrics used so far in TENGs for further enhancement in output power, as well as the fundamental issues regarding the materials. Finally, we show some strategies for obtaining the properties that the materials should have as effective dielectrics. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4979306]

I. INTRODUCTION

A. Background of triboelectric energy harvesting

In the last two decades, the various applications of mobile electronics such as smartphone and smartwatch have been a big part of our lives. The mobile devices have various functionalities such as health monitoring, medical care, environmental protection, infrastructure monitoring, and security, making human life better. However, this means that many devices for the functionalities are needed, thus, the total power provided to them will be quite high although the power for driving each unit can be down to micro-watt range. The fast development of Internet of things and sensor networks dramatically also changed the existing understanding about energy, which should be mobile, available, and sustainable nowadays. This is why we are using batteries for every device. However, it may not be the solution because so many batteries are needed and they have a limited lifetime. Thus, we have to monitor and exchange them, which is an impossible task and costs a great deal. It is essential to develop portable power generating device which provides energy with the battery for a self-powered system.

A new energy generating device, named as triboelectric nanogenerator (TENG), was demonstrated in 2012 and various TENGs have been demonstrated, proven as a cost-effective, simple, and robust technique for energy harvesting. Energy is generated when two materials are brought into contact with each other, based on the coupling effect of the triboelectric effect and electrostatic induction. Because it uses the mechanical energy sources available anywhere and anytime at our surroundings, such as winds and moving things, this energy harvester is appropriate for the portable applications although the energy is not big as much as the solar energy.

B. Portable power source for self-powered devices

The ultimate goal of the TENG is to realize the self-powered electronics without replacing the battery for a long time. Many portable devices are expected to be charged from the TENGs without
us knowing. Since the first demonstration of the TENG in 2012, rapid development of new device structures and new functional materials led to the significant increase of the power density up to several tens of mW, as shown in Fig. 1. Due to the increased output power, it was demonstrated that it was possible to power up the various portable electronic devices, as well as to fabricate the self-powered sensors.

In the contact-separation mode TENG, polydimethylsiloxane (PDMS) has been mainly used as a dielectric with Au nanoparticles (NPs) coated Au thin film as contact electrode. The TENG generated an areal output power density of 31.3 mW/cm$^2$, corresponding to an energy conversion efficiency of 14.9%. The injection of negative ions into the dielectric by the corona discharging method was considered to be effective in increasing the charge density on the surface of fluorinated ethylene propylene (FEP). The charge density was increased to around 240 µC/m$^2$ and the contact-mode TENG generated a maximum power density of ~31.5 mW/cm$^2$. Recently, Baik’s group reported a new type of TENG composed of three layers; a top layer with mesoporous polymer film on the top electrode (Al), a middle layer with Al film coated by Au NPs, and a bottom layer (Al), as shown in Fig. 2(a). By the sequential contact configuration of the TENG and direct electrical connection of the middle layer to the earth, the device generated a sustainable output power of 46.8 mW/cm$^2$, as shown in Fig. 2(b). The TENG was demonstrated as a portable power-supplying system that provides enough continuous dc power to charge a battery in smartwatch/phone.

C. Importance of dielectric in triboelectric nanogenerator

As mentioned above, the instantaneous areal power density has reached up to several tens of mW/cm$^2$. However, the increase of the output power does not mean the increase of the energy conversion efficiency. It tells us facts that the fabricated TENGs can generate the output powers at certain input conditions (i.e., large input force or optimized input condition). The areal output currents reported are also still less than 1 mA/cm$^2$, too low to provide enough energy with electronic devices. Actually, it is so hard to charge the smartphone/watch battery above 1% with the TENGs. Recently, it seems that there is no longer significant increase in the output current.

A key approach to improve the output performance of the TENGs from the materials’ aspect is to increase the triboelectric surface charge. Thus, the commercialization of the TENGs would be possible only if there are effective dielectrics because the output power is critically and basically dependent on the density of the charges transferred. So far, various dielectric materials such as polydimethylsiloxane (PDMS), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), fluorinated ethylene propylene (FEP), polyimide (PI) have been used without any modifications. Very recently, the modification of properties such as compressibility, surface potential, and hydrophobicity in a few TENGs has been reported.

![FIG. 1. The areal power densities and output currents of various TENGs reported during last 5 years.](image-url)
II. MATERIALS AS EFFECTIVE DIELECTRICS

Generally, different materials have different affinities for electrons. By rubbing a variety of materials against each other and seeing the charge transfer between them, the materials can be ordered according to their affinity for electron, called as triboelectric series. One such ordering for several materials is shown in Fig. 3.\textsuperscript{23} Materials shown highest (left) on the figure tend to have a greater affinity for electrons than those below it (right). Subsequently, when any two materials in the figure are rubbed together, the one that is higher can be expected to attract electrons.
A list that ranks various materials according to their tendency to gain or lose electrons in contact electrification, called as the triboelectric series.

from the material that is lower. As such, the materials accepting the electrons have the greatest tendency to acquire the negative charge, while those losing the electrons become positively charged.

**A. Polymer materials**

1. **Polydimethylsiloxane (PDMS)**

Polydimethylsiloxane (PDMS) is one of polymeric organosilicon compounds and one of the most widely used dielectrics in TENGs because it is easy to handle and produces high output power due to the excellent ability to gain electrons. It is quite viscoelastic because of the flexible polymer chain by their siloxane linkages, by a simple curing process. Thus, various patterns can be fabricated by using conventional patterning processes, useful for many applications. After polymerization and cross-linking, solid PDMS samples present a hydrophobic surface. This property made the electrical output of the TENGs less sensitive to the moisture content in air, compared with those made of the hydrophilic surface.

Wang group, for the first time, used the PDMS as an electron accepting material and fabricated the transparent TENG consisting of two polymer films made of PDMS and PET. Various patterns with various features, such as line, cube, and pyramid, are made by a simple patterning process, as shown in Figs. 4(a) and 4(b). They reported the maximum output voltage and current signal for pyramid-featured devices up to 18 V and 0.13 $\mu$A/cm$^2$ under bending cycles at a frequency of 1 Hz, which were almost 4 times as high as the previously reported TENG using flat films, as shown in Fig. 4(c). The film was quite transparent, enough for the film of the smartphone, as shown in Fig. 4(d). However, it is so sticky, thus, when it is released after the contact, some of the material can be detached and transferred to the metals.

2. **Polytetrafluoroethylene (PTFE)**

Polytetrafluoroethylene (PTFE) is a fluorocarbon solid consisting wholly of carbon and fluorine, produced by free-radical polymerization of tetrafluoroethylene. In general, it is very stable and non-toxic below 260 °C due to the presence of strong C–F bonds. The high electronegativity of fluorine results in a strong force to pull electrons during the physical contact. However, unlike the PDMS, it is poorly soluble in almost all solvents. A flexible multilayered TENG is composed of five layers, in which each layer has PTFE and Al foil, on a zigzag-shaped Kapton substrate. The Al foil had a lot of nanopores on the surface by the electrochemical anodization, while the flat PTFE was used. The device was attached on a shoe pad and generated approximately 250 V and 0.6 mA in output.
FIG. 4. (a) Schematic image of TENG, composed of PET/ITO and PDMS. (b) Structure characterization of the patterned PDMS thin film. (c) Output voltage and current of the TENG using PDMS thin film with flat surface and various patterned features, respectively. (d) The UV–vis spectra of various types of substrates and TENG devices and the photograph of a TENG device attached on the screen of a smartphone that indicates the high transparency of the device. Reproduced with permission from Fan et al., Nano Lett. 12, 3109 (2012). Copyright 2012 The American Chemical Society.

voltage and current, respectively. A sliding-based TENG, in which polyamide 6,6 (nylon) and PTFE films were chosen as the triboelectric layers, is shown in Fig. 5(a). On the polymer films, a layer of metal electrode was deposited on the side next to the glass slide. The two plates are kept in parallel to each other and the polymeric surfaces are brought into contact. The PTFE film was dry-etched using inductively coupled plasma (ICP) to make vertically aligned nanowires (NWs) with an average length of ∼1.5 µm, which increased the surface roughness and the effective surface area. When the plates in the TENG slid from the contact position to the separated position, Figs. 5(b) and 5(c) show that it produced extremely high voltage and current of 1300 V and 4.1 mA/m², respectively, approximately 0.4 W/m² in output power.²⁶

Actually, a flexible multilayered encapsulation structure showed its excellent reliability output performance in harsh environmental conditions for over 30 days.²⁷ The PTFE powder-based TENG was also stable for over a week to investigate the stability, corresponding to 7 × 10⁶ cycles, at a vibrating frequency of 10 Hz. The generated output current of 10 µA did not show any degradation.²⁸ Despite aforementioned advantages, it is so difficult to chemically reform for further enhancement of the output performance in TENG.
FIG. 5. (a) The schematic diagram showing the structural design of the TENG in two sliding states: the overlapping position (on the left) and the separation position (on the right). The magnified schematic of the surface between the two polymeric films, showing the fabricated NW array on PTFE surface. SEM image of the PTFE surface with etched NW structure at the tilted view of 30°, the inset is the SEM image in higher magnification. The photograph of a typical sliding-driven TENG on the measurement stage. (b) The open-circuit voltage ($V_{OC}$) and the short-circuit current density ($J_{SC}$) under the in-plane sliding with the displacement of 71 mm and the acceleration of 20 m/s². (c) The dependence of the output voltage (blue) and current density (green) and the power density on the resistance of the external load. Reproduced with permission from Wang et al., Nano Lett. 13, 2226 (2013). Copyright 2013 The American Chemical Society.

3. Polyvinylidene fluoride (PVDF)

PVDF has been also considered as one of the most widely studied dielectric materials in mechanical energy harvesting technologies because of its low cost, high flexibility, and biocompatibility. The easy production of a variety of nanostructures, such as NWs, nanofibers, nanotubes, was very useful in many applications, such as capacitors, batteries, and sensors. As a linear homopolymer composed by the repetition of CH$_2$–CF$_2$ monomers, PVDF is able to crystallize in four possible conformations named as $\alpha$, $\beta$, $\gamma$, and $\delta$ phase. The highest dipole moment is obtained with the alignment of all dipoles in the same direction, corresponding to the $\beta$-phase of the PVDF.

PVDF thin films were used in TENG as a dielectric in the triboelectric series without any modifications. The film generated an output power of 1.19 mW by the physical contact with the
Al foil under a periodic compressive force around 50 N. The output power significantly increased to 3.74 mW and decreased to 0.91 mW after forward and reverse polarization, respectively. Here, it was proposed that the dipole moment altered the surface potential level of the PVDF film, thus modulating the surface charge transfer between the PVDF and the Al electrode. PVDF nanofibers prepared by the electrospinning method and a TENG were also fabricated with the nylon nanofibers. The TENG also generated high output of 26.6 W/m². A fully self-powered and portable ultraviolet radiation level detection device was demonstrated by using the TENG as a power source.  

4. Other polymer materials

In addition to the polymer materials mentioned above, fluorinated ethylene propylene (FEP) and polyimide (PI) have been also used in TENGs fabricated so far. A pressure sensor with extremely high detection resolutions of 0.16 Pa based on triboelectric effects between FEP and latex membrane was reported. They also demonstrated heartbeat monitors, in which air pressure change in a chest piece caused by the heartbeat transmit via air-filled hollow tubes to the TENG generated an output voltage around 0.06 V. By using PI, a disk-type TENG was reported, composed of two disk-shaped components with four sectors each. This rotation-based TENG produced a large output current density of 29.0 mA/cm² at a rotating speed of 1000 rpm.

B. Strategies to develop the effective dielectrics

1. Surface chemical potential

The magnitude of the electrons flowing through the external circuit is strongly influenced by how many charges are transferred to the dielectric. The charge density transferred is closely related to the chemical properties of both surfaces, thus, the surface modification by appropriate functionalization methods is effective in increasing the charge density. In general, the transferred charge density (σ) on the surface of the dielectric is explained as

\[ \sigma = \frac{[(W - E_0)\varepsilon](1 + t/\varepsilon z)}{t/\varepsilon \varepsilon_0 + (1/\bar{N}_s(E)\varepsilon_0)^2(1 + t/\varepsilon z)}, \]

where \( W - E_0 \) is the difference in the effective work functions between two materials, \( \varepsilon, t, \varepsilon, \varepsilon_0, z, \) and \( \bar{N}_s(E) \) are the charge of an electron, distance of space, relative permittivity of dielectric, vacuum permittivity of free space, depth of dielectric film, and the averaged surface density of states. This shows that as the work function difference of two contact materials increases, the surface charge density also increases. According to this equation, most of the works on the surface modification of the dielectric have focused on the control of the surface potentials.

The chemical potential of organic materials is mainly determined by its functional groups exposed on the surface. Zhang group employed single-step fluorocarbon plasma treatment on the PDMS surface with octafluorocyclobutane for the reactive gas for the surface modification and pyramid array in Fig. 6(a). The plasma treatment was carried out by an ICP etcher and the fluorocarbon layer was completely covered after the 8-cycle plasma treatment. The output peak voltage achieves up to the maximum value of 265 V after the 8-cycle plasma treatment, an increase by a factor of 214% compared to that of TENG with the 0-cycle plasma treatment, as shown in Fig. 6(b). Shin et al. also reported polyethylene terephthalate (PET) films with the surface functionalized with poly-L-lysine solution and trichloro(1H,1H,2H,2H-perfluoroctyl) silane (FOTS) vapor by dip coating and self-assembling deposition, respectively.

2. Dielectric constant

Dielectric constant of the dielectric is one of the important parameters in determining the charge density transferred, thus, the output performance of the TENG. This parameter may be related with the maximum magnitude of the charges that can be sustained on the surface and inside the bulk. The surface modifications mentioned above will increase the density of charges on the surface, not inside the bulk. In general, the total transferred charge density (σ') can be expressed by
FIG. 6. (a) Schematic view of 3D structure of the high-performance TENG in top side. (b) Characterization of the output performance of the TENG with different surface chemical modifications (i.e., plasma treatment cycle) under the external force with frequency of 5 Hz in bottom side. Reproduced with permission from Zhang et al., Nano Energy 4, 123 (2014). Copyright 2014 Elsevier.

\[
\sigma' = \frac{-\sigma_0 d_{\text{gap}}}{d_{\text{gap}} + d_{\text{dielectric}}/\varepsilon_{\text{dielectric}}},
\]

where \(\sigma_0\) is the triboelectric charge density at the equilibrium state, \(d_{\text{gap}}\) and \(d_{\text{dielectric}}\) are the gap distance and the thickness of dielectric films, and \(\varepsilon_{\text{dielectric}}\) is a dielectric constant of dielectric films. According to the above equation, the charge density can increase as the dielectric constant increases.

One of the facile methods to increase the dielectric constant of the dielectric film is to make composites, composed of inorganic and organic materials. A composite composed of a barium titanate (BaTiO\(_3\)) NPs and a ferroelectric copolymer matrix, poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) was reported.\(^{35}\) The insertion of BaTiO\(_3\) into the P(VDF-TrFE), followed by the poling process, increased the dielectric constant from 10.9 to 12.4 at \(10^2\) Hz. Similarly, the PDMS film consisting of 10% SrTiO\(_3\) NPs in volume showed an excellent performance, where the maximum instantaneous output power is 6.47 W m\(^{-2}\) under periodic compressive force at frequency of 2.5 Hz.\(^9\)

3. Compressibility

In addition to the dielectric constant, the compressibility of the film is so important because the TENG is based on the dynamic motion. This means that the charge density transferred is influenced...
by the mechanical properties of the film. In metal/dielectric/metal structure, the charge density is expressed by $Q = CV$. The first derivative of charges with respective to time is as follows:

$$\frac{dQ}{dt} = \frac{dC}{dt} V + C \frac{dV}{dt}. \quad (3)$$

This equation can tell us that the rate of capacitance with the time is also an important parameter as well as the dielectric constant. As a simple method to increase the rate, a mesoporous film was fabricated by using polystyrene (PS) spheres as a sacrificial template. The TENGs showed a 10-fold power enhancement compared with those with flat film. They showed that the enhancement was due to the increase of the contact area in the capacitance by the increase in effective ($\varepsilon/d$) value. A mesoporous PDMS films impregnated with Au NPs as effective dielectrics were also reported by the same group. This film was fabricated by casting a mixture of PDMS solution and de-ionized (DI) water, evaporating water very slowly at room temperature as shown in Fig. 7(a). The Au NPs were accumulated only at the bottom side of the pores (Fig. 7(b)), which generated the electric potential by the friction between the Au NPs and PDMS. The porosity could be controlled by the content of

![Figure 7](image-url)

**FIG. 7.** (a) Schematic diagrams of the fabrication process for the AMTENG. (b) Top and cross-sectional SEM images of a mesoporous PDMS film with Au NPs (0.28 wt. %). The insets show the morphology of Au NPs and cross-sectional SEM images of the mesoporous film. (c) Porosity changes as a function of the DI water concentration ranging from 0 % to 50 %. The insets show SEM images of mesoporous films with various porosities. (d) Photographs of a fabricated large-area mesoporous PDMS thin film (30 cm × 30 cm). The insets show manual compression with a volume reduction of over 50 %. (e) The loading and unloading stress–strain curves as a function of the porosity ranging from 0 % to 59 %. Reproduced with permission from Chun et al., Energy Environ. Sci. 8, 3006 (2015). Copyright 2015 The Royal Society of Chemistry.
the water in the mixture and increased with the content, as shown in Fig. 7(c). They also showed that a large-area mesoporous PDMS thin film (30 cm × 30 cm) could be fabricated (Fig. 7(d)), demonstrating the capability of producing large-scale films. Due to the larger porosity of the films, it was clearly seen that the mesoporous film became quite compressible and flexible (Fig. 7(e)).

III. SUMMARY AND PERSPECTIVES

Here, we summarized the recent progress in the development of dielectric materials for the TENG with high output power generation. So far, many TENG technologies including device structures, operation modes, a few functional materials, as well as fundamental issues such as operation mechanism, were reported, contributing to the significant increase of the output power up to several tens of mW/cm². Due to increased output power and accumulated technologies, the successful demonstration of various applications such as portable power source and self-powered sensors is so meaningful to us and shows the possibility of the commercialization.

However, further enhancement in the output power is essential to speed up the commercialization, and we believe that new triboelectric material, in particular, effective dielectric should be developed because the charge density transferred to the dielectric determine the output power. For this, the dielectric should easily and quickly gain negative charges (i.e., electrons) from the metal and the charges should be transferred into the inside of the materials to gain the charges as much as they can. Finally, the materials should hold the charges for a long time for practical applications. Until now, many dielectric materials were proven to have these functionalities, not enough for sufficient generation of the out power. We believe that this review can be useful and helpful for designing energy harvesters which are able to provide sufficient energy with portable electronic devices.

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