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Liquid Doping Materials as Micro-carrier of Functional Molecules for Functionalization of Triboelectric Materials and Flexible Triboelectric Nanogenerators for Energy Harvesting and Gesture Detection

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Abstract:

The modification or functionalization of triboelectric materials is of great importance for improving triboelectric nanogenerator’s triboelectric performance. Traditionally, chemical introduction was the major method for functionalization of TENG materials which relied on certain reactive molecules and complex chemical process. The variety of functionalization was limited as majority functionalization molecules such as halogens are not chemical reactive. Here, high permittivity liquid was dispersed in polydimethylsiloxane (PDMS) matrix by emulsion mixing and regarded as functional molecules micro-carrier for functionalization of triboelectric materials. Due to the solubility of liquid, functionalized PDMS composite could be facilely fabricated by corresponding functional additive dissolved liquid, avoiding functional additive’s necessity of chemical reactivity and indicating great extensibility in functionalized triboelectric materials. Fluoroethylene carbonate (FEC) additive for fluorine functionalization and benzyl chloride additive for chloride functionalization were studied for demonstration of this concept. The PDMS composite possessed high permittivity and functional property synchronously and resulted enhancement of 5.7-fold in output voltage, 5.4-fold in current and 44.8-fold in power density as compared with pristine PDMS, which was obtained by fluorine functionalized composite, PDMS-FHD45. This work demonstrated that functional additive liquid doping composite was a promising method for functionalization of triboelectric materials for great extensibility.

Key words: Fluorine functionalization; Polydimethylsiloxane; High permittivity liquid; Fluoroethylene carbonate; Triboelectric materials

Introduction

Energy, which powers the human civilization, is the origin of successive science and technology revolutions in human history.[1] For centuries, fossil energy acted as the major energy sources of human society since first industry revolution but had consumed significantly under the rapidly increasing demand of energy.[2] Besides, the environment problems caused by fossil energy such as air pollution and global warming are also threatening our daily life.[2-4] The energy sources must be adjusted to renewable power sources which should be highly efficient, clean, sustainable and renewable power for the future human society.[3, 5] In 2012, Prof. Zhonglin Wang fabricated first triboelectric nanogenerator (TENG) for harvesting ambient mechanical energy and it had displayed promising potential owing to the merits such as good suitability and high energy conversion efficiency.[6-8] The well accepted TENG's working principle is the combination of triboelectric effect and electrostatic induction.[5, 9] Usually, TENG is composed of two separated dissimilar materials which have opposite electron affinities, regarding as electronegative and electropositive materials.[10-12] In general, constituent materials have directly influence on TENGs' energy density and it is critical to develop materials with high triboelectric performance, low cost, mass production facility for the upcoming TENG charging era.[4, 13-17]

Functionalization of TENG materials was one of the most effective methods for improving friction materials' triboelectric performance, such as halogens introduction because of halogens' strong electron affinity.[4] Some published works had proved its success.[6, 18-21] Generally, the functional molecules introduction required chemical reaction between reactive halogens contained molecules and substrate, which led to a complex process and limited choices in reactive molecules.[21-23] In our previous work, we proposed high permittivity liquid doping PDMS composite (PDMS-HD) instead of common solid doping PDMS. The preparation of PDMS-HD composite employed PDMS pre-solution state to form the precursor emulsion, in which the high permittivity liquid was well dispersed in PDMS pre-solution. With subsequent heat curing of PDMS solution, PDMS matrix was formed and the liquid was thus encapsulated in the matrix.[24-27] The introduced liquid could be well dispersed in PDMS matrix which not only reduced the effective thickness of pure PDMS but also increased the permittivity of composite like solid doping materials, resulting significantly improvement of triboelectric performance.[28-31] Moreover, the dispersed liquid droplets in the emulsion could be applied as micro-carrier of functional molecules if the dispersed liquid possessed good solubility and the concept had been widely applied in emulsion polymerization as reaction space for monomer polymerization.[32, 33] Similarly, the high permittivity liquid droplets in PDMS-HD composite should have the potential of micro-carrier for various functional molecules without chemical reactive group via simply dissolution and further result in various corresponding functional PDMS-HD composite with performance enhancement.

By latest research, it is notable that fluorine possessed stronger electron affinity than Si-O in PDMS.[34-36] Hence, it is reasonable to integrate the advantages provided by fluorine and other materials for preparing powerful materials which could meet the rising demands of TENG materials. Herein, we employed the advantage of aforementioned PDMS-HD to develop convenient and efficient method of fluorinate functional materials, in which the liquid droplets in PDMS matrix acted as the fluorinated molecule micro-carrier.[33] The fluorinated molecule was fluoroethylene carbonate (FEC) and dissolved in the high permittivity liquid which was the mixture of propylene carbonate (PC) and ethylene carbonate (EC).[37] The FEC solution was thus applied as the new doping liquid of PDMS to prepare fluorine functionalized composite (PDMS-FHD). The triboelectric performance was significantly enhanced on the basis of high permittivity doping PDMS-HD composite. The maximum enhancement was approximately 5.7 folds in voltage and 5.4 folds in current at 45% liquid filling ratio, as compared with pristine PDMS in same test condition. The corresponding instantaneous power density enhancement was also calculated as much as 44.8 folds.

PDMS-FHD composite exhibited good transparence and could be coated on fabric to prepare flexible and wearable TENGs for energy harvesting and self-powered gestures detection.[38] Furthermore, the method could be generalized to design functional composite via corresponding functional additive dissolved liquid, such as FEC additive for fluorine functionalization and benzyl chloride additive for chloride functionalization which had no requirement in chemical reactive group of functional molecules. This work provided and demonstrated a facile method for functionalization of TENG materials through corresponding functional additive dissolved liquid filling composite, which broadens the insights of functionalization of TENG materials beyond chemical method and further proves it as an adoptable and attractive method of great extensibility for efficient TENG energy harvesting.

2. Results and discussion

High permittivity liquid doping PDMS composite was made from curing of its emulsion precursor, as illustrated in Fig 1. The emulsion consisted of two immiscible liquids: PDMS solution which was continuous phase to encapsulate the dispersed phase, and high permittivity liquid acted as dispersed phase which were micro-droplets.[24, 33] The continuous phase of PDMS solution was cured by heat and the droplets of liquid thereby were encapsulated in the cured PDMS matrix. The introduced high permittivity liquid in cured PDMS matrix increased the permittivity and decreased the effective thickness of friction PDMS synchronously, which led to significantly enhancement of output performance. Moreover, emulsion system was a common phenomenon in our daily life from milk to cosmetics. One of the most famous application of emulsion in chemistry was the emulsion polymerization in which the dispersed phase droplets were applied as microreactors for polymerization.[32, 33] Inspired by this, we proposed that the dispersed high permittivity liquid phase in the composite could be regarded as micro-carrier of functional molecules on the basis of liquid doping materials, resulting functional TENG materials and avoiding the requirement of chemical reactive group. The functional molecules thereby were not limited to chemical reactive molecules such as silane coupling reagent. Fluorine was reported as better electron affinity than PDMS in TENG materials.[20, 35, 36] Here, fluorine was introduced into high permittivity liquid, the micro-carrier, to fabricate better performed TENG materials. On such purpose, FEC was chosen as the fluorine functional additive because it was the fluorine derivative of EC, and no other new chemical group was introduced when it was added to the high permittivity liquid and it was miscible with carbonate liquid. [39] The other chemical group influence on the composites triboelectric performance would be excluded. The fluorine in FEC was thus could be introduced in PDMS-HD composite by the FEC in high permittivity liquid solution without chemical reaction, indicating a simple method of fluorinated functionalization of PDMS and avoiding the necessity of chemical reactivity in chemical methods.

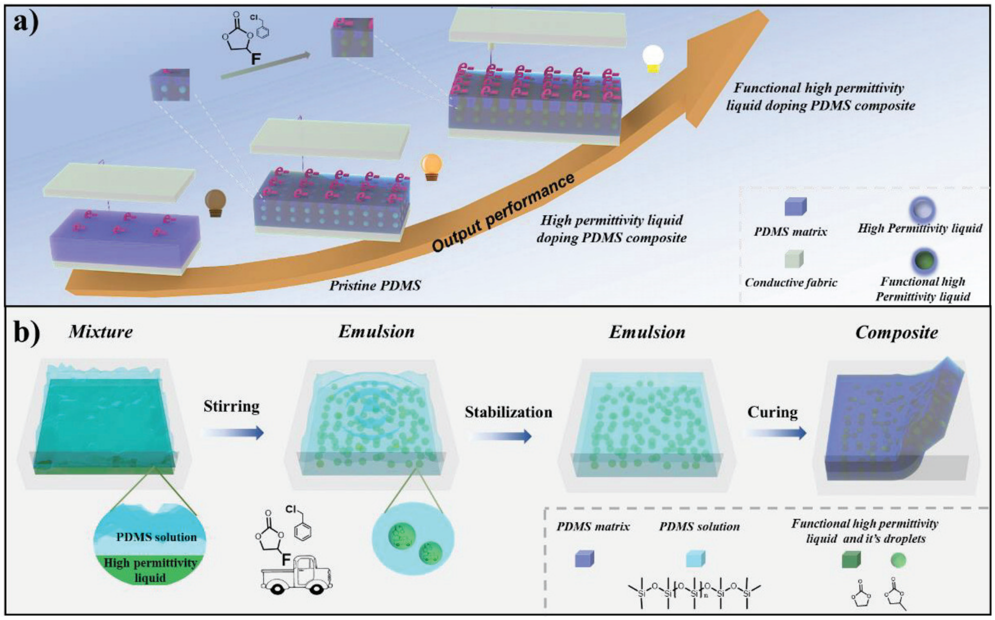


Figure 1. a) Scheme of functional high permittivity liquid doping PDMS composite. b) Fabrication of high permittivity liquid doping PDMS composite and fluorine functionalization.

A vertical contact-separation mode TENG was employed to evaluate the triboelectric performance of PDMS or PDMS composites. The TENG was composed of two separated square acrylic substrates which were connected by four sponges on the corners. The electropositive friction material was the Cu/Ni coated fabric (conductive fabric) which was adhered to another circular acrylic substrate with a diameter of 4.4 cm.[40] The circular acrylic substrate was then attached to the top square substrate, leaving a maximum gap distance of 5 mm space between conductive fabric and bottom square substrate. The PDMS or PDMS composites with conductive fabric electrode were adhered to the bottom substrates which were electropositive friction materials. The test condition was fixed in 100 N at frequency of 3 Hz for a consistent evaluation of triboelectric performance among different samples. According to the theory studies of vertical contact-separation mode of TENG, the TENG was not only an energy output device but also an energy storage.[29, 41] In consequence, the output performance of TENG had strong correlation with the capacitance of the device which was given by in theoretical equation

$$V_{oc} = \frac{\sigma_0 * x(t)}{\varepsilon_o} \tag{1}$$

in which, the ε_0 and σ_0 represented the vacuum permittivity and triboelectric charge density of triboelectric materials, respectively.[41] TENG's output performance has strongly dependence on the capacitance of friction materials. And the capacitance could be expressed by

$$C_{max} = \varepsilon_0 * S \frac{\varepsilon_r}{d} \tag{2}$$

Where the ε_r, d, S are permittivity, thickness and contact area of triboelectric materials, respectively.[29] The ε_r was described by an idea model.[24, 42, 43]

$$\varepsilon_r = \varepsilon_m * V_m + \varepsilon_f * V_f \tag{3}$$

ε_m and ε_f are the permittivity of matrix and filling particles; V_m and V_f are the volumetric fraction of matrix and filling particles. Consequently, the decrease of the pure PDMS's effective thickness as well as increase of permittivity could enhance the device's capacitance when the high permittivity liquid was filled in PDMS matrix.

2.1 Fluoroethylene carbonate (FEC) additive for fluorine functional PDMS-HD composite

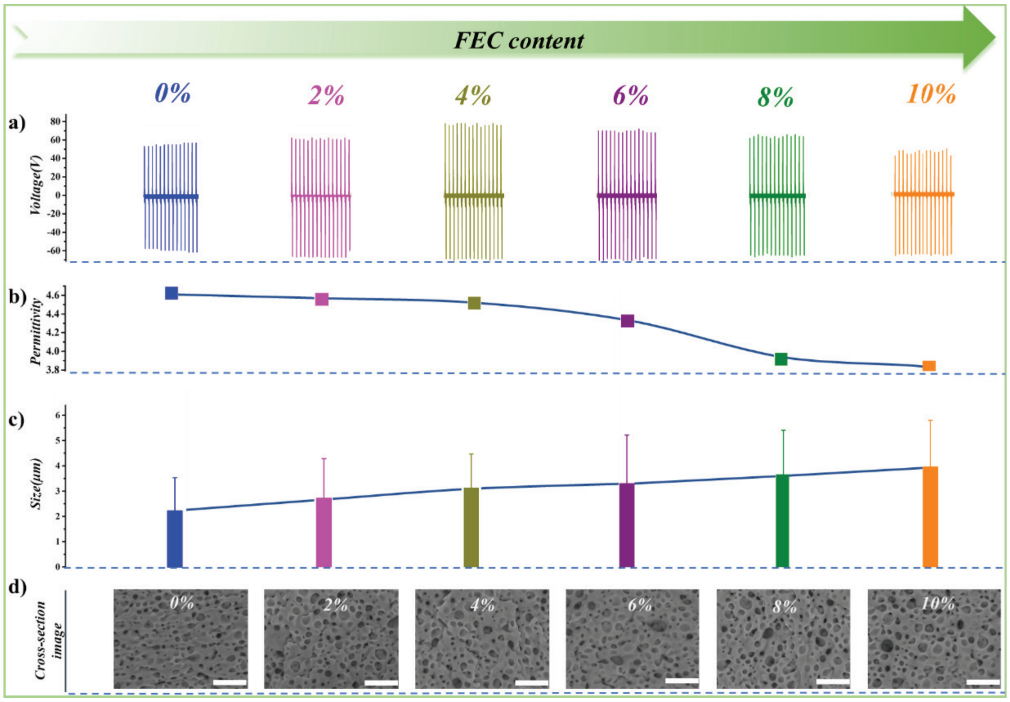


Figure 2. The performance of different FEC content's PDMS-FHD films at 30% high permittivity liquid mass filling ratio, a) output voltage, b) permittivity, c) PDMS-FHD composite pores' size, d) inner region SEM images of different FEC additive PDMS-FHD composite films. The scale bar is 20 μm.

The influence of high permittivity liquid's FEC additive content on PDMS composite's triboelectric performance was evaluated at first, as shown in Fig 2 and 3. The blank group was pristine PDMS film and its output voltage was around 20 V, with corresponding 0.76 μA of output current and 1.18 nC/cm^2 of transfer charge, as presented in Fig 4. While the high permittivity liquid was introduced to the PDMS matrix at 30% mass ratio (PDMS-HD30, 0% FEC content in doping liquid shown in Fig 2), the output voltage was enhanced to 61 V which was 2.9 folds of pristine PDMS as well as 2.8 folds of current and 3.1 folds of transfer charge. The results indicated that high permittivity liquid doping was an effective method of improving triboelectric performance of PDMS. FEC was then gradually added to the high permittivity liquid which used to prepare PDMS-FHD composite films on the basis of high permittivity liquid doping PDMS. The output voltage was increased from 67 V to 78 V when FEC content of high permittivity liquid increased from 2% to 4%. The current and transfer charge also exhibited similar tendency from 2.33 μA, 3.68 nC/cm^2 at 2% to 2.75 μA, 4.34 nC/cm^2 at 4%, as shown in Fig 3 and Tab S1. The enhancement could be ascribed to FEC in PDMS liquid composite that was featured with high electron affinity as fluorine in the molecule frame of FEC.[6, 18, 23, 44, 45] However, the triboelectric performance of PDMS-FHD composite films showed obviously declining as the content of FEC in doping liquid kept in increasing. The output voltage decreased gradually from 72 V at 6% to 67 V at 8%, then 65 V at 10% together with decreased current and transfer charge. The decay of output performance was contrary to the increased FEC content along with higher electron affinity. To figure out the reason of decay, the permittivities of composites were measured and showed a negative proportion to FEC content, 4.62 at 0%, 4.56 at 2%, 4.52 at 4%, 4.32 at 6%, 3.92 at 8%, 3.83 at 10% FEC content, as shown in Fig 2b. The lower permittivity undermined triboelectric performance of PDMS-FHD composite, which was contradictory to the electron affinity brought by FEC. The maximum enhancement of FEC was thus determined at 4% which showed around 28% in output voltage, 30% in current, 19% in transfer charge as compared with high permittivity liquid PDMS composite without FEC additive, proving an effective method of fluorinate functional PDMS composite. When it was compared with pristine PDMS film, the total enhancement was calculated as 3.9 folds in output voltage, 3.6 folds in current and 3.7 folds in transfer charge.

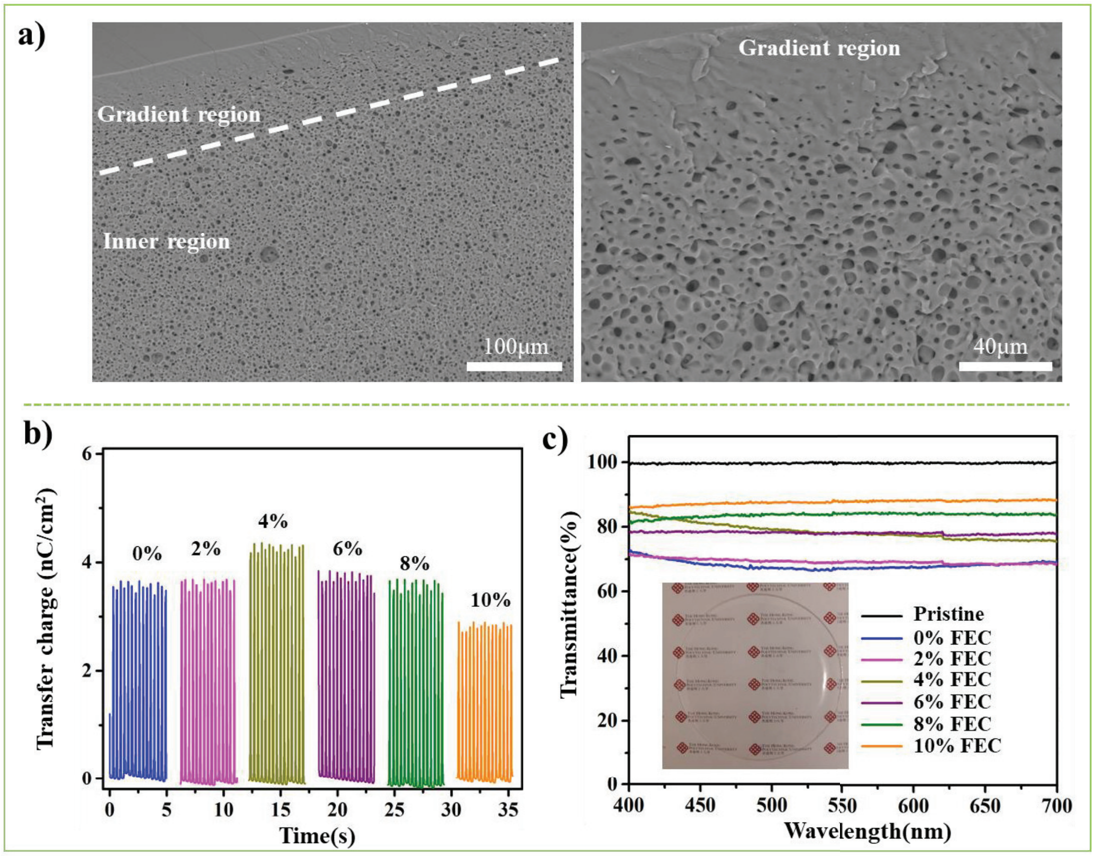
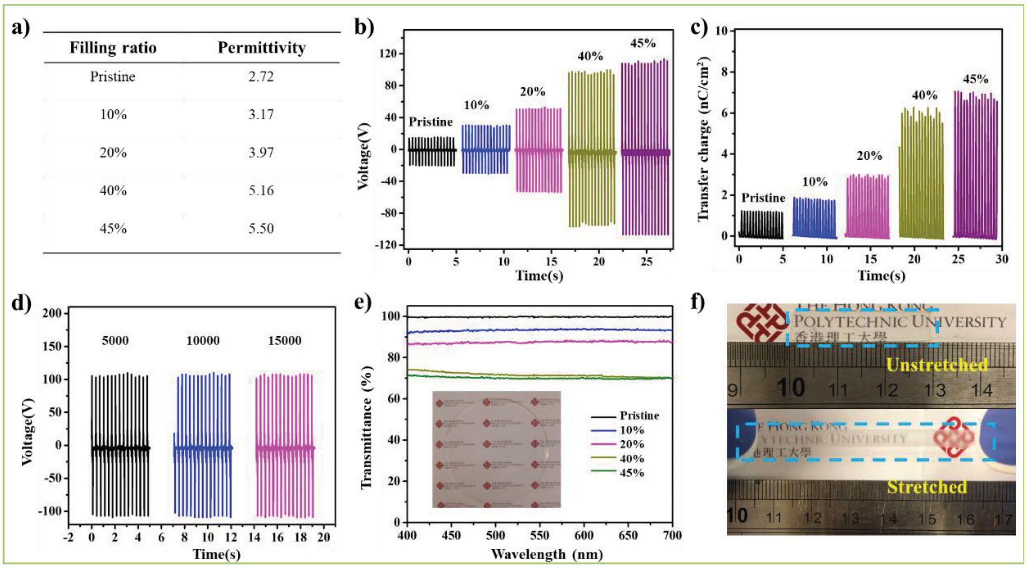


Figure 3. a) SEM images of PDMS-FHD composite film at 30% high permittivity liquid mass filling ratio contained 4% FEC additive. Cross-section of whole region and gradient region. b) Transfer charge of PDMS-FHD composite films at different FEC contents. c) Optical transmittance at visible region (400~700nm) of different FEC contents PDMS-FHD composite films, the insert figure was the image of 4% FEC additive PDMS-FHD film.

As stated in above paragraph, the doping liquid's permittivity directly influenced the capacitance of TENG which further influenced the triboelectric performance. However, FEC possessed permittivity of 79.7 which was little different with high permittivity liquid (calculated as 85 from the volume ratio of EC and PC).[39, 46] The triboelectric performances of PDMS-FHD composites were supposed to increase with the FEC content because of increasing electron affinity along with negligible decrease of doping liquid's permittivity. Another confusing result was the transmittances of PDMS-FHD films which were shown in Fig 3c. All PDMS composites films exhibited excellent transparency, whereas the transmittance of PDMS-FHD increased with the FEC content, which reached 87% at 10% FEC additive. From the basic principle of dispersed system, the transmittance was significantly decided by the size of dispersed phase droplets. In dispersed system, transparence is strongly influenced by the light scattering in visible region (400~700nm).[47, 48] The optical scattering was strong when the size of dispersed phase droplets and wavelength of visible light (400~700 nm) were approaching, which will induce opaque dispersed system. Considering the clear liquid of FEC solution, the transmittance should be stable as the same filling ratio of solution in PDMS matrix although with different FEC percent. The increase of transmittance implied that the size of droplets might be affected by FEC percent of filling liquid.

To investigate the PDMS-FHD composites, SEM was subsequently applied to study its structure, which were displayed in Fig 2c, 2d, Fig 3a and Support information. The cross-section images showed massive independent pores inside all liquid doping composite which originated from high permittivity droplets occupied space, as shown in Fig S1, S2, S3, S4 and S5. The introduced droplets thereby occupied pure PDMS, inducing increase of permittivity of PDMS composite and decrease of effective thickness of pure PDMS in whole PDMS composite. The triboelectric performance was subsequently enhanced as the capacitance of PDMS composite was enhanced. Besides, it was clear that very limited pores distributed in nearby region to upper surface of PDMS composite, which was contact area in friction. In consequence, the effective contact area would not be reduced by liquid doping materials, which was the major problem of solids doping PDMS.[28, 29] While in the inner region of PDMS composite, the droplets distribution become homogeneous as the well dispersed emulsion precursor. The sizes of PDMS-FHD composites' pores in different FEC content were presented in Fig 2c and Fig 2d. The sizes of PDMS-FHD composites' pores appeared stepwise increase with the addition of FEC, from 2.2±1.3 μm at 0% to 4.0±1.8 μm at 10%, as shown in Fig 2c. It also should be emphasized that the size statistics from cross sections images was for comparative study as it was not correspond to the actual droplets size, owing to the cutting of each droplet was not always through its respective center.[24] From the research of composite permittivity, small size of filler led to the large interfacial areas in the composite between the matrix and particle and subsequently promoted the exchange coupling effect through a dipolar interface layer, resulting high permittivity of composite.[43, 49, 50] In such PDMS-FHD composites, the sizes of filling droplets gradually increased with the gaining of FEC content, which further induced the decrease of composites' permittivity. In general, the triboelectric performances increased with the FEC content when it blew 4%, as the permittivity declining was negligible along with the gaining of electron affinity. However, the permittivity declining became dominated in triboelectric performance when the FEC content was above 4%, which offset the enhancement of electron affinity induced by FEC. The increase of transmittance could also be explained that the size of droplets deviated visible light region when FEC was gradually added, which alleviated the optical scattering.



Filling ratio	Permittivity
Pristine	2.72
10%	3.17
20%	3.97
40%	5.16
45%	5.50

Figure 4. The performance of PDMS-FHD composites with different high permittivity liquid filling ratio at 4% FEC additive. a) Permittivity. b) Output Voltage. c) Transfer charge. d) Durability test of PDMS-FHD45 after 5000, 1000, 15,000 cycles. e) The optical transmittance of PDMS-FHD composite films at different high permittivity liquid filling ratio with 4% FEC additive, the insert was digital image of PDMS-FHD45 film. f) Unstretched and stretched states images of PDMS-FHD45 composite film.

On the basis of aforementioned results, the FEC content of high permittivity liquid was determined to 4% for maximum of PDMS-FHD composite's triboelectric performance subsequently. The other mass filling ratios of high permittivity liquid with 4% FEC were measured for exploring the best triboelectric performance PDMS-FHD composite, 10%, 20%, 40%, 45%, which were termed as PDMS-FHD10, PDMS-FHD20, PDMS-FHD40, PDMS-FHD45 respectively. Principally, the permittivity of high permittivity liquid doping PDMS composites increased with the ratio of high permittivity liquid as the liquid could reduce the effective thickness of pure PDMS and increase the permittivity of whole composite. With the addition of high permittivity liquid in composites, the permittivities of PDMS-FHD composites increased gradually, 3.17 at 10%, 3.97 at 20%, 5.16 at 40%, 5.50 at 45%, as depicted in Fig 4a. The triboelectric performances of PDMS-FHD composite thereby increased as gaining of liquid filling ratios, which was showed in Fig 4a and Fig. 4b. The output voltage was 37 V at 10%, 53 V at 20%, 100 V at 40% and 114 V at 45%, respectively. As for the current and transfer charge, there were 1.28 μA, 1.88 nC/cm^2 at 10%, 2.16 μA, 2.98 nC/cm^2 at 20%, 3.70 μA, 6.28 nC/cm^2 at 40% and 4.10 μA, 7.06 nC/cm^2 at 45%, as shown in Table S2 and Fig 4c. The maximum enhancement was thus determined at 45%, which was 5.7-fold in voltage and 5.4-fold in current as compared with pristine PDMS. The durability of PDMS-FHD45 also was tested at 15,000 cycles, as shown in Fig 4d. The output voltage was around 110 V at 5,000 cycles, 110 V at 10,000 cycles and 109 V at 15,000 cycles, which indicated no obviously declining.

The transparencies of different filling ratios were displayed in Fig 4e, demonstrating gradually decrease as the filling ratio increased. The decrease was resulted from the scattering of visible light by micro-scale high permittivity liquid droplets in composite. The transmittances of PDMS-FHD composite films were 93% at PDMS-FHD10, 87% at PDMS-FHD20, 72% at PDMS-FHD40 and 69% at PDMS-FHD45 in visible region, and all films exhibited good transparency which kept the merit of high transparent pristine PDMS. PDMS-FHD45 was selected as the composite for further research owing to it high triboelectric performance. The insert digital image of Fig 4e was the PDMS-FHD45 film which was placed on a paper of colorful image, and the good transparent of the film made the colorful image clear. In Fig 4f, the stretchability of PDMS-FHD45 film was displayed by a 3×0.5 cm sample, which could be stretched over 7 cm. The stretchability thereby can be calculated as over 130%, indicating a flexible and stretchable TENG materials.

The triboelectric performances in other test conditions of PDMS-FHD45 composite were also investigated, as shown in Fig S6 and S7, Table S3 and S4. At first, the external force applied to TENG was fixed at 100 N to study the influence of frequency. The output voltage and current were proportional to frequency and the transfer charge was steady, 85 V, 3.01 μA, 7.08 nC/cm^2 at 1 Hz, 93 V, 3.63 μA, 7.07 nC/cm^2 at 2 Hz and 124 V, 4.37 μA, 7.10 nC/cm^2 at 3.3 Hz. Under steady force in these tests, the effective contact area and the surface charge of friction materials were maintained in similar. The transfer charge thereby maintained stable. However, high frequency led to rapidly contact and separation of two friction materials. The electric field between the two charged friction materials alternated rapidly and then promoted the output voltage and current. Then, the frequency was fixed at 3 Hz while the external force was varied. The corresponding output voltage, current and transfer charge were measured as 104 V, 2.88 μA, 4.14 nC/cm^2 at 50 N, 128 V, 4.61 μA, 8.88 nC/cm^2 at 150 N and 142 V, 5.07 μA, 10.13 nC/cm^2 at 200 N respectively. The rising tendency agreed well with other reported work, which could be attributed to enlarge effective contact area resulting from stronger force as the flexibility of PDMS-FHD45 composite.[51]

2.2 Benzyl chloride additive for chloride functional PDMS-HD composite

The FEC additive was not end of the functional modification of PDMS-HD. The additive of liquid filling PDMS was supposed to be a general as well as convenient method of functionalization. For instance, PC and EC were the widely used solvents in lithium-ion battery as it is featured with good solubility. Therefore, the functional molecules, which were neither chemical reactive nor limited to the carbonate or fluorinated molecules, could be carried by the PC and EC via simply dissolution. Moreover, the dissolved functional molecules in liquid droplets micro-carrier were prevented from directly contact with PDMS solution which might restrain the curing process of PDMS or lead to surface distribution induced less contact area in friction. The choice of functional molecules in functionalization TENG could thereby broadened. The droplets of filling liquid in PDMS-HD which carried functional molecules enabled the composite with designed function, indicating a promising functionalization method.

To demonstrate the potential of such method, a common reagent, benzyl chloride instead of FEC, was applied as new additive for enhancing the triboelectric performance of PDMS-HD composite as chloride was reported as good electron affinity. [20, 35, 36] Moreover, benzyl chloride is miscible with PDMS pre-cured solution with its low polarity but would be dissolved out as the PDMS matrix was formed after heat crosslinked curing process. The directly benzyl chloride addition to PDMS was not a good method as benzyl chloride could not be reserved in PDMS matrix to enhance its triboelectric performance as well as restraint of PDMS curing process. In this work, the benzyl chloride had higher solubility in carbonate than that it in PDMS solution, which thus could be carried by carbonate droplets in the emulsion precursor and further be reserved after the PDMS solution was cured. The filling ratio of liquid was fixed at 30% at first for investigating the benzyl chloride content’s influence on the triboelectric performance. As shown in Fig 5a, with the gradual addition of benzyl chloride to 6%

in mass, the output voltage was enhanced to 91 V, owing to the stronger electron affinity of C-Cl in benzyl chloride high permittivity liquid solution. While the percent of benzyl chloride was over 6%, the output voltage of composites declined gradually, 71 V at 8%, and 64 V at 10%. The output voltage decrease could be explained by the gradually decrease of composites' permittivity when benzyl chloride's content increases, as shown in Fig 5b. The effect on output performance was resulted from declining of permittivity counteract that from stronger electron affinity in chloride when the content of benzyl chloride was above 6%. The output current and transfer charge also exhibited similar tendency, as shown in Fig S8 and Table S5. The maximum enhancement was thereby determined at 6% of benzyl chloride functional PDMS composite, which was 149% in output voltage, 146% in output current and 140% in transfer charge of high permittivity liquid without any additive, and 4.6 folds in output voltage, 4.1 folds in output current, 4.4 folds in transfer charge of pristine PDMS film.

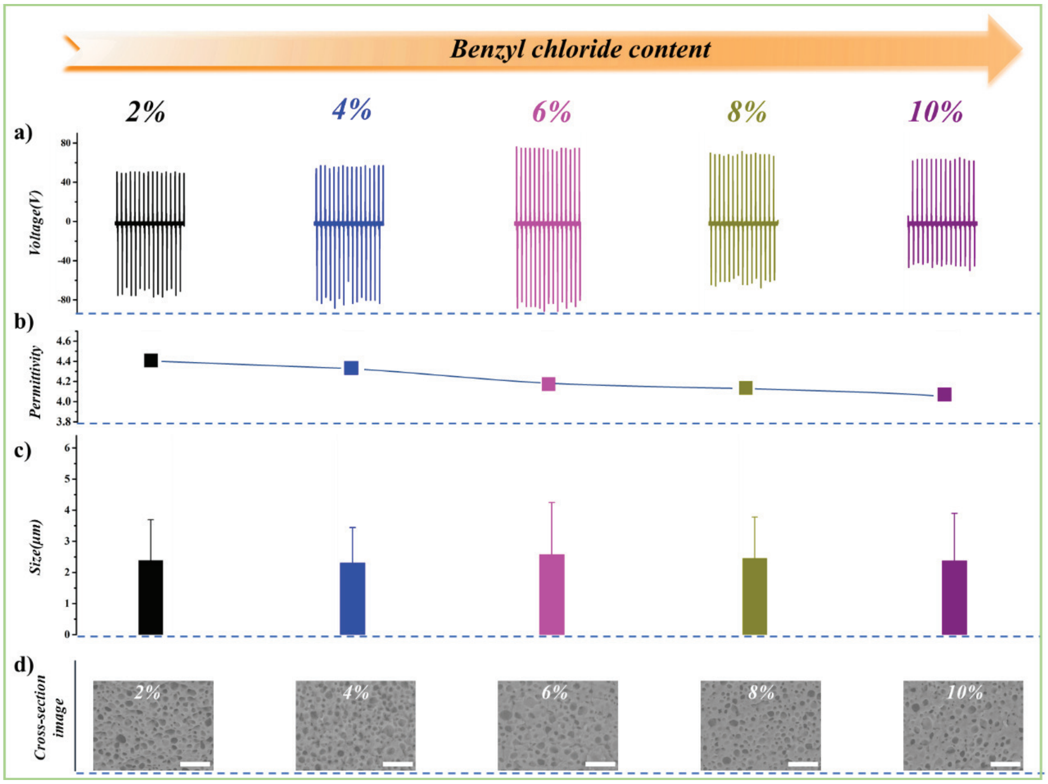


Figure 5. a) The performance of different benzyl chloride content's PDMS-HD films at 30% high permittivity liquid mass filling ratio, a) output voltage, b) permittivity, c) benzyl chloride functional PDMS-HD pores' size, d) inner region SEM images of different benzyl chloride additive PDMS-HD composite films. The scale bar is 20 μm.

The structure of different benzyl chloride content's PDMS-HD films at 30% high permittivity liquid mass filling ratio was studied by SEM, as shown in Fig S9, S10, S11, S12, S13 and 5d. As expected, the distribution of droplets in composites was similar with that of no additive or FEC additive, demonstrating limited distribution in nearby region to upper surface of composite. Pores distribution of FEC additive implied that additive had negligent influence on the droplets distribution, which thus could be applied to more functional molecules and avoid the surface distribution induced less contact area in friction. The size of pore in benzyl chloride additive composite maintained steady despites of the increase of benzyl chloride content, which had little difference with that of no additive. However, the permittivity showed obviously decrease when benzyl chloride was gradually added in liquid. The reason might be attributed to low permittivity of benzyl chloride in the liquid which reduced the permittivity of whole doping liquid as well as permittivity of PDMS composite.

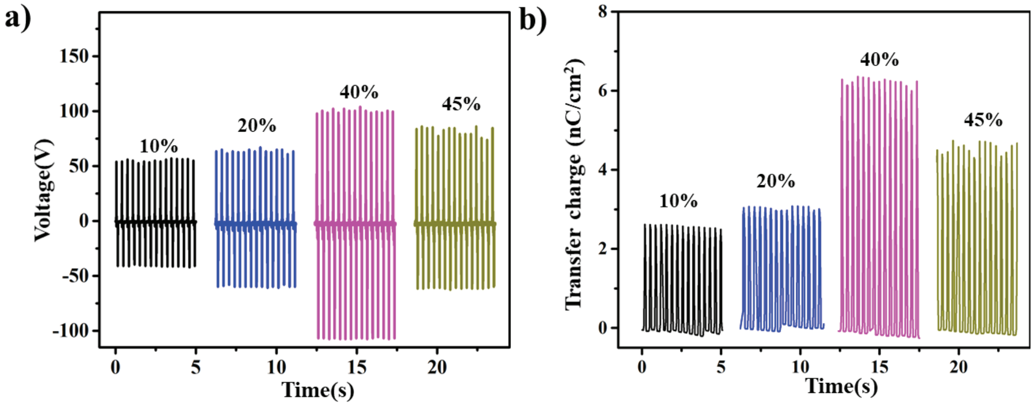


Figure 6. a) The output voltage of chloride functional PDMS-HD composite films with different high permittivity liquid filling ratio at 6% benzyl chloride additive.

Hence, the other filling ratios of high permittivity liquid with 6% benzyl chloride were prepared for further research. As displayed in Fig 6, the output voltages of such composites increased with the filling ratio of benzyl chloride dissolved high permittivity liquid when it is below 40%. The output voltage of composite was enhanced to 107 V at 40% filling ratio, which was 5.4 folds of pristine PDMS. Fig 6b and Table S6 showed that current and transfer charge were also increased to its peaks value of 4.23 μA and 6.36 nC/cm^2 or 5.6 folds in current and 5.4 folds in transfer charge of pristine PDMS at 40% filling ratio. The enhancement was originated from the gradually increase of composite's permittivity as high permittivity liquid was embedded in composite, as shown in Table S6. However, the output performance showed obviously declining at 45% filling ratio even its composite possessed highest permittivity. The declining came from insufficient curing of PDMS at high benzyl chloride content, in which the benzyl chloride was driven into PDMS solution under the force of distribution between carbonate and PDMS solution and further resulted in restrain of PDMS curing process.

From the results as presented above, the functional halogens additive in micro-carrier liquid could be an effective method to enhance materials' triboelectric performance which was not relied on chemical reaction and showed great extensibility of reagent from PDMS solution immiscible FEC to PDMS solution miscible benzyl chloride. The FEC is immiscible with PDMS solution and was carried by the droplets in emulsion precursor. The distribution of FEC in PDMS solution and cured composites was negligible. As for benzyl chloride, the reagent is miscible with PDMS solution. When it is at a low concentration, the majority of benzyl chloride was carried by the droplets in emulsion precursor. The curing process would not be affected by the benzyl chloride as negligible distribution in PDMS solution. As the benzyl chloride reached at a high concentration, benzyl chloride was driven into PDMS solution under the force of distribution between carbonate and PDMS solution and further restrained the PDMS curing process. However, directly benzyl chloride addition to PDMS was not a good method as benzyl chloride is miscible with PDMS solution and would inhibit the PDMS curing process even the concentration was at a low level. The two halogens are only representative and many other functional molecules can explored for study which was not presented in this study because of length limit. The distribution of micro-carrier droplets in PDMS matrix was not influenced, demonstrating a general method. Besides that, the additive directly affected the high permittivity liquid state which further affected doping liquid permittivity and dispersed droplets' size as the additive content increases. The materials' triboelectric performance thereby was affected. All factors should be taken into comprehensive consideration to maximize the triboelectric performance when functional additive was introduced.

2.3 Output performance of PDMS-FHD45 made TENG for energy harvesting and sensor

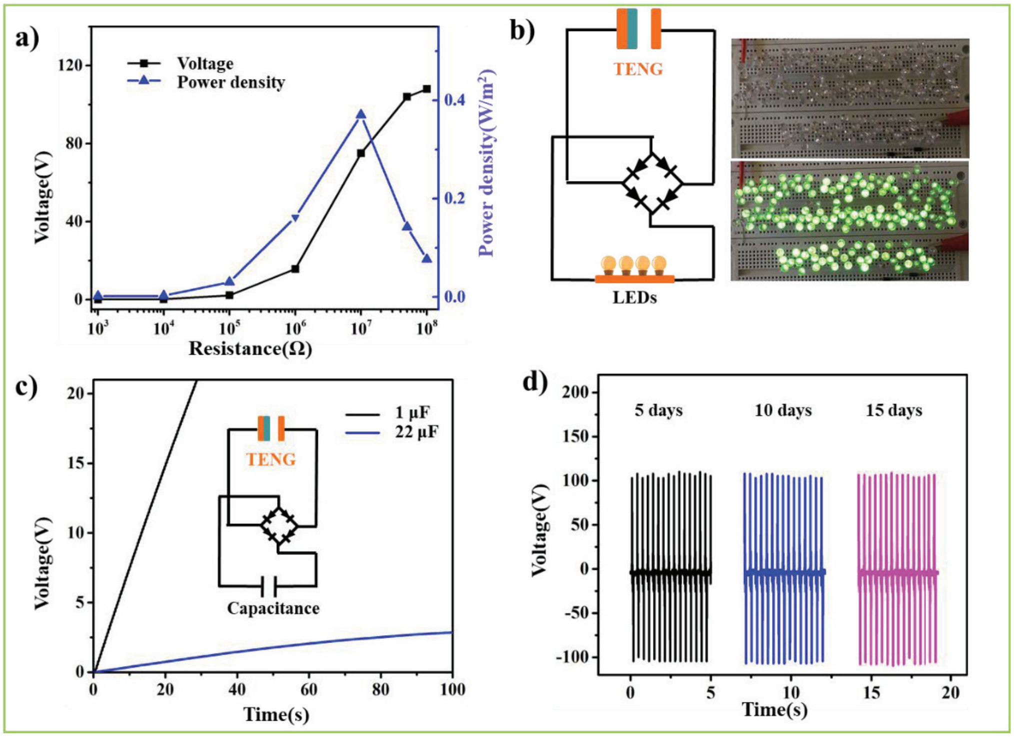


Figure 7. a) The output voltage and instantaneous power density of PDMS-FHD45 made TENG versus external load resistance. b)156 green LEDs were instantly lighted up by PDMS-FHD45 made TENG. A bridge rectifier was applied to adjust the output electric signal. C) Capacitor of 1 μF and 22 μF charged by PDMS-FHD45 made TENG. d) Stability test of PDMS-FHD45 after 5 days, 10 days and 15 days.

Evaluations were then conducted on PDMS-FHD45 composite TENG with an external force at 100 N of 3 Hz for the output performance, as this composite was found with best triboelectric performance in the above study. The PDMS-FHD45 composite fabricated TENG was connected to external loads in series circuit with different resistance values (10^3~10^8 Ω) for testing the output voltage. Fig 7a revealed that the output voltage with external resistor increased gradually with the gaining resistance values. The maximum output voltage was 108 V(single peak) which was obtained at 10^8 Ω. The instantaneous power density was calculated from $W = V^2/R$ and plotted in same figure. The instantaneous power densities displayed a gradually increase with resistance values while it was below 10^7 Ω. The peak value of instantaneous power density was 0.37 W/m^2 with an external resistance load of 10^7 Ω. The output power decreased with the resistance when it was over 10^7 Ω subsequently. The corresponding instantaneous power density enhancement was also calculated as much as 44.8 folds at an external load resistance of 10 MΩ as compared to pure PDMS film (Fig S14). The electricity power generated from PDMS-FHD45 was sufficient to drive some electronic devices and charge energy storage devices. As shown in Fig 7b and SI video, the TENG could light up 156 green LEDs with good brightness, while the output signal was adjusted by bridge rectifier. As for energy storage devices, two capacitors with different values were connected in circuit for demonstrating the potential of energy harvesting power source, as showed in Fig 7c. When the periodical force was applied to the TENG, the capacitor of 1 μF was charged from 0 V to 20 V within 28 s, indicating a charging rate of approximately 727 mV/s. The charging rate of 22 μF capacitor was approximately 29 mV/s. The stability also was an important factor in TENG application. Fig 7d showed the output voltage of PDMS-FHD45 fabricated TENG in different days after 5,000 cycles contact friction, which was 110 V at 5 days, 108 V at 10 days, 110 V at 15 days. The negligible declining to initial output voltage rendered the good stability of PDMS-FHD45 composite.

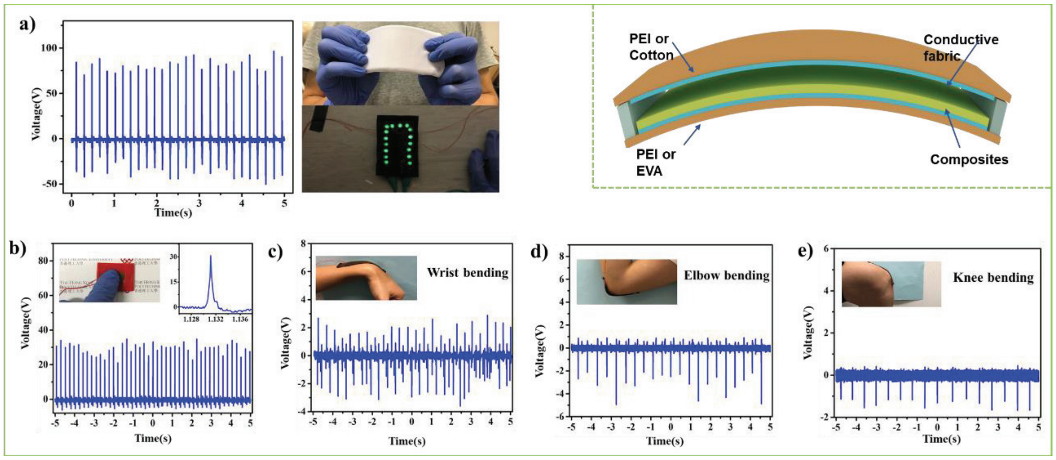


Figure 8. a) The output voltage and digital image of PDMS-FHD45 composite film made flexible TENG for energy harvesting, and the 16 green LEDs were powered up by flapping on the TENG. Electric signal generated from the gesture detecting TENG by b) finger tapping, c) wrist bending, d) elbow bending, e) knee bending.

Based on the above study of PDMS-FHD45 composite, we further utilized it for portable and wearable energy harvesting and self-powered sensor devices. Considering the comfort of the device in human body, cotton fabric was used as major substrate of the TENG device along with a thin EVA (ethylene vinyl acetate copolymer) sponge film of 3 mm. The PDMS-FHD45 composite film was attached on the EVA sponge film with conductive fabric as back electrode. Another piece of conductive fabric fixed on cotton fabric was then employed to cover the EVA film with sponges to supply elasticity and space between the conductive fabric and EVA film, as shown in Fig 8. By flapping the top substrate of the TENG, the output voltage generated from the friction of PDMS-FHD45 composite film and conductive fabric could reach over 90 V. To further demonstrate the potential of the device in powering electronics, and 16 green LEDs were directly connected to the device in series circuit. The Fig 8a displayed the TENG could light up 16 green LEDs when it was flapped by hands, rendering the TENG was an efficient energy harvesting device.

The flexibility as well as high output performance of PDMS-FHD45 composite were suitable for e-skin applications which required flexibility and high sensitivity in responding to externally applied force.[38] By particular designing, flexible TENG was fabricated for detection of human moving gestures. The TENG was composed of two thin PEI (Polyetherimide) films which acted as supported substrates. A piece of conductive fabric was coated by PDMS-FHD45 composite to supply the electronegative material in friction and back electrode of TENG respectively, which were then attached on the bottom PEI film substrate. Another piece of conductive fabric was adhered on the top PEI film substrate, playing as electronegative material and electrode synchronously. The flexibility of PDMS-FHD45 composite was the foundation of such TENG and the high output performance of PDMS-FHD45 enabled it as a sensitive self-powered gesture detection device. As shown in Fig 8b, 8c, 8d, 8e, the TENG was attached to the different moving parts of body such as the wrist, elbow and knee for detection of human moving gestures. The electric signal was thus generated without additional energy supply or storage device. For example, the TENG’s size was adjusted to fit finger tapping sensor. Once the TENG was tapped by finger, a sensitive output voltage signal was detected with great responsiveness in 6 ms, as well as stable repeatability. Furthermore, the electric signals shapes generated from the TENG sensor were different which could be applied to recognize various human body gestures. These results demonstrated the flexibility of PDMS-FHD45 composite and its potentials in E-skin.

To further demonstrate the output performance, the PDMS-FHD45 film was applied to assemble a single-electrode TENG device, in which conductive fabric was as the back electrode. The single-electrode TENG was connected to a designed circuit as shown in the Fig S15. The 4.7 μF capacitor was charged by single-electrode TENG with hand tapping at first and the voltage of capacitor achieved 2.6 V, at a charging rate of 43 mV/s. The circuit was then switched to other side to power the watch in the other circuits. The watch could be powered by the electricity in the capacitor, which originated from the TENG harvesting energy. The working time of watch was over 40 seconds as the capacitor supplied electricity. The powering watch experiment revealed the potentials of PDMS-FHD45 film in construction of high power density TENG device.

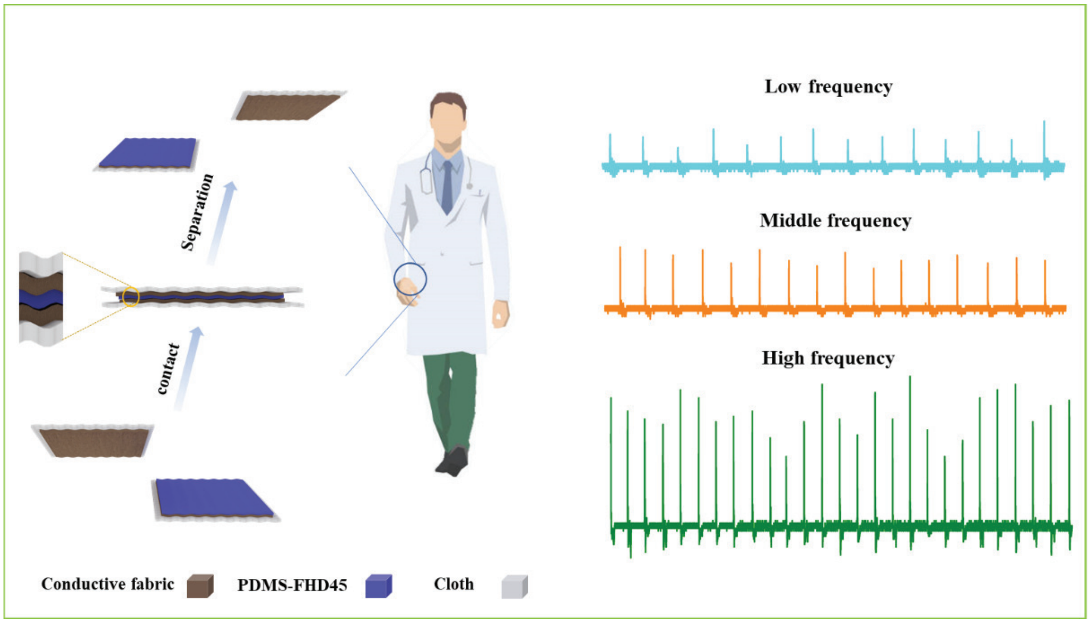


Figure 9. Single electrode mode TENG for monitoring of arm swinging.

A single-electrode mode TENG was also assembled to monitor arm swinging in walk for the purpose of further demonstrating the potential of PDMS-FHD composite in e-skin, as shown in Fig 9. The TENG was a piece of PDMS-FHD45 composite coating conductive fabric, in which conductive fabric was electrode and PDMS-FHD45 composite was friction material. The TENG was then attached on the hem of coat as it would rub with cuff in arm swinging of walk. To enhance the output signal, another piece of conductive fabric was adhered to cuff by double-sided tap, which was used as electropositive material. In detail, when the arm swang back and forth in walking, the hem and cuff was brough in contact and separation periodically, which induced triboelectricity in PDMS-FHD45 composite. The electrode thereby generated periodically potential through electrostatic induction. The signal was observed via connection of electrode and oscilloscope, which could monitor the arm swinging induced contact and separation. With different walking frequencies induced arm swinging, the output signal was varied and shows an increase with frequency.

3. Conclusion

In summary, a facile method was developed for functionalization of triboelectric materials on the basis of high permittivity liquid filling materials. The method employed the liquid droplets in PDMS-HD composite as functional molecules micro-carriers via corresponding functional additive in liquid, such as FEC additive for fluorine functionalization and benzyl chloride additive for chloride functionalization, which avoided chemical reaction. The composites thus possessed high permittivity and functional property synchronously, which induced significant enhancement in triboelectric performance. The fluorine functionalization composite, PDMS-FHD45 composite, exhibited the enhancement of approximately 5.7 folds in output voltage and 5.4 folds in current as compared with pristine PDMS. The corresponding instantaneous power density enhancement was also calculated as much as 44.8 folds at an external load resistance of 10 MΩ. The PDMS-FHD45 composite was then applied for energy harvesting which was sufficient to light up 156 green LEDs. PDMS-FHD is also featured good transmittance and stretchability. Flexible TENG fabricated by PDMS-FHD45 was used to detect human gestures, demonstrating widely application in e-skin. Nonetheless, this work demonstrated only two additives of functional molecules, and a plenty of additives which could dissolved in liquid were potential and valuable to explore. This work demonstrated that liquid filling composite prepared from emulsion states was not only an effective method for enhancing triboelectric performance but also a promising method for functionalization of triboelectric materials for flexible and wearable energy harvesting and self-powered sensing devices.

4. Experiment section

Materials and Characterization

Propylene carbonate (PC) and ethylene carbonate(EC) were the products of Alfa Aesar. PDMS (Sylgard 184) was the product of Dow Corning. Fluoroethylene carbonate (FEC) and benzyl chloride were brought from Dieckmann company. Cu/Ni coated fabric was applied as conductive fabric which was obtained from 3 M Corp. All reagents were used as received without further purification.

Button/key durability life test machine was applied to test triboelectric performance of all samples, ZX-A03, zhongxingda Shenzhen. The velocity of driving motion was around 0.10 m/s. The output voltage was measured by an oscilloscope of Keysight Infiniivision DSOX3024T with 8 M Ohm input impedance while the output current and transfer charge were collected by Keithley 6514 system electrometer of Tektronix, Inc. Hitachi UH5300 was used to study the transmittance of films. The SEM images were taken from Hitachi TM-3000. The dielectric constant data was calculated from capacitance. $C \quad = \varepsilon_0 * S\frac{\varepsilon_r}{d}$ The capacitance was test on LCR-6300,300kHz, GW Instek.

FEC or benzyl chloride high permittivity liquid solution and PDMS solution

PC and EC were mixed at 4:1 in volume ratio for high permittivity liquid.[52] FEC was then dissolved in the high permittivity liquid in different ratios of 2%, 4%, 6%, 8%, 10% for using as FEC solution. The benzyl chloride solutions were prepared in similar way. PDMS solution was the mixture of elastomer and curing agent at recommend mass ratio of 10:1from the company.

Preparation of PDMS-FHD composites and chloride functional PDMS-HD composites

The PDMS solution and high permittivity liquid or FEC solution were mixed in designed mass ratio. The mixture was then stirred vigorously for 3 mins till sticky emulsion was formed. The emulsion was casted on petri dish in thickness of around 540 μm and heated at 70°C for 3 h to fabricate thin film. After that, the film was cooled in air and then peeled off from the dish.

The preparation of chloride functional PDMS-HD composites was similar with PDMS-FHD, in which benzyl chloride solution was used instated of FEC solution.

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