Chemical Modification of Polymer Surfaces for Advanced Triboelectric Nanogenerator Development

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Abstract

Triboelectric nanogenerator (TENG) is a newly developed technique for harvesting mechanical energy from ambient environment with sparkly high output and extremely flexible structural designs. The operation of TENGs is based on the combined effects of triboelectrification and electrostatic induction. The charge density on triboelectric surfaces (mostly polymers) sets the foundation of TENG output. Meanwhile, the charge density on polymer surface is closely related to the surface chemical property. Therefore, engineering the surface chemical environment by appropriate functionalization is the most fundamental approach in controlling the TENG outputs. This article systematically reviews recent processes of chemical modifications of triboelectric polymers for advanced TENG developments. According to different functionalization techniques, four categories of chemical modifications, including fluorinated surface, ion injection, sequential infiltration synthesis and molecular-targeting

functionalization are thoroughly reviewed, and their contributions to TENG performance are discussed.

Keywords: Triboelectric Nanogenerator; Surface Modification; Polymer Surfaces; Mechanical Energy Harvesting

1. Introduction

The rapid development of mobile electronics has reconstructed the landscape of energy consumption. Miniaturization of energy sources with high portability and sustainability is greatly desired for powering a large variety of personal electronics and implantable biomedical devices. Currently, batteries are the predominant choice of such power sources. However, they may not be the ultimate solution since their operational lifetimes are limited and regular recharging or replacing is necessary, which give rises to their incompatibility, incompetency and even environmental concerns.[1] Based on this regard, self-powered charging system would be a desired power source for modern electronics. Ambient environmental mechanical energy is considered abundant and the most accessible energy source for powering small electronics.[2] Among many endeavors of harvesting mechanical energy effectively, the nanogenerator was invented using piezoelectric nanostructures as the functional building blocks, which offers high sensitivity, long life time, and potential superior efficiency.[3] During the last decade, numerous piezoelectric nanogenerators (PENGs) were developed to harvest energy from physical deflection,[4,5] acoustic waves,[6,7] air and fluid flow,[8-10] and body movements (e.g. walking, talking and breathing).[11-13] In 2012, triboelectric nanogenerator (TENG) was first reported on the basis of the traditional electrostatic energy harvesting principles.[14] Owing to its simple design and scalable/integratable nature, the area and volume power density of TENGs rapid reached 500 W/m^2 and 15 MW/m^3 , respectively within a few years.[15] An instantaneous conversion efficiency of 70.6% and a total conversion efficiency of 85% were achieved.[16,17] The high power output and large energy conversion efficiency made TENGs feasible in driving various commercial electronics, such as cell phones,[18,19] light bulbs,[15,19] alarms,[20,21] pacemakers,[22] and a large number of sensors[23-28] and light emitting diodes (LEDs),[29-

34]According to the device configuration, TENGs can be categorized into four modes: vertical contact-separation mode, contact-sliding mode, single-electrode mode, and freestanding triboelectric-layer mode,[35] which cover the functions of TENGs in converting various energy forms including water waves,[36-38] wind,[39,40] rain droplets,[30,41] vehicle[32,42] and human movement.[17,43,44] These two advantages promise TENGs in not only developing practical self-powered energy systems but also generating electricity at large scale. The development and broad applications of TENGs were extensively summarized in a number of recent reviews.[1,2,35,45-48]

The operation of TENG is on the basis of two combined effect of triboelectrification and electrostatic induction. The triboelectrification is the phenomenon that a material becomes electrically charged after intimate contact with a different object. When two dissimilar surfaces with distinct triboelectric polarity (i.e. tendency to gain or lose electrons) touch each other, electrons, holes or other charged ions/molecules transfer across the interface to compensate the difference of surface potentials. This charge separation is the primary driving force of mechanical to electric energy conversion in TENGs. Triboelectric materials (mostly polymer) are usually attached to metal electrodes, where electrostatic charges are induced. Once the device capacitance changes by displacement, current flow occurs between the conductive electrodes and thus outputs electric power. Therefore, controlling the charge density on the triboelectric surfaces is the most fundament strategy for improving the performance of TENG. In general, the charge density is determined by the amount of charge carrying locations and the tendency of these sites to gain or lose electron. These two factors can be regulated by morphologically and chemically modifying the triboelectric polymers. The number of charge carriers can be simply increased by enlarging the surface roughness factor. For instance, morphologies like nanowires,[49-

51]nanoparticles[31,52] or other nanoscale patterns[53-59] are frequently adopted to raise the surface area of triboelectric materials and thus enable more charge carrying site. On the other hand, the tendency of these sites can be controlled by altering their chemical properties. The objective of this article is to give a review of most recent advances in chemically engineering polymer surface and to discuss the contribution of four different modification techniques to enhance TENG performances.

2. Fluorinated Surfaces

The triboelectrification process exists in various material pairs. To maximize the charge transfer density, efficient TENGs are built on two surfaces with the most distinguished ability to gain or refuse electrons. Different surfaces' tendency of receiving and losing electrons were listed in several triboelectric series,[1,29,60] which are the guidance of material selection in TENG designing. Fundamentally, this ability/tendency is closely related to the electron affinity of the surface atoms. For instance, most electron-attracting polymers contain elements with strong electron affinity, such as fluorine (F). Therefore, one intuitively expected approach to increase the charge density is introducing extra F atoms onto the polymer surface by chemical modifications, so called fluorinated surfaces. In principle, surfacefluorination is achieved by chemically grafting F-containing unit, such as CF_3 group through either solution reactions or vapor treatments.

Shin et al. manipulated the triboelectric polarities of polyethylene terephthalate (PET) film by functionalizing its surface with positively charged amino group ($-\text{NH}_3$) and negatively charged $-\text{CF}_3$ group using poly-L-lysine solution and trichloro(1H,1H,2H,2H-perfluorooctyl)silane (FOTS) vapor, respectively.[61] The modification process started from the cleaning of PET substrates.

After that, the PET substrates were treated in oxygen plasma for 100 s, resulting in the formation of reactive hydroxyl groups (-OH) on the surface. At last, two pieces of plasma-treated PETs were individually soaked in poly-L-lysine solution for 5 min and exposed in FOTs vapor environment at 95 °C for 1h. During this process, target molecules (i.e. poly-L-lysine and FOTs) were anchored on the PET surface by covalently bonding with the reactive hydroxyl groups. To verify the surface functionalization, water contact angles of the pristine and treated samples were analyzed through static sessile drop experiments. The contact angles of poly-L-lysine-treated PET (P-PET), pristine PET, and FOTs-treated PET (F-PET) were 44°, 81° and 123°, indicating the hydrophilic and hydrophobic properties, respectively. The hydrophilic characteristic of P-PET was attributed to the positively charged amino groups that actively interact with the polar hydrogen bonds of water molecules. The hydrophobic feature of F-PET was a consequence of the -CF₃ group in the graphed FOTs molecules, which has low surface energy to interact water molecules. These results confirmed the presence of -NH₃ group on the P-PET and -CF₃ group on the F-PET surface.

After the chemical modifications, P-PET and F-PET demonstrated higher tendency to lose and gain electron due to the -NH₃ group and the fluorinated surface, respectively. In principle, TENG with these two surfaces should deliver significant electric output considering the enlarged difference of triboelectric polarities. Figures 1a and b compare the voltage output of TENGs with different friction pairs: (i) PET:PET, (ii) PET:P-PET, (iii) PET:F-PET, and (iv) P-PET:F-PET. A smallest V_{oc} of ~4 V was produced in pair (i) with a device area of 4 cm² and under an applied force of 0.5 MPa. P-PET and F-PET could improve the V_{oc} to ~110 V and ~205 V, respectively. The maximum V_{oc} of ~330 V was obtained with the TENG assembled from pair (iv). That was ~80 times enlargement compared to the V_{oc} of PET:PET pair, implying the effectiveness of this

amino and fluorine functionalization methods. The modified PET surfaces exhibited superior stability owing to the tight chemical bonds. No reduction of voltage or current output was observed during the periodical measurement of TENG with pair (iv) for over 4 weeks (Figure 1c). A V_{oc} of ~300 V and a short-circuit current density (J_{sc}) of ~200 mA/m² can be maintained within the entire time interval. These electric outputs were able to lighting up 250 blue LEDs with a rectified bridge circuit to convert alternating current (AC) to direct current (DC).

Similar FOTs functionalization was applied to polypropylene (PP) nanowires (NWs). Feng et al. fabricated PP NW array with anodic aluminum oxide (AAO) template and chemically modified the NW surfaces with two fluorine-containing molecules including FOTs and poly(2,2,3,4,4,4-hexafluorobutyl-5-((3,4-dihydroxyphenethyl)amino)-2,2,4,4-tetramethyl-5-oxopentanoate)fluoropolymer (Pdop-F). [62] Compared with the Pdop-F, FOTs was found to be more effective in implementing fluorine onto PP NW surfaces since the fluorine content in FOTs (48.6 wt%) was much higher than Pdop-F (23.8 wt%). Consequently, the charge density of FOTs treated PP NWs (65 $\mu\text{C}/\text{m}^2$) was about two times larger than that of Pdop-F treated PP NWs (30 $\mu\text{C}/\text{m}^2$). Both of these two values are substantially higher than the pristine PP NWs (3.3 $\mu\text{C}/\text{m}^2$). As a result, FOTs treated PP NWs achieved the highest voltage output of 1900 V and current density output of 19 mA/cm², which were sufficient to powering 372 red LEDs.

Another popular way to introduce fluorine is fluorocarbon plasma, *i.e.*, employing fluorocarbon (*e.g.* CF₄ and C₄F₈) plasma gas to treat the polymer surfaces. During this process, fluorinated and roughened surface can be achieved simultaneously. Zhang *et al.* reported a one-step fluorocarbon plasma treatment for chemically modifying polydimethylsiloxane (PDMS) film.[63] An inductively coupled plasma (ICP) machine was employed to perform the plasma treatment with C₄F₈ as the active gas and fluorine source. Figures 2a-c are the schematic and

scanning electron microscope (SEM) pictures of the hierarchical PDMS film used in the plasma treatment and TENG fabrications. After the fluorocarbon plasma, small holes emerged on the surfaces of PDMS islands. Figure 2d shows the voltage outputs of TENGs that assembled from pristine PDMS and PDMS with different cycles of C_4F_8 plasma treatment (12 s per cycles). 1-cycle treatment sharply increased the voltage from 124 V to 193 V. Subsequently, the voltage output could be further improved with the increase of treating cycles, which was ascribed to the increasing amount of F atoms. A maximum voltage of 265 V was attained with 8-cycle treatment. Further extending the treating cycles resulted in a decrease of voltage output. This output reduction was attributed to two reasons: the degradation of electrostatic induction caused by the thicker fluorocarbon layer; and the influence of the roughness factor on PDMS surfaces. From the SEM observation (Figure 2c), 1-cycle treatment can induce significant etching on the PDMS surfaces. This roughness was assumed to contribute to the output improvement. Within 8 cycles, the PDMS surface was found to be partially covered by fluorocarbon and the etching remained effective. After 8 cycles, fluorocarbon polymeric layer capped the entire PDMS surface and thus reduced the roughness factor, diminishing the etching contribution.

Since the electric output of this TENG was largely improved, the electron binding energy of PDMS was expected to be appreciably enhanced by the C_4F_8 treatment. This assumption was verified by the first principle calculations. The relative ability of losing one electron of pristine PDMS and C_4F_8 modified PDMS were analyzed by calculating the vertical ionization energies of two model complexes $(CH_3)_3Si(OSi(CH_3)_2)_2OSi(CH_3)_3$ and $CF_3(CF_2-CF_2)_2CF_3$, respectively. As shown in Figure 2e and f, the ionization energies of PDMS and C_4F_8 modified PDMS were 8.98 and 12.31 eV, respectively, affirming the latter has larger electron binding energy and higher tendency to gain electrons.

If the PDMS film is thin and treated before curing, this fluorocarbon plasma approach could create wrinkled PDMS film with chemically modified surfaces.[64] Figure 3a depicted the fabrication procedure of a wrinkled PDMS film and the corresponding TENG setup. PET/ITO film was used as the substrate for the spin-coated PDMS film as well as the counter electrode of the TENG. SEM and laser scanning microscope (LSM) characterizations in Figure 3b demonstrated the curved topology of PDMS with an average width of $\sim 15\ \mu\text{m}$ and height of $\sim 12\ \mu\text{m}$. The formation of this wrinkled surface was probably caused by the velocity from the fluorocarbon polymer. The disordered momentum of fluorocarbon ions would introduce the random deformation of PDMS. Another possible reason could be the different surface tension between the PDMS and the fluorocarbon polymer layer during the curing process.

The chemical composition and bonding state of the modified PDMS film was explored by X-ray photoelectron spectroscopy (XPS). Strong fluorine peak was identified in the spectrum of C_4F_8 treated PDMS, evidencing the appearance of fluorine atom on the surface. The element contents that were detected by XPS varied with the plasma treating time. When the plasma treating time increased from 50 s to 150 s, O content decreased from 13.29% to 4.4%, and F increased from 25.06% to 42.37%. Combined with the wrinkled surface, these extra fluorine atoms could greatly enhance the electric output of TENG. Figures 3c and d manifest the voltage, current and charge outputs of the flat PDMS, C_4F_8 -treated flat PDMS and C_4F_8 -treated wrinkled PDMS. Compared with the untreated PDMS, C_4F_8 flat PDMS and wrinkled PDMS improved the voltage output from 120 to 150 and 240 V, corresponding to 25% and 100% enhancement, respectively. The peak current and charge outputs of the C_4F_8 -treated wrinkled PDMS in a single cycle were 182 μA , and 528 nC, respectively, which were able to lighting up 72 commercial blue LEDs.

In addition to PDMS, PET surface can also be chemically modified by the fluorocarbon plasma approach.[65] In this case, a mixture of carbon tetrafluoride (CF_4) and oxygen (O_2) gases were used as the plasma source. Analogous to C_4F_8 plasma, CF_4 treatment could yield both chemical modification by fluorination and physical modification by roughening the polymer surface in nanoscale (Figure 4a). The electric potential of the PET before and after modification were measured with Kelvin probe force microscopy (KPFM). The surface potential was increased from 41 mV to 105 mV after the plasma treatment. This improvement was attributed to the enlarged surface charge density, which was induced by the fluorine modification and increased surface area. According to topography characterizations from the atomic force microscopy (AFM), the unmodified PET surface was very smooth with an average roughness of 2.2 nm and a root mean square roughness of 2.8 nm. After the plasma treatment, the average and root mean square roughness were increased to 27.4 and 34.4 nm, respectively. The maximum profile peak height was as high as 320 nm. This surface roughening effect was a result of the anisotropic etching by ionic bombardment due to the applied bias.[66] Based on the fundamental mechanism of TENG, considerable electric output could be anticipated after establishing the rough and fluorinated surfaces. Figures 4b-d present the V_{oc} , I_{sc} and charge transfer amount (Q) of pristine PET, plasma treated PET and polytetrafluoroethylene (PTFE) film. The V_{oc} , I_{sc} and Q of the modified PET reached approximately 220 V, 45 μA and 130 nC, respectively, which were over two times larger than those of the pristine PET film. These electric outputs even outperformed the PTFE film, which is considered as the most efficient triboelectric polymer with the strongest tendency to gain electrons,[1] reinforcing the effectiveness of the CF_4 plasma modification approach.

The fundamental mechanism of the CF₄ modification was studied in this work. XPS was employed to detect the elemental compositions and their local chemical environments on the pristine and modified PET surfaces. Strong fluorine peak emerged in the full survey spectrum of the modified PET sample and no fluorine peak was found from the pristine PET film. C 1s peaks were individually scanned with high resolution. As shown in Figure 4e, for the pristine PET, 66.3% of C-C, 18.4% of C-O and 15.3% of C=O bond can be recognized in the deconvoluted curves, agreeing well with the PET molecular formula. On the other hand, the deconvolution of C 1s peak in the modified PET exhibited apparently reduced amount of C-C (23.3%), increased percentage of C-O (33.9%) and similar amount of C=O (13.3%) (Figure 4f). Three new peaks were identified including CF (9.5%), CF₂ (11.4%) and CF₃ (8.6%). Based on these measurements, two possible reaction mechanisms were proposed for this fluorination process. During the plasma discharging, CF₄ gas was decomposed into free radicals such as ·CF₃ and :CF₂. These active radicals were eager to recombine into CF₄. However, the presence of O₂ suppressed this process by forming ·COF and CO₂, and releasing more ·F free radicals.[67] These free radicals reacted with PET macromolecules *via* two possible routes, named as “implantation” and “graphing” (Figure 4g). For the “implantation” path, free radicals replaced hydrogen or added to pi bonds of the aromatic rings, forming reactive saturated intermediates.[68] For the “graphing” path, :CF₂ radicals first replaced hydrogen, then further reacted with other free :CF₂, and eventually bonded to –CF₂-CF₂-chains.[69]

In summary, developing fluorinated surfaces is a straightforward and effective approach to chemically modifying triboelectric polymers. For the fluorocarbon plasma process, chemically and morphologically modified surfaces can be achieved simultaneously. Since the electron affinity of fluorine atom is extraordinarily high, fluorination could significantly enhance the

materials' ability of holding electrons, giving rise to drastic performance gain of TENG devices. However, for the same reason, this method is only effective for improving polymers with negative triboelectric polarity. Although the majority of current TENGs are built on polymers with negative polarity, materials with positive polarity are frequently used for certain applications (e.g. cottons for wearable electronics). Fluorination would obviously jeopardize their performance by suppressing their tendency of losing electrons.

3. Ion Injection

Ion injection is another chemical modification approach with relatively broad source and target selections since a number of ions could be the charge source. Typically, the triboelectric charge density is not able to reach the level of maximum surface charge density (MSCD), which is determined by the breakdown electric field of air, due to the limited potential differences between two conventional friction surfaces. This means most polymer surfaces can handle extra charges besides the portion acquired from triboelectrification. One intuitive sense to introducing additional charges is directly injecting charged ions into desired surfaces. Through electrostatic absorption, the injected charged ions can remain in the dielectric polymers for years. [70] The most common method to conduct ion injection is plasma treatment. Reactive ion etching (RIE) is a widely used technique to increase the surface roughness of polymer by generating NW morphology with argon and oxygen as the plasma gas.[71] During this process, corresponding argon and oxygen ions are spontaneously injected into the triboelectric polymer, resulting in chemical modulation of surface states. From this point of view, all polymer NWs that made from RIE will experience chemical modification by ion injection.

In addition to the plasma treatment, Wang et al. employed ionized-air gun to controllably implanting extra charges to the fluorinated ethylene propylene (FEP) surface and systematically studied the MSCD of FEP polymer.[70] Compared to other charge implantation methods such as ICP and corona discharging,[72] this hand-sized ionized-air gun is simple and convenient. Ionized-air gun can produce ions with both polarities via triggering the discharge of air inside the gun. The polarity of ion can be manipulated by either squeezing or releasing the trigger. Negative charges (CO^{3-} , NO^{3-} , NO^{2-} , O^{3-} and O^{2-}) were selected in this work since FEP has strong tendency to gain electrons (Figure 5a). In order to achieve the MSCD for high-performance TENG, the metal electrode that attached to the back of polymer layer was grounded. Under this circumstance, the injected negative charges are able to drive equal amount of electron away from the metal electrode to ground, leaving positive charges in the electrode. As a consequence, the electrical field of the double layer charge will be confined only within the FEP film. Since the dielectric strength of FEP is two orders of magnitudes larger than that of air, the grounded connection could allow a much larger charge density compared to the electrode-free FEP film, in which the maximum charge density will be limited by the breakdown voltage of the air.

To investigate the MSCD of FEP film, the charge density on the charge-injected polymer surface was instantaneously monitored by a Coulomb meter, which could measure the charge flow between the bottom electrode and ground (inset of Figure 5b). As shown in Figure 5b, every period of ion injection induced a charge transferring process with an area density of $\sim 40 \mu\text{C}/\text{m}^2$, indicating the same amount of accumulated negative charge on FEP surface. After 17 times of injection, the charge density was saturated at $\sim 630 \mu\text{C}/\text{m}^2$, which was the MSCD of this 50 μm -thick FEP film. This increment of charge density was subsequently investigated by assembling

the ion-injected FEP film into a conventional contact-separation TENG with an Al plate as the counter electrode. The short-circuit charge density ($\Delta\sigma_{SC}$) generated by this TENG should equal to the surface charge density (σ_0) on the FEP film. Figure 5c presented the recorded $\Delta\sigma_{SC}$ of TENG after each ion injection. With no injection, the initial $\Delta\sigma_{SC}$ was only about $50 \mu\text{C}/\text{m}^2$. One ion injection process could increase $\Delta\sigma_{SC}$ to $\sim 100 \mu\text{C}/\text{m}^2$. After that, $\Delta\sigma_{SC}$ was elevated gradually by multiple ion injection processes and ultimately arrived at $\sim 240 \mu\text{C}/\text{m}^2$ at the fifth injection. Further increasing the ion injection times only resulted in very small amount of $\Delta\sigma_{SC}$ enhancement. After the ninth injection, the charge transfer suddenly behaved differently, as marked in the red dashed box. The first pressing process induced a $\Delta\sigma_{SC}$ of $\sim 260 \mu\text{C}/\text{m}^2$. However, when Al was released and separated from FEP film, the $\Delta\sigma_{SC}$ dropped to $\sim 230 \mu\text{C}/\text{m}^2$, leading to the upward shift of the base line. In the following contact and separation process, the $\Delta\sigma_{SC}$ was maintained at the same level. This abrupt decrease of $\Delta\sigma_{SC}$ was attributed to the air breakdown during the first releasing process, which was caused by a voltage drop between Al plate and FEP polymer. The presence of this voltage drop was verified by the numerically calculated potential distribution across the TENG (Figure 5d). As shown in the bottom portion of Figure 5d, a voltage drop (V_{gap}) of $\sim 300 \text{ V}$ existed in the air gap. When this V_{gap} exceeded the breakdown voltage of air, the positive ions in the air discharging corona will partially screen the negative charge on the FEP surface, resulting in the reduced $\Delta\sigma_{SC}$.

As discussed above, the initial short-circuit charge density ($\Delta\sigma_{SC-I}$) from the first pressing motion would be larger than that from the remaining operation circles ($\Delta\sigma_{SC-R}$) after the ninth ion injection. Their relationship was summarized in Figure 5e, where two regions can be clearly recognized. At region I, the V_{gap} caused by the FEP charge was smaller than the air breakdown

voltage, where the $\Delta\sigma_{SC-R}$ was linearly increased with the enlargement of $\Delta\sigma_{SC-I}$. When $\Delta\sigma_{SC-I}$ reached the MSCD of $\sim 240 \mu\text{C}/\text{m}^2$, the $\Delta\sigma_{SC-R}$ started to deviate from $\Delta\sigma_{SC-I}$ due to the air breakdown (region II of Figure 5e). In this region, larger $\Delta\sigma_{SC-I}$ led to smaller $\Delta\sigma_{SC-R}$, implying that the discharging of the air was more intensive with higher $\Delta\sigma_{SC-I}$.

During this ion injection process, the MSCD of triboelectric polymers can be measured. In this work, the relationship between the MSCD (σ_{max}) and film thickness (d) of FEP was studied both theoretically and experimentally. As demonstrated by the calculated results in Figure 5f and 5g, when d decreased from tens of microns to hundreds of nanometers, the MSCD was enhanced by more than two orders of magnitudes, approaching $50 \text{ mC}/\text{m}^2$. Experimentally recorded MSCD of three FEP films with the thicknesses of 50, 75 and $125 \mu\text{m}$ followed the same trend of the calculated curve (Figure 5g). The good agreement of experimental and simulated results confirmed the conclusion that a thinner dielectric film is favorable for the TENG development *via* the improvement of surface charge density, which was consistent with other report.[15]

In addition to the MSCD investigation, this ion injection approach can substantially enhance the output of TENG by maximizing the surface charge density. As shown in Figure 5c, ion injection could enable ~ 5 times larger charge density on FEP surface. In principle, proportionally-enhanced open circuit voltage (V_{oc}) and short circuit current density (J_{sc}) should be obtained accordingly. Figure 6 compared the V_{oc} , J_{sc} , and the power output of TENG before and after the ion injection. Without injection, the spontaneous charge density from the friction could only deliver a V_{oc} of $\sim 200 \text{ V}$ (Figure 6a). When the surface charge density was boosted to MSCD by ion injection, the V_{oc} was increased to $\sim 1000 \text{ V}$ (Figure 6b). Similarly, the J_{sc} was increased from 18 to $78 \text{ mA}/\text{cm}^2$ *via* the ion injection under a pressing force of $\sim 20 \text{ N}$ (Figures 6c

and d). When deforming the TENG at ~ 300 N, the J_{sc} could reach as high as ~ 900 mA/cm² (Figure 6e). Under this testing condition, the actual power output of the ion-injected TENG was estimated by connecting the device with a series of loads with different resistances. As shown in Figure 6f, the voltage and current output increased and decreased gradually with the increase of the load resistance, respectively. The opposite trend of voltage and current output produced a maximum power output density of ~ 315 W/m² with the external resistance of 300 M Ω (Figure 6g).

In general, the ion injection approach is simple, effective and applicable to many triboelectric polymers. It is a fairly efficient technique and by far the most commonly adopted method of polymer surface modification for improving TENGs' output. Nevertheless, the fabrication conditions and processes are relatively complicated, which may bring obstacles for further scaling up, particularly considering the polymer sheets are extremely low-cost and roll-to-roll manufactured raw materials.

4. Sequential Infiltration Synthesis

Sequential infiltration synthesis (SIS) is a molecular infiltration process on the basis of atomic layer deposition (ALD) technique.[73-75] When certain polymers were implemented, the large permittivity of metalorganic ALD precursors allow the deep infiltration of inorganic compounds during ALD process, leading to inorganic/organic hybrid materials. SIS has been successfully used to convert the block co-polymer nanopatterns into more durable inorganic patterns and to improve the polymeric lithography resistance towards the subsequent etching.[76-78] Inspired by these developments, SIS was expected to be effective in tailoring the internal composition and

electrical properties of polymer films, which may provide an ultimate solution for modifying triboelectric materials in bulk volume.

Based on SIS, Yu and coworkers reported an internal AlO_x doping of several triboelectric polymers, including PDMS, polyimide (Kapton) and poly(methyl methacrylate) (PMMA).[79] AlO_x molecules were found to be capable of penetrating into these polymers as deep as $\sim 3 \mu\text{m}$, which effectively tuned the bulk electrical property of the films. TENG devices using the modified polymer films exhibited enhanced power output; and this enhancement remained effective after the surface of polymer film was polished off for more than $2 \mu\text{m}$. AlO_x was selected as the dopants since trimethyl aluminum (TMA, ALD precursor of Al_2O_3) has desirable permittivity in a number of polymers such as polystyrene (PS), PP, polyethylene (PE), and poly(vinyl chloride) (PVC) and PMMA.[73] The SIS doping process was carried out in a homemade ALD system by sequentially introducing TMA and H_2O vapor to the polymer film at 80°C with controlled exposure time and cycles. Figures 7a and b show the cross-sectional SEM images and corresponding energy dispersive spectroscopy (EDS) elemental mappings of the pristine PDMS film and the same film after 5-cycle sequential TMA/ H_2O infiltration (marked as AlO_x -doped PDMS), respectively. PDMS elements including silicon (Si), oxygen (O) and carbon (C) were all identified with a uniform distribution in the pristine film and no aluminum (Al) signal was detected (Figure 7a-ii-v). For the SIS-treated PDMS, Al signal was clearly detected and was concentrated within the top $\sim 3 \mu\text{m}$ region, revealing the effective infiltration depth (Figure 7b-ii). Similarly, both O and C elements exhibited a concentrated signal within the top $\sim 3 \mu\text{m}$ region matching well with Al distribution (Figure 7b-iv and v). The concentrated O element was originated from Al-O bonds formed after H_2O molecule infiltrated into polymers and reacted with TMA. The unreacted methyl groups on TMA could be the main source

responsible for the concentrated C signal. This elemental distribution analysis evidences the successful deep infiltration of both precursors in the polymer film and no surface coating of Al_2O_3 was identified.

XPS characterizations further confirmed the presence of Al element in the PDMS after the SIS infiltration. As shown in figure 7c, a small peak of Al 2p appeared at the low binding energy region from the AlO_x -doped PDMS film. The high resolution scan of Al 2p signal demonstrated a peak shift from 75.6 eV to 74.7 eV after the SIS treatment, which was caused by the formation of the defective aluminum oxides such as Al_2O and AlO (Figure 7d).[80] The nonstoichiometric aluminum oxide may introduce extra charge carrier sites and thus improve the charge capacitance of the modified PDMS film. This hypothesis was verified by the dielectric constant measurement (Figure 7e). SIS doping increased the dielectric constant of PDMS films from ~ 2.4 to ~ 2.7 within the test frequency range, implying that modified PDMS was capable of storing more charges compared with the pristine one.

Similar to previously discussed two strategies, the SIS doping could also arbitrarily tune the electron affinity of triboelectric polymers and modulate the charge attraction/repulsion ability. For the AlO_x doping case, aluminum oxide will lower the electron affinity of PDMS since AlO_x is a triboelectric positive material with high tendency to lose electrons. As a consequence, electron would be injected from AlO_x -doped PDMS to PDMS upon their friction, leading to a positively charged surface in the doped PDMS and negatively charged surface in the pristine PDMS (Figure 8a). On the contrary, two PDMS films without modification could not induce such a charge redistribution due to the identical surface potential. Therefore, the AlO_x doping process should be able to significantly raise the TENG performance. Figures 8b-d show the V_{oc} , J_{sc} , and the total amount of charge transferred under short-circuit condition (ΔQ_{sc}) of TENGs

with two configurations: PDMS-PDMS and PDMS- AlO_x -doped PDMS. For pair of PDMS- AlO_x -doped PDMS, the average peak values of the V_{oc} , J_{sc} , and ΔQ_{sc} reached 2.3 V, 2.2 $\mu\text{A}/\text{cm}^2$ and 45 $\mu\text{C}/\text{m}^2$, respectively, which were comparable to TENGs that built with typical triboelectric couples such as teflon-metal pair.[15, 17] In comparison, only 0.3 V of V_{oc} , 0.3 $\mu\text{A}/\text{cm}^2$ of J_{sc} and 5 $\mu\text{C}/\text{m}^2$ of ΔQ_{sc} were obtained for the untreated PDMS pair.

One unique advantage of this SIS doping method is the simultaneous surface and bulk modification of the polymer's electrical property. The bulk doping capability allowed that the performance gain of TENGs could survive even after polishing off 2 μm -thick polymer materials. Figure 8e presents the V_{oc} variation as a function of the removed thicknesses. ~95% of V_{oc} was remained after 2 μm -thick material was polished. Such a durable TENG performance was contributed by the deep penetration (~ 3 μm) of AlO_x dopants. Further polishing the film dramatically reduced V_{oc} due to the expose of unmodified PDMS. A minimum value of ~0.3 V was received after removing 5 μm polymer, which was comparable to the TENG output with the pristine PDMS pair.

The up limit of this SIS doping process was revealed by varying the infiltration cycles and measuring the related TENGs output. As shown in Figure 8f, the peak V_{oc} was improved from 0.3 V to 1.9 V by only 2 cycles of SIS, suggesting the high effectiveness of this polymer modification approach. The V_{oc} kept increasing with the increment of SIS cycles and eventually saturated at ~2.4 V after 10 cycles of infiltration. Almost stable values were recorded when further increasing the cycle numbers. This V_{oc} variation is believed to be a consequence of the unique reaction process of AlO_x in the polymer material. During the first 10 cycles of infiltration, TMA diffused into PDMS and accumulated inside the polymer film, resulting in the rapid

increase of V_{oc} . After 10 cycles, more deposition might cover the entire PDMS surface and prevent further inside infiltration. Thus the growth mode switched back to regular ALD deposition of continuous Al_2O_3 film on the surface. Because additional cycles of infiltration contributed no internal doping, the electric property and TENG output would not exhibit any further change.

The underlying mechanism of this SIS strategy shares certain similarity with the aforementioned ion injection approaches. Both of them control the surface charge density of triboelectric polymer by introducing extra charged ions or molecules. However, compared to other chemical modification techniques, the SIS doping process extends the modification region from the surface to bulk portion of triboelectric polymers. This improvement is important for developing high-performance TENGs with good resistance to the surface wearing issue. Moreover, the SIS doping is versatile in tailoring broad range of triboelectric polymers since a variety of metalorganic molecules possess high permittivity in most polymer chains.[81] With proper selection of doping precursor and precise control of infiltration condition, SIS doping could be a promising strategy to engineering electric and dielectric properties of many polymers, and improving the performance of functional polymer based devices, such as TENGs.

5. Molecular-Targeting Functionalization

The chemical modification process through molecular-targeting functionalization is closely related to the chemical sensing function of TENGs. TENG is a good platform for developing various sensors including motion and chemical sensors.[46] By recording the output variation, TENG-based motion sensors can detect different types of mechanical deformations such as human touch and sound. Meanwhile, TENGs can also be used as self-powered chemical sensors

since the amplitude of the triboelectric signal is proportional to the surface charge density that is largely influenced by the surface chemical state. The operation principle of the TENGs-based chemical sensor relies on the surface charge density variation induced by targeting molecules. When the target molecules are attached on the surface of triboelectric polymers, possible charge transfer could emerge between the chemical species and triboelectric materials, leading to the change of TENG output.[21, 82-84] In this section, the TENG-based chemical sensors are discussed with an emphasis on surface functionalization for detecting specific molecules.

Li et al. reported a self-powered phenol sensor based on the β -cyclodextrin (β -CD) enhanced triboelectrification process.[85] Figure 9a presents the schematic of the TENG device with PTFE and β -CD decorated TiO_2 NWs as two electrodes. TiO_2 NWs were grown on Ti foil with an average diameter and length of 73.4 nm and 1.92 μm . In this structure, β -CD was a bifunctional component that can recognize phenol molecule and enhance the TENG performance at the same time. On one hand, β -CD molecule is composed of a hydrophobic internal cavity and hydrophilic external side chains. This special structure allows it to capture guest molecules with appropriate polarity and dimension, and forming a host/guest inclusion complex. The diameter of β -CD cavity is particularly suitable for the selective absorption of phenol, which making it a particular molecular probe for phenol.[86] On the other hand, β -CD can alter the overall TENG performance by conducting charge transfer with TiO_2 NWs. Specifically, β -CD is binding on TiO_2 surface *via* hydroxyl groups. Electrons could thus be injected from the hydroxyl groups to TiO_2 surface due to the coordination effect between the ligand and the metal under visible light (Figure 9b).[87] Consequently, the positive charges on TiO_2 surface that produced from the triboelectrification with PTFE were partially neutralized. This means PTFE can extract extra electrons from TiO_2 after β -CD functionalization, and further increase its surface charge density,

and therefore improve the TENG output. The influences of β -CD concentration on the triboelectric output were studied with a 4 cm $\times$ 4 cm TENG (Figure 9c). Both current and voltage signals were proportionally increased with the augment of β -CD concentration (Figure 9d). When TENG was treated with 80 mM β -CD, the electric output reached ~ 55 V, which was more than 8 times larger than the unmodified devices. A voltage plateau emerged at the region of β -CD concentration larger than 80 mM, which may be caused by the saturation of β -CD on TiO_2 surface. This experiment strongly evidenced the TENG performance-gain function of the β -CD modification.

The phenol detecting ability of this β -CD tailored triboelectrification was evaluated on TENGs modified by a fixed β -CD concentration of 80 mM. The constant volumes (20 mL) of phenol solution with varied concentrations were introduced to treat the β -CD decorated TiO_2 NWs. As shown in Figure 9e, the current output was clearly dependent on the phenol concentration. At the region of 10-100 mM phenol, the current signal decreased almost linearly with the increase of the phenol concentration. The reduction of electric output is ascribed to the phenol absorption onto the TiO_2 NWs surface via the β -CD cavity. After the whole surface was covered by phenol, the triboelectrification process might only happen between PTFE and phenol instead of the original PTFE and TiO_2 . Whereas, compared with TiO_2 , phenol has lower tendency to give electron to PTFE, and therefore jeopardized the TENG output. To render a direct view of the detecting efficiency, the current ratio $((I_0 - I)/I_0)$ was plotted as a function of phenol concentrations, where I_0 was the original current output and I was the current output after phenol treatment. As shown in Figure 9f, the sensitivity of the TENG sensor was calculated to be $0.01 \mu\text{M}^{-1}$ in the sensing range of 10-100 mM.

Besides the good sensitivity, this β -CD modified TENG sensor exhibited excellent selectivity and reusability. The detecting performance of this sensor for a number of other organic species that possessed similar molecular structures with phenol were tested and presented in Figure 9g. With the same concentration of 50 mM, the recorded current ratio from phenol detecting was appreciably larger than all other organic species, implying the good selectivity of this sensor. Additionally, after the sensing process, the device could be completely recovered by ethyl alcohol rinsing without losing any electric output. The exceptional sensitivity, selectivity, reusability, low cost, environmentally friendly and self-powered characteristics promise this β -CD modified TENG in future phenol sensing field.

Jie et al. developed a self-powered TENG sensor for dopamine (DA) detection with PTFE-Al triboelectric pair. [88] The operation of this DA sensor relies on the chemical modification of PTFE with the polydopamine(PDA). Under slightly alkaline condition, DA molecule would go through a self-polymerization and produced PDA chains on the PTFE surfaces (Figure 10a). Figure 10b schematically depicts the PDA modification process, where PTFE film was first soaked in the buffer solution containing different concentrations of dopamine. After adjusting the PH to 8.5, considerable amount of PDA was formed on the PTFE surface, turning the film color from white to brown and increased the hydrophobicity of PTFE. Since the electron affinity of PDA layer was substantially smaller than PTFE, the PDA layer would significantly reduce the surface charge density of the PTFE film, and therefore reduced the TENG output.

Figure 10c manifests the current output ratio of TENG under a series of DA concentrations. In general, current output diminished with the increase of DA concentration. As shown in the inset of Figure 10c, a proximately linear relationship was identified between the current ratio and Napierian logarithm of the DA concentration within the testing range (10 μ M and 1 mM). The

detection limit of this TENG sensor was found to be 0.5 μM , indicating its good sensitivity. The selectivity of the TENG sensor was further studied by purposely introducing other interference factors into the DA solution including uric acid (UA) and ascorbic acid (AA). Conventional electrochemical detections of DA usually suffer from the fouling effect resulted from the oxidation of UA and AA. However, in this TENG sensor, UA and AA can be well excluded since these two molecules have poor interaction between PTFE. Figure 10d compares the current ratio of the TENG sensor after exposing to DA, UA and AA solution with same concentration. As expected, only DA considerably altered the current signals, suggesting the good selectivity of this sensor.

Compared to conventional chemical monitoring techniques, TENG-based chemical sensors share common characteristics such as high sensitivity, selectivity and reusability. Meanwhile, since polymers are typically the active materials in TENG, existing principles of molecule detection relying on polymer reactions can be seamlessly transferred to TENG sensors. Most importantly, the self-powered capability of TENG-based chemical sensors greatly promise them in developing battery-free sensing systems with exceptional long life span.

6. Conclusion

Chemical modifications have been evidenced to be an effective approach for controlling the TENG output through regulating the surface charge density of triboelectric polymers. By enhancing the surface charge density, numerous polymers can be utilized to build high-performance TENGs without losing their intrinsic merits. The largely broadened material selections allow more flexible structural designs of TENGs. Compared to the vast research efforts of pursuing new configurations and functions, chemical properties and surface

functionalization of triboelectric polymers are relatively less explored despite their fundamental role in controlling the charge density and overall triboelectric performance. Both theoretical calculations and experimental endeavors are highly desired for promoting the existing or discovering new chemical modification techniques. Computational predictions would facilitate our understanding of surface chemical states and consequently guide experimental explorations. Developing innovative chemical functionalizing process for the teflon family can potentially uplift the limit of TENG outputs. Chemical modification, particularly to the bulk properties, would bring practical impacts to output enhancement, device configuration optimization and working lifetime extension of commercial TENG devices in the near future.

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Figures and Captions

Figure 1. (a) Schematic of TENGs built with four different contact pairs: (i) PET:PET, (ii) PET:P-PET, (iii) PET:F-PET, (iv) P-PET:F-PET. (b) Open-circuit voltage (V_{oc}) of corresponding TENGs, showing substantial performance gain after the chemical modifications. (c) Stability test of TENG with pair (iv), presenting no output reduction within one month. Reprinted with permission from ref 61. Copyright 2015, American Chemical Society.

Figure 2. (a) Schematic of fluorocarbon plasma modification process. (b) SEM and (c) high-magnification SEM images of PDMS hierarchical structures after plasma treatment. (d) The variation of voltage output versus plasma treating cycles. (e,f) Calculated vertical ionization energy of model complexes of (e) pristine PDMS layer and (f) plasma deposited fluorocarbon layer. Higher ionization energy was obtained from the fluorocarbon treated film, meaning the promoted electron attracting capability of the modified PDMS. Reprinted with permission from ref 63. Copyright 2014, Elsevier.

Figure 3. (a) Schematic of the wrinkled PDMS fabrication procedures, including spin coating of PDMS on PET/ITO substrate, C_4F_8 plasma treating and TENG assembly. (b) SEM and laser scanning microscope (LSM) image of the wrinkled PDMS film. (c) Voltage output of TENGs made from untreated, C_4F_8 plasma treated and wrinkled PDMS films. (d) The current and charge comparison of corresponding TENGs. Reprinted with permission from ref 64. Copyright 2015, Wiley-VCH.

Figure 4. (a) Schematic illustration of ICP plasma modification process and the modified PET surface. (b) Open-circuit voltage, (c) short-circuit current, and (d) induced charge of TENGs assembled from pristine PET, plasma treated PET and PTFE films. (e,f) High-resolution XPS characterization and deconvolution of the C1s peak from the pristine (e) and modified (f) PET surfaces. (g) Schematics of two fluorination mechanisms during the plasma treatment. Reprinted with permission from ref 65. Copyright 2015, Wiley-VCH.

Figure 5. (a) Schematic illustration of injecting negative ions onto FEP surface with air ionization gun. The back electrode was grounded to maximizing the surface charge density. (b) In situ measurement of charge transfer from the ground to back electrode of FEP film during the step-by-step ion injections. (c) The variation of short-circuit charge density as a function of ion injection cycles. (d) Schematic and numerically calculated potential distribution across the Al and FEP gap, showing the presence of voltage drop in the gap, which could cause the breakdown of the air. (e) The relationship between the initial short-circuit charge density ($\Delta\sigma_{\text{SC-I}}$) from the first pressing motion of TENG and the short-circuit charge density ($\Delta\sigma_{\text{SC-R}}$) in the remaining cycles. Inset is the magnified curve for comparing $\Delta\sigma_{\text{SC-I}}$ and $\Delta\sigma_{\text{SC-R}}$. (f) Theoretically calculated relationship between the maximum surface charge density (σ_{max}) and the film thickness d of FEP. (g) Plot of the above curve in the range of 20-150 μm region and three points of experimentally measured σ_{max} for the d of 50, 75 and 125 μm . Reprinted with permission from ref 70. Copyright 2014, Wiley-VCH.

Figure 6. (a,b) V_{oc} of TENG (a) before and (b) after the ion injection process. (c,d) J_{sc} of TENG (c) before and (b) after the ion injection process with a pressing force of ~ 20 N. (e) J_{sc} of TENG after ion injection with a deformation force of ~ 300 N. (f) The V_{oc} and J_{sc} variations of ion injected TENG versus different external load resistances. (g) Power density variation of ion injected TENG as a function of different external load resistances. Reprinted with permission from ref 70. Copyright 2014, Wiley-VCH.

Figure 7. (a, b) Cross-sectional SEM images (i) and EDS mappings of a pristine PDMS film (a) and an AlO_x-doped PDMS film (b) for Al, Si, O, and C elements (ii-v). (c) Full range XPS spectra acquired from pristine PDMS and AlO_x-doped PDMS. Small Al 2p peak was identified on the spectrum of AlO_x-doped PDMS. (d) Al 2p scan for pristine PDMS, AlO_x-doped PDMS film and ALD grown Al₂O₃ on silicon substrate. The peak position shift indicates the presence of defective oxides in AlO_x-doped PDMS film. (e) Dielectric constant measured from pristine PDMS and AlO_x-doped PDMS, showing increased dielectric constant of PDMS due to the AlO_x doping. Reprinted with permission from ref 79. Copyright 2015, Wiley-VCH.

Figure 8. (a) Schematic of charge redistribution between pristine PDMS and AlO_x-doped PDMS films upon contact as a consequence of triboelectrification. (b) The V_{oc} , (c) J_{sc} and (d) charge transfer amount under short-circuit condition (ΔQ_{sc}) of TENGs built from PDMS with and without AlO_x doping. The inset of Figure 2c is the enlarged current output (dashed square box on Figure 2c) generated by one pressing and releasing cycle. (e) Normalized V_{oc} of TENGs as a function of the material thickness that was polished off. Voltage output of AlO_x-doped PDMS film without any polishing was defined as unit. Insets are Al element EDS mapping of AlO_x-doped PDMS films before (left) and after (right) ~5 μm polishing. (f) V_{oc} variation versus the doping cycles of AlO_x on PDMS film. Reprinted with permission from ref 79. Copyright 2015, Wiley-VCH.

Figure 9. (a) Schematic of TENG device with β -cyclodextrin ($\beta\text{-CD}$) modified surface for phenol detection. (b) Schematic illustrations of electron transfer from hydroxyl group of $\beta\text{-CD}$ to TiO_2 nanowires. (c) A photograph of as-fabricated TENG device. The scale bar is 2 cm. (d) Voltage output increment of $\beta\text{-CD}$ modified TENGs with the increase of $\beta\text{-CD}$ concentrations. (e) Current density reduction of phenol treated TENGs with the increase of phenol concentration. (f) The determination of sensitivity and detecting range of the TENG sensor in terms of both current and voltage output. (g) The current ratios of TENGs treated by various chemicals, showing particular effective sensing function for phenol. Inset is the demonstration of reaction mechanism between $\beta\text{-CD}$ and organic species. Reprinted with permission from ref 85. Copyright 2015, Royal Society of Chemistry.

Figure 10. (a) Schematic of the reaction mechanism for dopamine (DA) polymerization. (b) Schematic illustration of polydopamine (PDA) deposition on PTFE surface and the influence of PDA on the voltage output of TENG. Insets are photographs of water droplet on the surface of pristine (i) and PDA modified (ii) PTFE. (c) Sensitivity characterization of the TENG sensor for the DA detection. Inset is a plot showing the linear relationship between the current ratio and Napierian logarithm of the DA concentration. (d) Selectivity determination of the TENG sensor by introducing interference factors including ascorbic acid (AA) and uric acid (UA). Large current ratio can only be obtained in the solution that contains DA, implying the good selectivity. Reprinted with permission from ref 88. Copyright 2015, American Chemical Society.