Doctor of Philosophy

TRIBO-POLARITY ENHANCEMENT OF POLYVINYLIDENE FLOURIDE FOR TRIBOELECTRIC NANOGENERATOR AND THEIR APPLICATIONS

The Graduate School of the University of Ulsan

School of Mechanical Engineering

VU DUY LINH

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Supervisor: Professor KYOUNG KWAN AHN

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VU DUY LINH

School of Mechanical Engineering

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APPLICATIONS

This certifies that the dissertation of
VU DUY LINH is approved by

Committee Chairman: Prof. DOO MAN CHUN

Committee Member: Prof. KOO HUYN CHUNG

Committee Member: Prof. KYOUNG KWAN AHN

Committee Member: Prof. BYUNG RYONG LEE

Committee Member: Prof. JI SUNG JANG

Department of Mechanical and Automotive Engineering

University of Ulsan, Korea

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Nomenclature

TENG	Triboelectric nanogenerator
LS-TENG	Liquid-solid triboelectric nanogenerator
TECD	Triboelectric charge density
EDL	Electric double layer
PVDF	Polyvinylidene fluoride
PVDF-TrFE	Polyvinylidene fluoride-trifluoroethylene
PVDF-HFP	Polyvinylidene fluoride-co-hexafluoropropylene
PDMS	Polydimethylsiloxane
PTFE	Polytetrafluoroethylene
PET	Polyethylene terephthalate
PP	Polypropylene
CFO	cobalt ferrite nanoparticles
FOTS	1H,1H,2H,2H-Perfluorooctyltriethoxysilane
GO	Graphene oxide
F-GO	Functionalized graphene oxide
SiNPs	Silica nanoparticles
ITO	Indium tin oxide

TMC	Benzenetricarbonyl trichloride
DMSO	Dimethyl sulfoxide
DMF	N,N-dimethylformamide
NaOH	Sodium hydroxide
DMAP	4-(Dimethylamino)pyridine
DCC	N,N0-dicyclohexylcarbodiimide
FSiP	FOTS/SiNPs/PVDF
FP	FOTS/PVDF
HCOENPs	Hydrophobic cellulose oleoyl ester nanoparticles
FE-SEM	Field emission scanning electron microscope
AFM	Atomic force microscopy
FTIR	Fourier transform infrared
XPS	X-ray Photoelectron Spectroscopy
LED	Light-emitting diode
P	power density (W/m^2)
A	Contact area (m^2)
I	Output curent (A)
V	Output voltage (V)

Q	Accumulated charges (C)
R	Load resistance (Ω)
C	Capacitance (F)
C_{max}	Maximum capacitance (F)
σ'	transferred charge density (C/m^2)
d_m	Membrane thickness (m)
ε_0	Vacuum permittivity (8.854×10-12 F/m)
ε_m	Membrane permittivity (F/m)
σ_0	Charge density in the equilibrium state (C/m^2)
d_{gap}	Gap distance between triboelectric layer and droplet (m)

ABSTRACT

Recently, in place to bolster the rapid expansion of the Internet of Things (IoT) and sensor systems in the application of wearable and portable devices, sustainable and green power sources are required. Therefore, energy harvesting from the natural surroundings has generally been considered a viable answer to the expanding electricity consumption brought on by innovative advances. Although liquid-solid triboelectric nanogenerator (LS-TENG) has been taken into consideration as a remarkable promising renewable clean energy source for electronic devices, their performances are still limited to be practically utilized owing to the weak polarity and inadequate functional groups of triboelectric materials. Thus, enhancing TENG performance is a critical issue to be concerned for both practical and industrial applications. Hence, in this study, the tribo-polarity of polyvinylidene fluoride (PVDF) was enhanced and acted as a triboelectric layer of the LS-TENG. PVDF was modified via two strategies: creating a more polar β phase to increase the dipole moment or adjusting the fluorine-containing functional groups with low surface energy. The results of β content, dielectric constant, hydrophobic, and polarization have demonstrated the increase of tribo-polarity in the PVDF membrane. In addition, the TENG based on the modified PVDF membrane was shown superior triboelectric performance. In particular, the highest power density of TENG was obtained at 2.08 W/m^2, a 10-fold improvement over the pristine PVDF-TENG. In this manner, a new material for the triboelectric layer is presented to effectively improve the output performance, stability, and durability of TENGs, which are promising for use in practical applications related to harvesting hydrokinetic energy, self-powered sensors, and other applications.

Keywords: tribo-polarity, triboelectric nanogenerator, liquid-solid, polyvinylidene fluoride, hydropower energy harvesting, self-powered sensors.

INTRODUCTION

1.1.Overview

1.1.1. Liquid-solid triboelectric nanogenerator

In recent years, climate change and energy shortages have given urgency to human life and industrial development, hence the development of clean and renewable energy sources has become imperative. Among the available renewable energy sources, raindrops, ocean waves, human footfalls, and airflow have gigantic energy potential, but most of this potential is wasted because of the difficulties associated with effective energy harvesting [1]. Therefore, a suitable technology is essential to capture those energy sources. In this respect, various types of energy harvesting techniques have been studied for the transformation of mechanical movement to create electricity, including piezoelectric, electromagnetic, pyroelectric, and triboelectric [2-5]. Among them, the triboelectric nanogenerator (TENG) was first reported by Wang and his group in 2012 as a promising method for generating electricity. A typical structure of a TENG device is shown in **Figure 1.1**. Based on the coupling of triboelectrification and electrostatic induction, the triboelectric charges can generate by the physical contact on the surfaces of two dissimilar materials. Therefore, the

Figure 1.1 Schematic illustration of the structure and photographic images of the triboelectric nanogenerator [9].

electricity can be produced by TENG from various energy sources such as wave water, wind, human motion, and so on [6-8]. Since its birth, the structures and functions of various TENGs have been researched to increase output performance and energy conversion efficiency. The power density and total efficiency have rapidly improved over the years and reached up to 500 W/m^2 and 85%, respectively [9-11].

In addition to the incredibly rapid development of solid-solid contact TENG, liquid-solid TENG (LS-TENG), which uses liquid itself as a triboelectric material, has been attracting significant attention owing to it has many benefits such as wear-resistant, lightweight, small size, cheap, simple fabrication, and environmental friendliness [12]. The LS-TENG devices are based on the basic concept that liquid makes contact with a dielectric solid surface and generates electricity. Due to the form flexibility of liquid, liquid-solid contact has a greater contact area, higher contact affinity, and lower friction coefficient than solid-solid contact. Although the exact electrostatic effect is still unclear, the working principle of liquid contact with solid has been tried to explain by the movement of the triboelectric charge on the surface of the materials. Wang et al. defined its technique for understanding the shift in electron transfer during the contact electrification process, having a significant influence on LS-TENG research as shown in **Figure 1.2** [13, 14]. Firstly, the liquid contact with the virgin surface without pre-existing surface charges (**Figure 1.2a**), the atom or molecules of a liquid are randomly distributed. Further, these atoms or molecules directly interact with the solid surface leading to the first electron transfer and called ionic formation (**Figure 1.2b**). Under the transfer of the liquid, the liquid molecules, adjacent to the solid surface, could be broken into the formation and left ions on its surface (**Figure 1.2c**). In the second step, some ions in the liquid would be formed with ions on the solid surface due to electrostatic interactions, forming an electric double layer. Due to this basic working principle of the LS-TENG devices, we can classify the fundamental working modes into three modes: single-electrode mode, sliding free-standing mode, and contact-separation mode.

Figure 1.2 The process of an electric double layer formation at a liquid-solid interface in two-step: electron transfer at virgin surface and ion adsorption at the charged surface [14].

1.1.2. *Working mechanism of LS-TENG*

The working mechanism of a single-electrode mode LS-TENG device can be seen in **Figure 1.3** [15]. The device includes two layers: an aluminum (Al) film as the electrode and polydimethylsiloxane (PDMS) film as the contact layer. In **Figure 1.3**, the positive charges of liquid would be created when droplet contact electrification with the pipette tube before impacts to PDMS film. When the droplet approached the PDMS surface, the electrical equilibrium of the surface broken led to the difference of positive potential between the contact layer and the electrode layer. The electron flow will be generated due to the attraction of the ground on the electrons of the Al electrode. After the droplet completely rolled off the contact surface, the electron flow was in the reverse direction because of the changing of

charge potential. Moreover, another working mechanism has been demonstrated a sliding water droplet mechanism when liquid and PDMS have a triboelectric phenomenon. As know that triboelectricity can be generated when the droplet falls on the film. The surface of PDMS will be charged to a negative charge because PDMS is negative in triboelectric series and the electrical double layer is formed. When the droplet left the surface, the charge was still maintained due to the nature of the dielectric electret, therefore, an electron flow appeared until charge equilibrium was achieved.

Figure 1.3 The working principle of a single-electrode mode LS-TENG device when droplet was pre-charged due to triboelectrification [15].

Due to the amorphous property of the liquid, it is hard to add the electrode to the surface of the liquid. Therefore, the sliding free-standing mode is the perfect choice for the LS-TENG device. The working principle of a sliding free-standing mode LS-TENG has been shown in **Figure 1.4** [16]. In this TENG device, the contact layer was made by the insulating film (PTFE thin film) and copper film (Cu) as the electrode. When water is in contact with a solid surface, tribo-charges appear on the solid surface. At the first step, the positive charge in the liquid contacted the tribo-layer surface, resulting in the electrons being attracted to the upper surface. The left-hand electrode (LE) will be fully covered by positive charges. Then, when the liquid column slides towards the right-hand electrode (RE). The positive charges

will flow from LE to the RE in which a current flow will be generated. When the liquid column reaches the overlapping position of the RE all the positive charges will then be driven to the RE. Subsequently, a backward sliding of the liquid column from the RE to the LE should drive the flow of the positive charges in the same direction, forming a reverse current in the load.

Figure 1.4 (a) Working principle of a sliding free-standing mode LS-TENG, (b) the short-circuit current showing the aforementioned four stages and short-circuit current, open-circuit voltage under 40 mbar and 1 Hz working condition [16].

The contact-separation mode is the most convenient way for the TENG structure device, especially in the case of solid-solid contact TENG. However, the LS-TENG fabrication device becomes more complicated due to the amorphous liquid. To solve this problem, several models have been studied and developed such as contact-separation style, lateral-sliding style, pressing-releasing style [17-19]. As shown in **Figure 1.5** [20], the basic device of contact-separation mode LS-TENG is formed by two parts, first is PTFE layer coated on an Al electrode and a load cell was connected on the top of the Al electrode, second is the Cu electrode was placed inside the liquid to ensued that the distance between the electrode and liquid surface was maintained about 5 mm. When the PTFE layer is separated from the liquid surface, the LS-TENG is initially in electrical equilibrium (**Figure 1.5(i)**). The PTFE

Figure 1.5 Working principle of contact-separation mode L-S TENG [20].

became negative and the liquid surface became positive when they contact with each other (**Figure 1.5(ii)**). When the PTFE is lifted from the liquid surface, effective charge separation occurs due to the hydrophobic properties of the material. During this induction, electron flow will be generated between Al and Cu electrodes (**Figure 1.5(iii)**). Then the PTFE back to the original position, and the electrical also tries to back to the equilibrium, therefore, the electron flowed in the opposite direction (**Figure 1.5(iv)**).

1.1.3. *Affecting parameters of LS-TENG*

It can seem that LS -TENGs are extremely diverse in device design and working mode, therefore, the study of LS-TENGs affecting parameters becomes complicated. Most of the current research focuses on many factors affecting the output performance and durability of the LS-TENG devices. Based on the structure of the device, the affecting parameters can be classified into two groups liquid phase and solid phase properties of the LS-TENG.

In the solid phase, there are two important parts: the contact layer and the electrode layer. Firstly, about the electrode layer, the choice of materials is critical. The high electric conductivity of the selected material will increase the electronic get from the contact layer, thereby increasing the output performance. On the other hand, the flexible property is also quite important to fabricate the TENG device with different models. Over the past few years, aluminum, silver, gold, and copper is a common electrode material for LS-TENG devices. This material is attributed to its high conductivity, good flexibility, commercial availability, and well-researched properties [21-24]. Moreover, a lot of other conductive material has been proposed due to their common flexible, stretchable properties and high chemical stability including carbon nanotubes (CNTs), graphene, nanowire-based materials, and organic or polymer-based materials [25-28].

Apart from the electrode layer, the contact or hydrophobic layer plays a role important to increase the TENG output performance. Due to the positive triboelectric properties of the liquid, the contact layer material should have high negatively charged. To quantitatively standardize the triboelectric effect, the triboelectric charge density (TECD) was measured to

rank materials. Besides that, the negative charge of material can be increased by using corona discharging of the air through using the air-ionization gun. After using corona discharging, the TECD could increase more than 5 times compared to the initial material [29]. The hydrophobic surface was also researched a lot in improving output performance. Several ways have been used to fabricate high hydrophobic surfaces such as nanostructures or hierarchical structures, artificial lotus leaf structures, and plasma treatment [30-32]. It is noteworthy that the surface morphology of the contact layer affects the velocity of the liquid on the contact layer and the bouncing motion between the liquid-solid surface. The hydrophobic surface is characterized by contact and sliding angle. High contact and sliding angle will increase the current output in the droplet single-electrode contact mode [33].

In the liquid phase properties, two kinds of liquid have been used in TENG are metal liquid and water. There are many choices for the metal liquid, including mercury, galinstan, etc. due to its liquid state at room temperature [19, 34, 35]. Moreover, metal liquid has excellent fluidity and conductivity, though, their effect of them on TENG devices has not been studied in any paper. The metal liquid is just mentioned as a replacement material for solid metal and works as an electrode layer. Opposite that, the properties of water carefully studied include the water forms (droplet, waves, flow), ion type, and concentration of other materials soluble in water. The water form properties have been researched through the working principle of the TENG. It is known that the water form is the main factor affecting the contact area and frequency of the liquid on the solid surface. With a larger contact area and higher frequency, the output power will obtain a higher result. The droplet water has been investigated to find out the effect of droplet volume, falling height, and tilting angle on L-S TENG output performance [36]. It can be seen that a droplet volume is proportional to the velocity of the droplet. Therefore, the inertial force is affected by the droplet volume and can be expressed as $\rho v^2/D$, where ρ is density, v is velocity and D is the diameter of the droplet. However, the inertial force when the droplet moves down on the solid surface is still affected by the velocity of the droplet increases with time (ϑ_t)due to the falling height (h) and tilting angle (θ). This relationship is expressed by the equation

$$\vartheta_t = \sqrt{2gh}\,sin\theta \qquad\qquad (1-1)$$

Due to the increment of the kinetic energy, ϑ_t increases, when falling height (h) increases, leading to an increase in the current output. Likewise, higher θ attributed to the increase of ϑ_t in Equation (1-1). However, the current output reaches saturation when the angle exceeds 45° and then dropped down when the inclination angle is over 75°

1.1.4. Tribo-polarity of triboelectric material

In 2015, Zi et al. suggested that performance figures of merit (FOM_P) be used to define the output electrical of TENG [37]. FOM_P is made up of two figures of merit: a structural figure of merit (FOM_S) and a material figure of merit (FOM_M), both of which are associated to structure and surface charge density. They began their research with the lateral-sliding mode TENG (**Figure 1.6**) and utilized the finite element method (FEM) to model the V-Q plot under a 100 MΩ external load resistance (**Figure 1.6b**). The output energy per cycle is represented by the ringed area of the closed-loop in the V-Q curve, and the loops are referred to as energy output cycles (CEO). The total cycle charge Q_C is defined as the difference between the maximum and minimum transmitted charge in each steady state of the CEO. Particularly for cycles with high external load resistances, the Q_C was always less than the maximum transferred charge $Q_{SC,max}$. As a result, they devised a series of methods to create the short circuit condition, $Q_C = Q_{SC,max}$, and achieved cycles for maximized energy output (CMEO). The maximum output energy (E_m) can be used to compute the following equation

$$E_m = \frac{1}{2}Q_{SC,max}\left(V_{OC,max} + V'_{max}\right) \qquad\qquad (1-2)$$

As stated in Equation (1-2), E_m contains $Q_{SC,max}$, which is proportional to the triboelectrification area (A). Area A should be placed in the denominator of this term to eliminate the influence of the TENG size on the output energy. They confirmed that the E_m/Ax_{max} decides the merits of TENG for the reasons described above. In addition, the triboelectric charge density is proportional to $Q_{SC,max}$, $V_{OC,max}$, and V'_{max} in Equation (1-2).

As a result, E_m is proportional to the square of the surface charge density σ. FOM is presented as a dimensionless structural FOM

$$FOM_s = \frac{2\varepsilon_0 E_m}{\sigma^2 A x_{max}} \qquad (1-3)$$

where ε_0 is the permittivity of the vacuum. FOM_P of TENG can be defined as

$$FOM_P = FOM_s \sigma^2 = \frac{2\varepsilon_0 E_m}{A x_{max}} \qquad (1-4)$$

Figure 1.6c demonstrates how to optimize the FOM_S by changing the value of x_{max}, and **Figure 1.6d** shows the relationship between the modes: $CFT > CS > SFT > LS > SEC$, where CFT, SFT, and SEC stand for contact freestanding mode, sliding freestanding mode, and single electrode contact mode, respectively. There is also a proposal for a standard technique

Figure 1.6 (a) Schematic diagram of the lateral-sliding mode TENG, (b) the CEO under load resistance R = 100 MΩ, (c) the FOMs for lateral-sliding mode, (d) the maximum structural FOM (FOMS,max) of different structures extracted from FEM simulations, and (e) the abs solute charge density measured by contacting different materials with solid gallium and liquid galinstan [13].

for quantifying the triboelectric characteristics of materials. The triboelectric charge density of the same liquid metal may be used to quantify the triboelectric performance of various materials. As shown in **Figure 1.6e**, the consequences of contacting different materials with solid and liquid gallium.

According to the triboelectric phenomena principle, the polarity of a material, or its capacity to gain or lose electrons, is exactly proportionate to the amount of charge generated by contact electrification. In recent years, polarity control of materials has received a lot of attention and research as a vital aspect of optimizing TENG performance. The tribo-polarity of various materials was investigated in several investigations, and the results were arranged

Figure 1.7 The triboelectric series is divided from the most negative tribo-polarity to the most positive tribo-polarity [13].

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from the most negative to the most positive tribo-polarity to construct the triboelectric series illustrated in **Figure 1.7**. The highest output power may theoretically be generated by using appropriate materials as triboelectric layers at the top and bottom of the triboelectric series [13, 38].

The polarity of triboelectric materials is determined by their chemical properties and is intimately linked to the surface, functional groups. The higher electronegativity of the functional group leads to the greater its capacity to acquire electrons and produce additional charges. Because the fluorine functional group is the most electronegative, negative materials such as polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), and polyvinylidene fluoride (PVDF) are commonly used. The positive materials, on the other hand, are the amino group, which includes polyethylene terephthalate (PET), polyamide (PA), polyurethane (PU), and other nitrogen-containing polymers. These groups have an exceptional capacity to gain and lose electrons, which is a key consideration when choosing a triboelectric pair. Chemical modification is regarded as an effective way to modify the polarity of a material surface to further broaden its application and increase its output performance, despite the large range of triboelectric materials available [39-41].

1.1.5. *PVDF membrane as a triboelectric layer*

In the LS-TENG, the liquid is intentionally employed as positive charge material, hence the utilization of a solid layer with high negative triboelectric properties is an effective way of generating more electrostatic charges, which provides a higher output performance [42, 43]. PVDF, a highly non-reactive polymer has been widely used as a material for manufacturing TENG devices owing to its high flexibility, good mechanical properties, reasonable cost, and the simplicity with which different membranes made of this material can be fabricated [44, 45]. Although PVDF has been widely used for TENG devices, their performances are still not sufficient to be practically utilized for powering portable devices. Therefore, much research has been developed on different processing methods to increase the TENG power performance based upon PVDF membrane polarizability control [29, 46-

48]. Fundamentally, the tribo-polarity of the PVDF membrane lies in its fluorine functional groups and geometrical structure. Consequently, there are two ways to enhance the negative polarity of PVDF: creating a more polar β phase to increase the dipole moment or adjusting the fluorine-containing functional groups with low surface energy.

PVDF has the simplest repeat unit based on the arrangement of CF_2-CH_2 monomers, resulting in its polymorphism, generally α, β, γ, and ε. **Figure 1.8** shows a typical chain conformation for α, β, and γ crystalline phases of PVDF [49]. The polar crystalline phase (β phase) is among them, and it has an all-trans configuration, with fluorine and hydrogen atoms aligned in opposite orientations. Therefore, the polar β phase in PVDF has excellent polarization properties, which increases the electrostatic induction with other materials [50, 51]. However, whereas α is the most common phase and the simplest to obtain, it is hard to obtain the β phase under normal circumstances.

Figure 1.8 Semi-crystalline α, β, and γ conformations of PVDF [49].

It could be quite fascinating to perform α to β transformation via mechanical deformation owing to various advantages such as simple technique, high efficiency, and large production. Nevertheless, after reducing the mechanical strain, the polymer molecular structure might revert to its original state, resulting in a drop in β phase content. In addition, large strains, typically 400–500%, are required to induce atomic phase transitions, which are not suitable for creating composite materials that can successfully combine the benefits of PVDF with other inclusions, especially at high filler content. It leads to uncontrolled reorganization and agglomeration of the filling material [52-54].

Another strategy to improve the β phase is to employ various monomer units in the polymerizing process, including all-trans configurations like chlorotrifluoroethylene (CTFE), chlorofluoroethylene (CFE), and trifluoroethylene (TrFE). This method, however, requires sophisticated synthesis techniques and expensive materials [55, 56].

Another way to enhance the content of the β phase is to add fillers such as carbon nano-tubes (CNTs), $BaTiO_3$ nanoparticles, and clays into PVDF to form nanocomposites. However, performance optimization of the TENG devices due to the synergistic effect between ferroelectric polymers and piezoelectric ceramics still needs to be improved [57-60].

1.2. Research objectives

The main objectives of this dissertation are to provide some effective method for fabricating the PVDF membrane with high tribo-polarity based on two strategies: creating a more polar β phase to increase the dipole moment or adjusting the fluorine-containing functional groups with low surface energy. In addition, the fabricated PVDF membrane was applied to the triboelectric layer to boost the output performance of the TENG. The scope of these research objectives has been summarized as follows.

Based on the first strategy to enhance the tribo-polarity of PVDF membrane, the combination of ferromagnetic cobalt ferrite nanoparticles, $CoFe_2O_4$ (CFO), and PVDF was studied to increase the polar β phase. Owing to the moderately high magnetization, high coercive force, and relatively large magnetic anisotropy of the CFO nanoparticles, the content of the β phase in the CFO/PVDF membrane could be significantly increased. Moreover, the addition of CFO nanoparticles was controlled to optimize the highest β phase in the CFO/PVDF membrane. Then, the output performance of CFO/PVDF TENG was investigated to confirm the advantage of the polar β phase in PVDF.

As is well-known, fluorine element, which is the most electronegative element, is able to increase polarizability and dipole moment of the PVDF. Based on the second strategy to enhance the tribo-polarity of PVDF membrane, 1H,1H,2H,2H-Perfluorooctyltriethoxysilane (FOTS), which contains a huge of fluorine elements, was used to graft on the PVDF membrane through the epitaxial growth process. The epitaxial growth gives the favorable opportunity for simple and large-scale fabrication in the preparation of PVDF membrane, the modified membrane is generated by a two-step approach. Firstly, SiNPs are coated on the hydroxylated PVDF membrane through chemical bonding and then grafted by FOTS to create the FOTS/SiNPs/PVDF (FSiP) membrane. The tribo-polarity enhancement of the FSiP membrane was demonstrated via the improvement of the dielectric constant and hydrophobic properties. Thus, the TENG based on the FSiP membrane exhibits outstanding triboelectric performance.

Based on the advantage of the two above strategies, we tried to enhance the tribo-polarity of the PVDF membrane by using both methods: polar β phase enhancement and adjusting the fluorine-containing functional groups. The surface of graphene oxide (GO) was functionalized by using FOTS to form the high polarization functionalized graphene oxide (F-GO). After that, the F-GO/PVDF membrane was fabricated via a blade coating method. The addition of F-GO in the PVDF membrane can significantly increase the content of the β phase, dielectric constant, and hydrophobic properties, which is a critical point for enhancing the output performance of the TENG.

In addition, the TENG based on different proposal membranes were investigated to prove the ability as a power source for the electronic systems in practical application. The proposal TENG shows the high durability, stability, as well as water-resistant, which have great prospects for hydraulic energy harvesting and a self-powered sensor for the liquid flow rate measurement in a harsh environment. However, some limitations of the proposed methods remain and are discussed.

1.3. Limitation of the dissertation

In this thesis, the tribo-polarity enhancement of PVDF through two strategies: creating a more polar β phase and adjusting the fluorine-containing functional groups has been confirmed. Based on this, the output performance of the proposal TENG exhibited significantly increased. However, some limitations can be remarked as follows.

In the fabrication method, the fabricated membranes are only based on the two above strategies with a simple process. For the higher tribo-polarity, different fabrication methods should be applied to optimize the structure and characteristics of the membrane. Moreover, mass production should be investigated.

The output performance of TENG has been significantly improved after using PVDF membrane with tribo-polarity enhancement, however, the performance still needs to be enhanced. The application of the TENG devices in practical application as a power source

for electronic systems and self-powered systems are some limitations. These limitations will be concerned and researched in the near future.

1.4.Disstertation outline

The reminder of this thesis is organized as follows. The using material, fabrication procedure of the membrane and TENG devices, and characterization of the triboelectric membrane are present in Chapter 2. In Chapter 3, the PVDF membrane is driven the polar β phase to enhance the output performance of TENG. The tribo-polarity and output performance of the TENG based-PVDF membrane is improved via adjusting the fluorine-containing groups and is introduced in Chapter 4. Chapter 5 provide the method to increase both the β content and fluorine elements in the PVDF membrane for tribo-polarity enhancement. Finally, the conclusions of the study and the discussion for future works are presented in Chapter 6.

MATERIALS AND METHODS

2.1.Materials

Polyvinylidene fluoride (PVDF) powder (M.W. ~ 534 000), GO nanosheets, and 1H,1H,2H,2H-Perfluorooctyltriethoxysilane (FOTS, 98%), $CoFe_2O_4$ nanoparticles (CFO, 30nm, 99%), silica nanoparticles (SiNPs, 99.5% trace metals, 10–20 nm), 1,3,5-Benzenetricarbonyl trichloride (TMC, 98%) were acquired from Sigma-Aldrich, St. Louis, MO, USA. A PVDF membrane (Sigma-Aldrich) has an average thickness of 50 μm.

Dimethyl sulfoxide (DMSO, 99%) and N,N-dimethylformamide (DMF, 99,5%) were purchased from Samchun Chemical, Seoul, Korea.

Sodium hydroxide (NaOH, 97%), hexane, anhydrous ethanol was acquired from Daejung Co. Ltd., Korea.

4-(Dimethylamino)pyridine (DMAP, 99%) and N,N0-dicyclohexylcarbodiimide (DCC, 99%) and were supplied from Thermo Fisher Scientific, Boston, MA, USA.

Indium tin oxide (ITO) glass (Sigma-Aldrich) with surface resistivity of 8 to 12 Ω/sq was used as the electrode.

Silicone tube, Kapton tape, Silver epoxy paste, double-sided tape, copper tape, and copper conductor were purchased from the local market.

2.2.Fabrication procedure of the TENG

2.2.1. Fabrication of CFO/PVDF TENG

Figure 2.1 shows the fabrication of the CFO/PVDF membrane by using a sol-vent-casting process. At first, PVDF powder and CFO nanoparticles were separately dissolved in DMF solution to obtain the 10 wt% PVDF and 1 wt% CFO solution. Then, the CFO solution was added to the PVDF solution in various amounts to obtain the desired CFO/PVDF ratio (2.5, 5, 7.5, 10 wt%). After that, the fabricated solution was successfully bladed onto the ITO

film and dried at 80 °C to ensure the DMF evaporation. Each membrane was designated as follows CFO/PVDF-A, where A is the content of CFO in the PVDF matrix.

The CFO/PVDF TENG device operates through single-electrode mode by using CFO/PVDF membrane as the solid phase, ITO layer as the electrode, and deionized water as the liquid phase. After coating, the fabricated membranes were cut into a dimension of 2×2 cm2. The output signals of current and voltage were measured through a copper wire connected to the ITO layer.

Figure 2.1 Schematic diagram of CFO/PVDF membrane fabrication.

2.2.2. Fabrication of FSiP TENG

Figure 2.2 illustrates the preparation procedure of the epitaxial growth for tuning the PVDF surface polarizability via SiNPs coated and FOTS functionalized. Firstly, the membrane was treated with alkaline solution (7.5 M NaOH) for 3 h at 70 ◦C to generate hydroxyl functionality. The hydroxylate PVDF membrane was washed with DI water and soaked in a TMC solution (0.5 wt%) at 25 ◦C for 30 min. Thereafter, the TMC-modified membrane was then absorbed in a SiNPs solution (0.1 wt %) for 1 h under gentle stirring to make the epitaxial growth of SiNPs on the PVDF membrane surface. After that, the treated membrane was cleaned with DI water and further fluorinated by being soaked in FOTS solution (1.0 wt%) for 24 h to form FOTS/SiNPs/PVDF (FSiP) membrane. Besides, the FOTS/PVDF (FP) membrane was fabricated by fluorinating the hydroxylate PVDF membrane with FOTS by the same above method.

After that, each FSiP, FP, PVDF membrane was cut into a size of 2 cm × 2 cm sample so that all of the TENG devices are the same contact surface area for every experiment. These samples were attached to copper tapes as an electrode layer on one side of each membrane before being added to the glass substrate. Finally, a copper wire was bridged the electrode of the TENG by Silver epoxy paste to measure the electrical data.

Figure 2.2 Schematic diagram the procedure for epitaxial growth on PVDF membrane with silica nanoparticles (SiNPs) coated and FOTS functionalized.

2.2.3. Fabrication of F-GO/PVDF TENG

Functionalization of GO nanosheets: The goal of the process is to graft the FOTS hydrolysate onto the GO nanosheets as illustrated in **Figure 2.3**. The -COOH group on GO nanosheets reacted with the -OH group on hydroxylated FOTS as a result of DCC dehydration and DMAP catalysis. First, 0.25 g GO was dissolved into 50 mL DMSO for 4 h under sonication vibration to obtain a homogeneous GO solution. The GO solution was then supplemented with 5 g DCC and 0.37 g DMAP. Simultaneously, the hydroxylation of FOTS solution was prepared by adding 1 mL FOTS and 2 mL DI water into 50 mL DMSO under 2 h magnetic stirring. Then, two solutions were thoroughly mixed and continuously stirred at 50°C for 24 h to initiate the grafting reaction between GO and FOTS. The suspension was then separated using high-speed centrifugation and rinsed thoroughly with acetone and DI water. Finally, the functionalization of GO nanosheets (denoted as F-GO) was dried at 60°C for 24 h under vacuum to achieve a constant weight.

Preparation of F-GO/PVDF TENG: The fabrication of F-GO/PVDF membranes via a blade coating method was shown in **Figure 2.4**. 1 g PVDF was dissolved in 10 mL DFM at 60°C for 3 h with constant stirring, and different content of F-GO suspensions was separately prepared by dispersing in DFM and sonicating for 4 h. Then, the F-GO suspensions were introduced drop by drop to the PVDF solution and were stirred at 60°C to form a homogeneous solution. For comparison, other neat PVDF and GO/PVDF solutions have also been made in the same manner. The material components of the coating solution was displayed in **Table 2.1**. The several prepared solutions were then sequentially blade-coated onto the ITO film (40 × 30 × 1.1 mm) and evaporated at 80°C in the oven for 12 h. The fabricated membrane covers the ITO surface with dimensions of 30 × 30 mm. Finally, the top electrode was formed of copper wire and was attached to the coated membrane to make TENG devices. The ITO layer, which forms the bottom electrode, was linked to another copper wire.

Table 2.1. The material components of the coating solution.

Membrane name	PVDF (g)	DFM (ml)	GO (mg)	F-GO (mg)	F-GO/PVDF ratios (wt. %)
PVDF	1	10	0	0	/
GO/PVDF	1	10	5	0	/
F-GO/PVDF-0.1	1	10	0	1	0.1
F-GO/PVDF-0.25	1	10	0	2.5	0.25
F-GO/PVDF-0.5	1	10	0	5	0.5
F-GO/PVDF-1	1	10	0	10	1.0
F-GO/PVDF-2	1	10	0	20	2.0

Figure 2.3 Schematic illustration of functionalization of GO.

Figure 2.4 Preparation of F-GO/PVDF membranes and TENG devices.

2.3. Characterization of triboelectric membrane

2.3.1. Microstructure

To get an observation of membrane surface, we observed under field emission scanning electron microscope with energy-dispersive X-ray spectroscopy (FE-SEM, model JSM-6500F and model JSM-7600, JEOL, Tokyo, Japan). The samples were placed on the copper grid, which was coated with carbon film then covered with a layer of platinum. Moreover, The membrane surface roughness was measured by atomic force microscopy (AFM) (MFP-3D Stand Alone AFM, Oxford Instruments, UK).

2.3.2. Chemical properties

Fourier transform infrared (FTIR) spectroscopic data (model Nicolet iS5, Thermo Fisher Scientific, Boston, MA, USA) was used to evaluate the functional groups and chemical bonding of each membrane sample. Dried samples were mixed with KBr at a 1:100 ratio to make a pellet under the pressure of 200 kg/cm^2. The FTIR spectra were recorded in the range of 4000–450 cm^{-1} with a resolution of 2 cm^{-1}. The content of the β phase could be estimated using the measured infrared absorption according to the Lambert-Beer law.

$$F(\beta) = \frac{A_\beta}{(K_\beta/K_\alpha)A_\alpha + A_\beta} \tag{2-1}$$

where A$_\alpha$ and A$_\beta$ represent the absorbance at the wavenumbers 764 and 840 cm^{-1} for the α and β phase, K$_\alpha$ (6.1 ×10^4 cm^{2}mol^{-1}) and K$_\beta$ (7.7 ×10^4 cm^{2}mol^{-1}) denote the transmittances at the wavenumber considered.

X-ray photoelectron spectroscopy (XPS) is widely used in the material surface analysis because of its relative simplicity in use and data interpretation. To examine the functional groups on the membrane surface, the XPS (XPS, ESCALB-MKII250 system, Thermo Fisher Scientific, Boston, MA, USA) was hired.

2.3.3. Physical properties

For ferroelectric properties, the membranes were characterized through an HP3325B synthesizer/function generator and a TREK 10/40 high-voltage amplifier. High voltage AC power supply has the specification (0 - 40 kV), 0.5 A, and frequency 1 Hz. The capacitor of (0.68 µF) was used. The P-E hysteresis loop measurement had been done by increasing the voltage gradually to get the curve of the hysteresis, then the saturation polarization (P$_s$), Remnant polarization (P$_r$), and coercive electric field (E$_c$) were measured.

Dielectric characterize of the membrane were obtained using an impedance analyzer 3522-50 LCR Meter (Hioki, Nagano, Japan) with a frequency from 10^3 to 10^7 Hz.

The hydrophobicity of the film was investigated through the water contact angle by the sessile drop method (SmartDrop, FemtoFAB, Waltham, MA, USA).

2.3.4. Output performance measurement of TENG

A peristaltic pump (Ecoline VC-360) was used to transport the working water through the TENG. The TENG system is set up following the photograph in **Figure 2.5**. The silicone tube with a diameter of 6.35 mm is used to transport the water on the triboelectric surface of the TENG. The operating conditions of the TENG system were set at 50 μL per water droplet with a frequency of 2 Hz, dropping height of 7.5 cm, and an inclination angle (α) of 30°-45° The output current and voltage of the PIL-TENG devices were recorded using digital multimeters (DMM7510, Keithley Instruments) with an internal load resistance of 10 MΩ.

Figure 2.5 Illustration photography of the FSiP-TENG experimental system.

Chapter 3

DRIVING THE POLAR β PHASE OF PVDF MEMBRANE

3.1.Introduction

The triboelectric layer, therefore, is critical to the energy performance of the water-based TENG, depending on the operating mechanism and structure design. Previous studies have shown several methods aimed at improving efficiency performance by adding auxiliary materials, surface treatments, or structural designs based on various triboelectric properties such as surface potential, permittivity, and structural properties were investigated [61, 62]. According to the different methods for triboelectric effect enhancement, ferroelectric is one of the key materials with lightweight, flexible, high strength, have attracted considerable attention. Furthermore, ferroelectric materials specialize in converting mechanical and thermal stimuli into electrical responses due to their special piezoelectric and thermoelectric properties [46, 48, 55, 63].

Unlike inorganic ferroelectric materials which have hardness, brittleness, and involve tedious manufacturing processes, ferroelectric polymers have flexibility, treatability, and impressive physics, making them promising candidates for wearable and implantable electronic devices for triboelectric devices [52, 53]. PVDF is suggested as a useful material that can fabricate a triboelectric layer for water-based TENG owing to its large polarizability in the crystal structure and strong surface potential [64]. PVDF is composed of a CF_2CH_2 monomer chain, which is arranged into various stages to form the α, β, γ, and ε phases. In general, the α phase outperforms the PVDF phase element due to its remarkable thermodynamic stability. On the other hand, the α phase does not exhibit ferroelectricity due to its nonpolar molecular chain conformation. While the polar crystal phase (β phase) has a zigzag structure with fluorine and hydrogen atoms are oriented in opposite directions. Furthermore, compared to other polymers, PVDF with a high phase composition has a greater dielectric constant and a bigger negative charge [65-67]. Therefore, increasing the β phase of the PVDF membrane is a critical point for optimizing the output energy of water-based TENG devices.

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In this chapter, we propose a realistic approach to synthesizing a high level of β phase content for a triboelectric layer of the TENG devices by constructing ferromagnetic cobalt ferrite, (CFO), as fillers in the PVDF matrix. Due to the moderately high magnetization, high coercive force, and relatively large magnetic anisotropy, the addition of CFO nanoparticles could be significantly increased the content of the β phase in the CFO/PVDF membrane, which significantly impacts the performance output of the CFO/PVDF TENG.

3.2. Results and discussions

3.2.1. Characterization of CFO/PVDF membrane

As demonstrated in **Figure 3.1**, the surface morphology of PVDF and CFO/PVDF-5 membrane was examined with FESEM images. Compared to PVDF membranes, CFO/PVDF-5 has a rougher surface and contains more granular particles owing to the distribution of CFO in the PVDF matrix. In addition, this is due to the phase separation of the CFO and PVDF, which has a substantial impact on the β phase conformation and the dielectric constant of the membrane. Moreover, AFM images (**Figure 3.2**) from a near-field microscope were used to clearly distinguish between non-polarity (α) and polarity (β) on the membrane surface [67]. The membrane surface exhibits multiple spherical morphologies corresponding to β (marked by red circles) and β / α hybrid phase regions (marked by blue

Figure 3.1 FE-SEM image of (a) PVDF and (b) CFO/PVDF-5 membranes.

circles), respectively. In addition, the smooth areas coincide with the α phase of the membrane. Therefore, after adding the CFO nanoparticles, the content of the β phase significantly increases. Due to the negatively charged on the surface of CFO nanoparticles, these nanoparticles establish a bond with the positive CH_2 of PVDF via ionic dipole interactions, having resulted that the preferential development of the polar β phase.

Figure 3.2 AFM image of (a) PVDF and (b) CFO/PVDF-5 membranes.

For more perceptible, FTIR was used to quantify the effect of CFO on the phase structure of the PVDF membrane. The α phase is indicated by the peaks at 764, 984, and 1391 cm^{-1}, while the β phase is indicated by the peaks at 840 and 1284 cm^{-1}, as pictured in Figure 3.3(a), [68]. Following Equation 2-1, the content of the β phase in different PVDF and CFO/PVDF membranes were calculated and shown in Figure 3.3(b). Consequently, the application of CFO nanoparticles dramatically enhanced the content of βphase. For example, the content of the β phase in the CFO/PVDF-5 membrane reached a maximum value of 77.7%, while the β phase content of the PVDF membrane was 51.2%, indicating the advantage of CFO nanoparticles over the β phase formation of PVDF structure. However, at CFO concentrations above 5 wt%, the content of the β phase begins to decrease. This can be explained by the agglomeration of a high concentration of CFO nanoparticles on the film surface [50].

Figure 3.3 (a) FTIR spectra of pure PVDF and CFO/PVDF membranes and (b) the corre-sponding content of β phase.

In addition, CFO nanoparticles are a renowned magnetic material with an excellent dielectric constant that impacts the TENG electrical output. As a result, **Figure 3.4** investigates the dielectric constant of the pure PVDF and CFO/PVDF membranes relying on frequency dependence. The pure PVDF membrane has a dielectric constant of 10.4 at 10^2 Hz and subsequently declines as the frequency increases, demonstrating the same pattern as prior research [69, 70]. Furthermore, the dielectric constant of the CFO/PVDF membranes follows the same trend as the pure PVDF membrane in the frequency range of 10^2-10^6 Hz and increases as the concentration of CFO increases. Therefore, the dielectric constant of the CFO/PVDF-10 membrane reaches the highest value of 17.9 at 10^2 Hz, which is 1.72 times larger than the PVDF membrane.

Figure 3.4 Dielectric constants of pure PVDF and CFO/PVDF membranes at a different frequency.

3.2.2. Working mechanism

The working principle of water-based TENG in this study is illustrated in **Figure 3.5** based on triboelectric and electrification effects. In the initial state, the water droplet was pre-charged contained with air and silicone tubing to get the positive charges before approaching the CFO/PVDF membrane surface (**Figure 3.5(i)**) [71, 72]. When the positively charged droplet contact with the CFO/PVDF layer (**Figure 3.5(ii)**), the electrical balance is disrupted resulting in an electrical potential imbalance between the CFO/PVDF membrane and the ITO electrode. Electrical currents are generated due to the attractiveness of the ITO electrode towards electrons at the ground. Because of the self-balancing property of the potential difference, it tends to return to equilibrium (**Figure 3.5(iii)**). The electron flow then changes direction due to the generation of potential difference as the droplet exits the CFO/PVDF layer (**Figure 3.5(iv)**). In this situation, an alternating current output could be generated until the next water droplet is generated to provide a continuous current.

Figure 3.5 Working mechanism schematic of the water-based TENG.

3.2.3. Electrical output performance

Based on the fundamental working mechanism of the TENG, the transferred charge density ($\boldsymbol{\sigma'}$) in this device could be presented as follows [64]:

$$\sigma' = \frac{\sigma_0 d_{gap}}{d_{gap} + d_m/\varepsilon_m} \qquad (3-1)$$

where d_m, ε_m refer to the thickness and permittivity of the CFO/PVDF membrane, d_{gap} is the gap distance and σ_0 is the charge density in the equilibrium state. The enhanced polar β phase facilitates charge carrier migration and increases charge density in equilibrium [73]. Therefore, as a result of the high β phase of the CFO/PVDF membrane, charge accumulation at the solid interface may increase, the static electric field acting on the triboelectric surface may increase, and TENG performance may be further improved. In addition, this calculation shows that when the dielectric constant grows, the transfer charge density of the membrane improves as well, gaining the benefits of TENG electrical output.

Therefore, characterization of the power output of the pure PVDF TENG and CFO/PVDF TENG has been shown in **Figure 3.6** to illustrate how CFO content affects the TENG electrical output. In general, the electrical output of TENGs exhibits is highly stable, which is advantageous for the operation of electrical systems. Specifically, the peak voltage and current of PVDF-TENG were found about 11.4 V and 1.26 μA, respectively, which seem to be smaller than that of other CFO/PVDF TENG. After adding the CFO nanoparticles, the peak voltage and current of CFO/PVDF TENG were approximately 12.6, 17.2, 14.9, 12.8 V and 1.67, 2.27, 1.95, 1.49 μA, respectively, corresponding to CFO content of 2.5, 5, 7.5, 10 wt%. Similarly, the transferred charge (**Figure 3.6c**) of the CFO/PVDF TENG exhibits a similar trend as the output current under varied CFO content in PVDF. Notably, CFO/PVDF-5 TENG achieves the maximum electrical output, which enhances the current of 80%, voltage of 51%, and transferred charge of 66% compared to the values obtained for the PVDF TENG. This significant improvement is attributed to greater charge transfer as a result of better β phase composition and dielectric constant, which has been discussed in the above section. However, when the content of CFO nanoparticles exceeds 5% by weight, the output signal of CFO/PVDF TENG starts to deteriorate. This is due to a decrease in β phase content

in the CFO/PVDF membrane. Furthermore, high CFO concentra-tion might create agglomeration on the membrane surface, which reduces charge transfer to the surface.

Figure 3.6 (a) Voltage and (b) current of PVDF and CFO/PVDF based TENG, (c) comparison of transferred charge of their TENG.

With the goal of demonstrating the capabilities as a power source for electronic devices, the power density of the PVDF and CFO/PVDF-based TENG was examined under various load resistance (R) ranges ranging from 1 MΩ to 500 MΩ. The following formula was used to compute the power density (P)

$$P = \frac{I^2 R}{A} \tag{3-1}$$

As a result, in **Figure 3.7a**, the highest power density of CFO/PVDF TENG is 90.3 mW/m^2 corresponds to a load resistance of 20 MΩ, which is 2.4 times more than pure PVDF TENG. Moreover, the output current of CFO/PVDF-5 TENG decreases as the loading resistances rise (**Figure 3.7b**). Meanwhile, power density increases until a load resistance value are reached to 20 MΩ, then decreases as resistance increases. These findings suggest that the CFO/PVDF-5 TENG system might be used as water-based energy harvesting equipment, where the triboelectric layer made of PVDF and CFO nanoparticles provides better performance.

Figure 3.7 (a) Power density of PVDF and CFO/PVDF based TENG at load resistance of 20 MΩ, (b) current and power density of the CFO/PVDF-5 TENG with different load resistance.

Furthermore, the high durability and stability of CFO/PVDF-5 TENG were demonstrated in **Figure 3.8**. Before being used for the triboelectric layer, the CFO/PVDF-5 membrane was processed to bath sonication at various intervals. The peak voltage of this TENG remained steady after the CFO/PVDF-5 membrane was treated for 20 minutes, indicating that CFO/PVDF-5 TENG has exceptional mechanical endurance in harsh conditions. Furthermore, the voltage signal remains 90% after working for more than 10000 cycles,

Figure 3.8. (a) Durability of CFO/PVDF-5 TENG following sonication treatment at various periods, (b) stability of CFO/PVDF-5 TENG operated for 10000 cycles.

which demonstrated the high stability of the TENG. According to the findings, the CFO/PVDF-5 TENG has a high potential for harvesting water energy in a variety of situations such as rainfall, ocean, wastewater, and so on.

3.3. Chapter summary

In conclusion, the electrical output of the water-based TENG was boosted by modifying the crystal morphology and dielectric constant of the PVDF membrane using CFO nanoparticles. Based on the large magnetic anisotropy, the dielectric constant of CFO/PVDF membranes progressively improved when the content of CFO was increased from 2.5 to 10 wt% and efficiency finally approached over 80% when compared to pure PVDF membrane. More crucially, the content of the β phase improves and reaches the maximum of 77.7% in the CFO/PVDF ratio of 5 wt%. It was attributed to an increase in charge distribution, resulting in greater electrostatic charge movement on the triboelectric interface. As a result, the highest power density of the TENG rises from 37.5 to 90.3 mW/m^2, which was increased approximately 2.4 times. Furthermore, the proposed TENG generated by the CFO/PVDF-5 membrane has tremendous potential for mechanical power generation and a self-powered sensor in a hostile environment because of its high durability and stability.

ADJUSTING THE FLUORINE-CONTAINING GROUPS IN PVDF MEMBRANE

4.1. Introduction

In the LS-TENG, the liquid is intentionally employed as positive charge materials, hence the utilization of a solid layer with high negative triboelectric property is an effective way for generating more electrostatic charges, which provides a higher output performance [43]. Although polyvinylidene fluoride (PVDF), which is regarded as a high negative triboelectric property, excellent chemical compatibility, and physical robustness, has been widely used for TENG devices, their performances are still not sufficient to be practically utilized for powering portable devices. Therefore, much research has been developed on different processing methods to increase the TENG power performance based upon PVDF membrane polarizability control [29, 47, 48]. Fundamentally, the surface polarity of the PVDF membrane lies in its fluorine functional groups and geometrical structure. Consequently, there are two ways to enhance the negative polarity of PVDF: creating a more polar β phase to increase the dipole moment or adjusting the fluorine-containing functional groups with low surface energy. A number of techniques have been reported following these two strategies, such as electrospinning, chemical modification, phase separation, self-assembly, hydrothermal synthesis [74-77]. It is demonstrated that the combination of inorganic oxide nanoparticles and the fluorine enhancement could boost the negative polarity of the PVDF membrane by far.

Silica nanoparticles (SiNPs) are a well-used inorganic oxide material with decent strengths for use in energy harvesters such as excellent retention ability, low electric loss, high resistivity, and high dielectric constant. For instance, the SiNPs with modified functional groups such as alkyl chains, fluorine groups, and phenyl groups have been widely studied for a number of applications. Among the functionalities of SiNPs, the fluorine element plays a critical role in hydrophobicity, dielectric constant, and surface potential, which was widely used in solid-solid TENG devices [68, 78-81]. For example, Yan et al. [82]

used an in-situ polycondensation method to introduce SiO2 nanoparticles with modified fluorine functional groups on the surface of the poly (vinylidene fluorideco-hexafluoropropylene) (PVDF-HFP). Compared to raw PVDF-HFP based TENG, the modified-PVDF-HFP TENG showed significantly improved output performance and excellent droplet-repellency. Roy et al. [83] grafted allicin onto cellulose nanofibers (CNFs) film using a 'thiol-ene' click chemistry. The peak current and voltage of the modified film-based TENG could gain 5.13 μA and 7.9 V, more than 5 times greater than the TENG-based pristine cellulose. However, the processing methods exhibit several restrictions of complex operating conditions, limited yields, as well as the saturated effect of optimized material. On the other hand, utilizing SiNPs with modified functional groups for LS-TENG devices has rarely been reported [84, 85].

Herein, we describe a new surface polarity tuning PVDF membrane that can be served as a triboelectric material for TENG devices through the epitaxial growth process with outstanding water-resistant and dielectric properties. As the epitaxial growth gives the favorable opportunity for simple and large-scale fabrication in the preparation of PVDF membrane, the modified membrane is generated by a two-step approach. Firstly, SiNPs are coated on the hydroxylated PVDF membrane through chemical bonding and then grafted by FOTS to create the FOTS/SiNPs/PVDF (FSiP) membrane. The tribo-polarity enhancement of the FSiP membrane was demonstrated via the improvement of the dielectric constant and hydrophobic properties. Thus, the TENG based on the FSiP membrane exhibits outstanding triboelectric performance.

4.2. Results and discussions

4.2.1. Characterization of FSiP membrane

The hydroxyl group on the PVDF surface was firstly generated by treating it with an alkaline solution. After that, the epitaxial growth via the chemical bonding method was used to coat SiNPs and fluorine elements on the membrane surface. To confirm the functionalization of the membrane before and after epitaxial growth, the FTIR spectrum was

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employed to analyze the chemical structure as exhibited in **Figure 4.1**. Regarding the PVDF and other membranes, the peak of CH_2 vibration group was found at 1410 cm^{-1}, and the stretching of CF_2 was found at 1170 and 1210 cm^{-1}, respectively. Otherwise, the new appearance of the vibration band at 1080 cm^{-1} is represented to silicon groups, recommending the successful SiNPs growing on the surface of the FSiP membrane. The intensity enhancement of 1170 cm^{-1} and 1210 cm^{-1} for both FP and FSiP membrane indicates the existence of FOTS, indicating the success of fluorinated enhancement on the surface membrane [86]. In addition, the fluorine (F1s) peak for the FSiP membrane showed higher intensity compared to the FS membrane (**Figure 4.2**), suggesting more fluorine elements were grown on the membrane surface. It can be explained by coated SiNPs on the PVDF membrane surface before the fluorinated process. The abundant hydroxyl functional groups of SiNPs facilitate the surface fluorination process via well-established silane chemistry to low-energy membrane surfaces [85]. The successful epitaxial growth by using SiNPs and FOTS on the PVDF membrane was the extraordinary significance for the enhancement of hydrophobicity and surface potential.

Figure 4.1 FTIR spectra of PVDF, FP, FSiP membranes surface.

Figure 4.2 XPS spectra of PVDF, FP, FSiP membranes.

The surface morphology and roughness characterized of each tribo-membrane were examined by using FE-SEM and AFM as presented in **Figure 4.3**. It is apparent that the PVDF surface exhibits a high porosity surface and in the inset image, the pore walls were smooth (**Figure 4.3a**). Nevertheless, a number of pores on the FP and FSiP membrane surface were broken due to the hydroxyl group generation process (**Figure 4.3b, c**). Furthermore, various nanoscale protrusions on the FSiP membrane surface were observed in **Figure 4.3c** ascribed to the silica nanoparticles by means of chemical bonding on the membrane surface. These SiNPs protrusions on the pore walls are promised to provide multiple kinetic barriers leading to increment water resistance [84]. When considering the surface roughness before and after epitaxial growth (**Figure 4.3e-f**), it is pointed out that the rising of root mean square roughness (Rq) was principally attributable to the hydroxyl group generation process. Meanwhile, the Rq values of the FP and FSiP membranes were 183 nm and 192 nm, which is no obvious difference. Therefore, the SiPNs growing process on the FSiP membrane surface was around 10 nm equivalent to the size of the SiPNs (10-20 nm). According to the increasing nanoscale protrusions surface structure and surface roughness

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increases, the hydrophobic property of the modified membranes is greatly improved, which will be proven by the contact and sliding angle in subsequent sections.

Figure 4.3 FE-SEM images of (a) PVDF, (b) FP, (c) FSiP membranes surface, the inset image shows a magnified view, and AFM images of (d) PVDF, (e) FP, (f) FSiP membranes surface.

4.2.2. Working mechanism

Figure 4.4a presents the schematic structure and digital photograph of FSiP-TENG. One side of the PVDF membrane was grown by SiNPs and FOTS to form a thin polarization layer, and the other side deposited a Cu layer as an electrode. Then, the FSiP-TENG was fixed on the glass substrate and arranged into the device for testing electricity generation. The operating principle of this TENG is described as a single-electrode mode as exhibited in **Figure 4.4b** based on electrostatic induction and triboelectric effect. In the beginning state, before approaching the triboelectric layer (**Figure 4.4b(i)**), the water droplet already contains positive charges during contact electrification with the air and the silicone tube [45, 46]. As the positively charged droplet reaches the FSiP membrane (**Figure 4.4b(ii)**), the electrical equilibrium broken leads to the difference of positive potential between the FSiP membrane and the Cu electrode. The electron flow is created by the attraction of the Cu electrode to the electrons from the ground. Since its intrinsic feature tends to be back to the equilibrium state, i.e. balance the potential difference (**Figure 4.4b(iii)**). Successively, the electron flow reverses direction owing to the creation of a negative potential difference when the water

Figure 4.4 Schematic structure and working principle of the FSiP-TENG.

droplet moves out of the FSiP surface (**Figure 4.4b(iv)**). In this case, an AC output can be generated until the next droplet is brought about to generate a continuous electricity flow.

4.2.3. *Electrical output characteristics*

The fundamental working mechanism of the LS-TENG is occurred originated from the electrostatic induction and the triboelectrification of the droplet and solid surface. Thus, it is quite important to ensure that the solid surface has a high dielectric constant and hydrophobic property to enhance the TENG performance [87, 88]. In this work, the frequency-dependent dielectric properties of each membrane were measured with a frequency from 1 to 10^7 Hz, shown in **Figure 4.5a.** The dielectric constant of the PVDF membrane was found ~10.8 at the frequency of 1 Hz and then shows a downward trend accordingly to the increase of frequency, which is almost the same as other reports [89]. After modifying the membrane, the dielectric constant raised sharply. As a consequence, the dependence of the dielectric constant of FP and FSiP reached a value of 12.8 and 15.3 at 1 Hz, respectively. As is well-known, the dielectric constant is closely connected to the polarizability of the elements present in the triboelectric membrane. Fluorine in FOTS, which is the most electronegative element, is able to increase polarizability and dipole moment. Therefore, FOTS is considered a major factor for the dielectric constant improvement in the epitaxial growth process. From previous work [89], in a tribo-membrane as a capacitor, the accumulated charges (Q) is given by

$$Q = CV \left[1 - e^{\frac{t}{RC}} \right] \qquad (4-1)$$

where C, V, t, and R are the capacitance, output voltage, charging time, and resistance, respectively. Assume that V is constant, the maximum capacitance (C_{max}) of the membrane can be calculated by

$$C_{max} = \varepsilon_0 A \frac{\varepsilon_m}{d_m} \qquad (4-2)$$

where ε_0 is the vacuum permittivity (8.854×10-12 Fm^{-1}), ε_m is the dielectric permittivity of the triboelectric membrane, A is the contact area (4 cm^2), and d_m is the membrane thickness

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(50 μm). Therefore, ε_m is proportional to C_{max}, which is proportional to Q. In agreement with this concept, the increasing charge density is related to the increasing dielectric constant that indicated the enhancement of output performance. Additionally, the process of SiNPs coating leads to fewer defects at the interface of the surface membrane as presented in **Figure 4.3c**, suggesting the enhancement of the dielectric constant. Meanwhile, the dielectric loss of FSiP membranes remained at a low level compared to other membranes in **Figure 4.5b**, except

Figure 4.5 Frequency dependence of (a) dielectric constant and (b) dielectric loss of PVDF, FP and FSiP membranes.

those in the higher frequency range due to the interfacial polarization. It is believed that low dielectric loss leads to low heat production, which is attributed to the working stability of the membrane [90].

The water contact angle and sliding angle were measured (**Figure 4.6**) to prove the hydrophobic property of the membrane. The water contact angles of the FP and FSiP membrane obtain a value of 143.5° and 151.6°, respectively, while the lower contact angle of 125.6° is noticed for the pristine PVDF membrane. The cause is the increment of fluorine element and silica nanoparticles, which open the way for the reduction of the surface tension and low surface energy, leaving the high hydrophobicity of the membrane. Furthermore, the water sliding angle of the membrane was estimated to evaluate the contact angle hysteresis. The water sliding angles of PVDF, FP, and FSiP are 33.9°, 24.5°, and 17.2°, respectively, which demonstrated the excellent hydrophobicity of the FSiP membrane. Following Young's equation [68], the surface energy of the solid is given by.

$$\gamma_S = \gamma_{SL} + \gamma_L cos\theta_0 \qquad (4-3)$$

where θ_0 is the contact angle of the smooth surface, γ_S is the surface energy of the solid, γ_{SL} is the interfacial tension of solid-liquid, and γ_L is the surface tension of the liquid. When the contact angle is higher than 90°, the surface energy of the solid decreases with an increase of contact angle. Moreover, the relation between contact angle and surface roughness can be determined by the Wenzel equation [91].

$$cos\theta_w = R_f cos\theta_0 \qquad (4-4)$$

where θ_w is the contact angle of the rough solid surface, R_f is the ratio of the surface area to its smooth projected area. Based on the Wenzel model, it could be concluded that the water contact angle increases with an increase of surface roughness, which is fitted with the result of surface roughness as presented in the above section.

Figure 4.6 Contact angle and sliding angle of PVDF, FP and FSiP membranes.

To demonstrate the influence of the surface polarity tuning on the LS-TENG output performance, the output power characteristics of the TENG with other PVDF modification membranes were investigated. **Figure 4.7** exhibits the current and voltage of all three TENG including PVDF-TENG, FP-TENG, and FSiP-TENG when the water flow rate of 1.5 ml/s. As expected, the FP-TENG shows the current and voltage of 1.13 μA and 10.2 V, respectively, which is 2.0 times and 1.5 times greater than the PVDF-TENG. While the current and voltage of FSiP-TENG gain the highest value approximately 2.39 μA and 15.2 V, which boosts the current by 4.1 times and voltage by 2.2 times, compared with the PVDF-TENG. This is consistent with the hydrophobic property and dielectric constant results. The tuning of the surface polarity by fluorine elements is useful to the creation of triboelectric charges under liquid-solid contact. Furthermore, the low surface energy of the fluorine element leads to the ease of charge separation and facilitates the charge accumulation, resulting in an increase of TENG performance [48].

Figure 4.7 (a) Current, (b) voltage, and (c) comparison of current and voltage of TENG for PVDF, FP and FSiP triboelectric membranes.

As a promising way for harvesting energy through water movement, it is required to evaluate the FSiP-TENG performance with regard to water conditions. Therefore, the relationship between this TENG performance and the variety of water flow rates was investigated. **Figure 4.8** shows the influence of water flow rate on the current and voltage, in which the water flow rate range of 1.0 ml/s to 7.0 ml/s, respectively. As can be seen, the current and voltage grow steadily from 1.52 μA to 5.79 μA and from 13.5 V to 28.3 V as the water flow rate increase from 1.0 ml/s to 5.0 ml/s, respectively. Additionally, the frequency of current and voltage peaks also increases from 1.5 Hz to 4.5 Hz when the flow rate increase from 1.0 ml/s to 5.0 ml/s. Meanwhile, the corresponding transferred charge of FSiP-TENG goes along with a similar variation tendency, which increases from 37.1 nC to 152.2 nC as shown in **Figure 4.10**. On the other hand, no obvious change could be realized in the

corresponding voltage and current of FSiP-TENG, when the flow rate continues to increase to 6 ml/s and 7 ml/s. Accordingly, there are two fundamental causes to elucidate the influence of water flow rate on the TENG power performance. Firstly, the applied force on the FSiP membrane surface is raised along with the increase in velocity of the water flow, thus generating more triboelectric charges for power performance enhancement [74]. Secondly, under a higher flow rate, the forming speed of the electric double layer (EDL) increases whereas the thickness of EDL is deduced, which is proving to the triboelectric charges transferring for achieving higher power performance and electrical peak frequency [92, 93].

Figure 4.8 (a) Output current and (b) voltage of the FSiP-TENG depending on the water flow rates.

Nevertheless, the charging and discharging of the FSiP-TENG are limited by material properties, hence the electrical equilibrium does not respond in time due to the higher water flow rate. Therefore, the triboelectric output of TENG tends to instability and has no increment. Moreover, the current, voltage, and transferred charge are proportional to the water flow rate with the linearity correlation coefficients of 0.976, 0.982, and 0.983, respectively. Based upon this linearity, the FSiP-TENG has good potential for application in a self-powered flow rate sensor.

Figure 4.9 Comparison of the current and voltage under varying flow rates.

Figure 4.10 The transferred charge under varying flow rates.

With the intention of proving the ability as a power source for the electronic systems, the power density of FSiP-TENG was measured as prepared TENG (friction area was 2×2 cm^2, the water flow rate was 5 ml/s) with external load resistors. As a result, the output voltage gradually increases from 17.7 V to approximately open-circuit voltage when the load resistances increase from 1 MΩ to 500 MΩ (**Figure 4.11a**). On the contrary, the current output exhibits a downside trend accordingly to the increased loading resistance. The estimated power density of FSiP-TENG is presented in **Figure 4.11b**. The graph indicates that the output power density increases until reaching a specific load value and then decreases under the growth of load resistance. The highest power density of the FSiP-TENG device attains a value of 420 mW/m^2 when a load resistance reaches 20 MΩ. Especially, as shown in **Figure 4.12**, the highest power density of FSiP-TENG is approximately 10.8 times greater than the PVDF-TENG (39 mW/m^2), and 2.7 times greater than the FS-TENG (154 mW/m^2). Moreover, the TENG device is bridged directly to a LEDs bank without requiring any regulated circuit, and about 120 LEDs are successfully lit up when water flows through the TENG.

Figure 4.11 (a) Output current and voltage at the working flow rate of 5.0 ml/s and load resistances range of 1 MΩ to 500 MΩ and (b) the highest power density of FSiP-TENG at different load resistances and the inset is 120 white LEDs are directly lit up by the TENG.

Figure 4.12 Output power density of PVDF, FS, FSiP based TENG at loading resistances ranging from 1 MΩ to 500 MΩ.

A comparison of the LS-TENGs based on the modification of PVDF membrane reported in other works is presented in **Table 4.1**. It is clear that the majority of the previous papers focused on blending PVDF and fluorine-containing materials to fabricate the triboelectric membrane. However, this work proposes the modified surface of the PVDF membrane by FOTS and SiNPs, which is not only a simpler way but also more effective than the previous TENGs solution. Meanwhile, the maximum power density of FSiP-TENG is much greater than other PVDF-based TENGs, it is indicated that surface polarity tuning through epitaxial growth is an excellent method to enhance the triboelectric characteristic of the PVDF membrane. Additionally, the working flow rate of FSiP-TENG is twice or three times lower than that of other PVDF-based TENGs, hence it promises to develop water energy harvesting easily applications even when a relatively low flow rate condition.

Table 4.1. The comparison of LS-TENG output power performance based on modification PVDF membrane.

Triboelectric material	Current (μA)	Voltage (V)	Power density (mW/m^2)	Flowrate (ml/s)	References
Fluorinated-PVDF	0.37	20	4.00	~	[94]
PVDF	0.95	20.9	26.5	15.0	[92]
PVDF/Ionic liquid	2.56	16.95	26.1	12.5	[75]
PVDF/PP	2.40	29.7	95.8	15.0	[93]
SiO$_2$/P(VDF-TrFE)	3.20	20	62	~	[95]
FSiP	5.79	28.3	420	5.0	This work

For scavenging water energy in practical applications, the high durability and stability of TENGs are indispensable. The aqueous solution at different pH has been used to investigate the stability of the FSiP-TENG, and the current is presented in **Figure 4.13a**. Notably, for pH ranging from 5 to 9, the output current has no obvious difference, suggesting the good stability of FSiP-TENG in weak acidic and basic media. In contrast to PVDF-TENG, the generated electricity decreases dramatically when pH has a slight change from 7 (**Figure 4.13b**). To demonstrate the durability of the epitaxial growth on the PVDF for the TENG performance, the FSiP membranes were treated in bath sonication at different times before using them for the triboelectric layer. The output current of this TENG could remain stable after the FSiP membrane was treated over 20 min (**Figure 4.13c**), suggesting the excellent mechanical durability of TENG in high abrasive environments. In addition, the stability and durability of the output signal for more than 15000 cycles are obtained in **Figure 4.14**. According to the results, the FSiP-TENG has perfectly potential for harvesting water energy under different environments such as rainwater, seawater, wastewater, etc.

Figure 4.14. Stability of FSiP-TENG operated at flow rate of 5 ml/s for 15,000 cycles.

Figure 4.13. Output current of (a) FSiP-TENG and (b) PVDF-TENG using aqueous solution at different pH, (c) output current of FSiP-TENG using the sample after treatment by sonication process at different times.

4.2.4. *Practicability in self-powered sensing*

According to a high-output performance and good stability, the FSiP-TENG has the potential application in streamflow sensing. **Figure 4.15a** presented the output current of FSiP -TENG depending on the water flow rate from 0.5 ml/s to 8 ml/s. It is noted that the output current gradually increases from 0.11 μA to 0.90 μA as the water flow rate enhances from 0.5 ml/s to 6 ml/s. On the contrary, upon further raising of water flow rate (up to 8 ml/s), the output current is no obvious change, and the output peaks tend to decrease stability. The effect of water flow rate on the output performance of TENG was presented in the working principal part. When the velocity of water flow increases, the number of ion adsorption on the triboelectric layer also increases, hence enhancing the electrical power output. However, the ionic adsorption capacity in the Stern layer reached the limit if the flow rate continues to increase, resulting in no increment of output performance. From this result, regression analysis of flow rate based on output current is determined in **Figure 4.15b**, which demonstrates a strong linear relationship between the current and flow rate from 0.5 ml/s to 6 ml/s. Therefore, the regression equation is given by:

$$I = 0.144\nu + 0.034 \tag{4-5}$$

where I is the output current (μA), ν is the velocity of water flow (ml/s). The fitting relation is obtained with high sensitivity $k = 0.144\ \mu A/ml.\,s^{-1}$ and correlation coefficient $R^2 = 0.9997$. Moreover, the increased velocity of water flow could reduce the charging and discharging time of the TENG, which is decreased the time interval between two cycles (ΔT) of output current (**Figure 4.15c**). The curve fitting of the data is shown in **Figure 4.15d** and follows the relationship:

$$\Delta T = \frac{0.624}{\nu + 1.302} \tag{4-6}$$

This regression analysis shows a high correlation coefficient $R^2 = 0.9807$, while the water flow rate increased from 0.5 ml/s to 8 ml/s, suggesting that the velocity of streamflow could be calculated without regard to the amplitude of the output performance. This implies that the PSPE-TENG can sense the velocity of different aqueous solutions with high sensitivity and accuracy. According to this phenomenon, the PSPE-TENG could be applied

as a multifunction sensor system to sense different objectives, such as flow rate, ion concentration, and ion detection at the same time. Therefore, the ability for ion concentration sensing of this TENG was investigated by changing the salinity of the aqueous solutions as shown in **Figure 4.15e**. The proportional relationship between ion concentration (C) and triboelectric charge generation (Q_d) as follows [96]:

$$Q_d \propto -logC \equiv pC \qquad (4-7)$$

According to this equation, the triboelectric charge generation is linearly proportional to pC, which is a conception of pH. The plot **Figure 4.16** is shown the regression analysis of pC based on output voltage to confirm such a phenomenon. Thus, the output performance of TENG tends to decrease with a higher ion concentration,[43, 97, 98] which has the same trend line as output experiment data. The output voltage of PSPE-TENG gradually decease from 6.3 V to 0.6 V as the NaCl concentration change from 0 M to 0.7 M. As expected, the relationship between the output voltage and salinity could be linearly fitted, when the NaCl concentration is in the range of 0 M to 0.4 M, and follow the equation:

$$V = -13.26C + 5.99 \qquad (4-8)$$

where V is the output voltage of PSPE-TENG, and C is the NaCl concentration. In this part, high sensitivity $k = -13.26 \, \text{V/mol} . \text{L}^{-1}$ and correlation coefficient $R^2 = 0.9814$ are obtained. Considering the output tendency with the presence of NaCl in water, the PSPE-TENG can be expanded as a self-powered sensor to determine further specific ion concentrations in an aqueous solution. Additionally, following other advantages of TENG device such as simple structure, low cost, flexibility, and miniaturization, the PSPE-TENG is a good potential candidate for application in self-powered streamflow sensors.

Figure 4.15 (a) Output current of FSiP-TENG depending on the water flow rate, (b) regression analysis of flow rate based on output current; (c) calculate the time interval between two peaks of current working on different water flow rates, (d) regression analysis of flow rate based on time interval; (e) output voltage of FSiP-TENG depending on NaCl concentration, (f) regression analysis of NaCl concentration based on output voltage.

Figure 4.16 The regression analysis of pC based on the output voltage.

4.3.Chapter summary

In summary, we demonstrated the surface polarity of the PVDF membrane could be substantially enhanced by silica nanoparticles grafting and fluorinated functionalized via the epitaxial growth process. The large polarization difference plays a vital role in dramatically improving the dielectric constant and the hydrophobic property of the FSiP membrane, hence the performance of FSiP-TENG is significantly increased. The FSiP-TENG exhibits outstanding triboelectric performance with a current of 5.79 μA and voltage of 28.3 V under a flowrate of 5.0 ml/s. Especially, the highest power density of FSiP-TENG can reach 420 mW/m2, which is 2.7 and 10.8 times higher than that of FP-TENG and PVDF-TENG, respectively. This work renders promising TENG devices which show the ability to light up 120 white LEDs under lower water energy excitation than other types of PVDF-based TENGs. Furthermore, the features of the high durability, stability, as well as water-resistant of the proposed TENG induced by the FSiP membrane have great prospects for hydraulic energy harvesting and a self-powered sensor for the liquid flow rate measurement in a harsh environment.

INCREASE THE β CONTENT AND FLUORINE ELEMENT IN PVDF MEMBRANE

5.1. Introduction

For LS-TENG, the tailoring of the nanomaterials and PVDF hybrid membrane has received much attention. Several studies have indicated driving the crystallization of the β phrase by adding additives, such as carbon-coated zinc oxide, graphene oxide, BaTiO$_3$, CoFe$_2$O$_4$, and SnO$_2$ [59, 90, 99-103]. Furthermore, TENG performance based on PVDF has demonstrated promising results by incorporating their nanomaterials into the PVDF membrane [74, 77]. However, the PVDF hybrid membranes are challenging to regulate because both the distribution of the nanomaterials and the β phase formation must be controlled. Additionally, the nanomaterials were frequently employed as-prepared, without any surface functionalization, meaning that only electrostatic interaction is the main factor to control the desirable polymer morphology. In this regard, the agglomeration of additional nanomaterials or precipitation on the surface of the PVDF membrane could easily occur, thereby restricting TENG performance enhancement [50, 51, 104].

Based on the advantage of the two above strategies, we tried to enhance the tribo-polarity of the PVDF membrane by using both methods: polar β phase enhancement and adjusting the fluorine-containing functional groups. The surface of graphene oxide (GO) was functionalized by using FOTS to form the high polarization functionalized graphene oxide (F-GO). After that, the F-GO/PVDF membrane was fabricated via a blade coating method. The addition of F-GO in the PVDF membrane can significantly increase the content of the β phase, dielectric constant, and hydrophobic properties, which is a critical point for enhancing the output performance of the TENG.

5.2. Results and discussions

5.2.1. Characterization of F-GO/PVDF membrane

To assess the impact of functionalized GO nanosheets on PVDF membrane characterization and TENG output electricity, GO/PVDF and F-GO/PVDF membranes with the same GO and F-GO content in PVDF at 0.5 wt.%, as well as a neat PVDF membrane were utilized for the experiment. As illustrated in **Figure 5.1**, the surface morphology of

Figure 5.1 FE-SEM image of the (a, b) neat PVDF; (c, d) GO/PVDF; (e, f) F-GO/PVDF membranes at different magnifications.

membranes was explored by FE-SEM image. The microstructure of the neat PVDF membrane is dense and smooth, however, some visible voids that appear on the surface may be caused by an air bubble during the blade coating process (**Figure 5.1a**). In comparison to the neat PVDF membrane, GO/PVDF and F-GO/PVDF membranes show rough surfaces and contain a high proportion of granular particles and small pores owing to the excellent distribution of GO nanosheets in PVDF. It has been noted that the significant specific interaction between oxygen-containing groups on the GO and fluorine in PVDF increases the polar phase of the membrane. Moreover, the number of granular particles on the F-GO/PVDF surface is higher than GO/PVDF, which may be caused by the hydrophobic property of the fluorine group in FOTS increases the affinity forces between GO and PVDF [105].

XPS and FTIR spectroscopy is a strong techniques to describe the chemical structure on the membrane surface. **Figure 5.2** depicts the fill-scale XPS spectra of neat PVDF, GO/PVDF, and F-GO/PVDF membranes. We can recognize that both GO/PVDF and F-GO/PVDF membranes show F1s, C1s, and O1s transitions while O1s peak is negligible in a neat PVDF membrane. It is considered to be the appearance of oxygen on the GO nanosheets. Moreover, the Si2p peak corresponds to the XPS spectra of FOTS only appearing in F-GO/PVDF membranes, which strongly demonstrates that the functionalization of GO nanosheets was successful by employing FOTS hydrolysate grafting. Interestingly, F-GO/PVDF membranes show a higher F1s peak than other membranes, indicating the asymmetric distribution of GO nanosheets in the membrane and confirming an increase in the polar phase of the membrane [106].

Figure 5.2 XPS spectra spectra of PVDF, GO/PVDF, and F-GO/PVDF membranes.

Figure 5.3 displays the FTIR spectra of each membrane in the 700 - 1500 cm^{-1} region. sThe typical peaks at 1170 and 1410 cm^{-1} are referred to as CF$_2$ stretching and CH$_2$ vibration, separately [105]. The intensity of both of the following peaks is the same, confirming that the addition of GO nanosheets had not affected the chemical composition of PVDF. On the contrary, the α phase is associated with peaks at 764, 984, and 1391 cm^{-1}, and the β phase is associated with peaks at 840 and 1284 cm^{-1}, demonstrating the changes in the crystalline structure of the PVDF membrane. Following Equation 2.1, The calculated β phase composition in neat PVDF, GO/PVDF and F-GO/PVDF membranes are 52.9%, 70.5%, and 81.7%, respectively. It has been verified once again that GO nanosheets are the key factor in the enhancement of the crystallinity of F-GO/PVDF membranes.

Figure 5.3 FTIR spectra spectra of PVDF, GO/PVDF, and F-GO/PVDF membranes.

Like the previous works, polarization, hydrophobic properties, and dielectric constant are the main factor influencing the triboelectrification between the water droplet and solid.[73, 88, 107] The transferred charge density (σ') in the TENG device could be presented as follows [50].

$$\sigma' = \frac{\sigma_0 d_{gap}}{d_{gap} + d_m/\varepsilon_m} \qquad (5-1)$$

where d_m, ε_m refer to the membrane thickness and dielectric constant of the triboelectric membrane, d_{gap} to the gap distance and σ_0 to the charge density at the equilibrium state. The enhanced polar β phase can promote electrical charge carrier transfer, which increases charge density in the equilibrium state. Therefore, as a result of the high polarization strength, the accumulation of charge at the solid interface could be increased, which boosts the electrostatic fields acting on the triboelectric surface, which further enhances the TENG performance. Additionally, following this calculation, as the dielectric constant increases,

the transferred charge density of the membrane increases, resulting in the advantage of TENG electrical output.

The three above characteristics were measured and shown in **Figure 5.4** to **5.6** to explain the effect of F-GO on the TENG output performance. Under the electric field, the electrical hysteresis loop (P-E) of PVDF, GO/PVDF, and F-GO/PVDF membranes show the polarization property at 1 Hz and room temperature (**Figure 5.3**). As we know that the quantity of β phase present determines the intensity of polarization in the PVDF membrane [100, 108]. Therefore, the PVDF membrane with the lowest β phase content shows a weak P-E loop while those of the other two membranes show a high polarization strength. It is noteworthy that the strongest polarization achieved in the PVDF membrane containing F-GO is 0.11 μC/cm^2, which is 2 times higher than the neat PVDF membrane.

Figure 5.4 P-E hysteresis of PVDF, GO/PVDF, and F-GO/PVDF membranes.

For the TENG devices, a high dielectric constant is a critical element in generating high energy output [48]. **Figure 5.5** presents the dielectric constant of the different membranes as frequency-dependent. It seems that the dielectric constant of these membranes decreased over frequency from 10^2 to 10^6 Hz, which is typical dielectric behavior according to earlier publications[69, 70, 89]. The dielectric constant of the F-GO/PVDF membrane is remarkably higher than that of the other two membranes, resulting in higher capacitance of the membrane, which is advantageous for charge storage and producing improved TENG performance. The addition of GO nanosheets might be the main cause of the rise in the dielectric constant. GO nanosheets are well-known due to their high dielectric constant, which allows them to expand the membrane interface. Furthermore, the fluorine element enhancement in F-GO may be another reason for the high dielectric constant of F-GO/PVDF.

Figure 5.5 Frequency dependence of dielectric constant of PVDF, GO/PVDF, and F-GO/PVDF membranes.

In liquid-solid contact for energy generation, the water droplet should be easily separated from the membrane surface, which indicates that increasing hydrophobic characteristics is also crucial. Therefore, the water contact angles and sliding angles were measured and summarized in **Figure 5.6**. The neat PVDF membrane shows a contact angle of 115.5°, whereas the GO/PVDF and F-GO/PVDF increase the contact angle to 129.6° and 141.1°. In contrast, the sliding angle of neat PVDF, GO/PVDF, and F-GO/PVDF are 35.1°, 22.3°, and 15.8°, respectively. This suggests that the hydrophobic property would significantly increase with the incorporation of F-GO nanosheets and PVDF, resulting in enhanced TENG performance.

Figure 5.6 Contact angle and sliding angle of PVDF, GO/PVDF, and F-GO/PVDF membranes.

5.2.2. Working principle

When a droplet touches the F-GO/PVDF layer, friction occurs between F-GO/PVDF layer and the droplet, resulting in the generation of a negatively charged F-GO/PVDF surface and a positively charged droplet (**Figure 5.7a(i)**). It electrostatically induces an electric potential between the bottom electrode and the droplets. When the droplet touched the Cu electrode, it passes the originally disconnected components (ITO and Cu electrode) to the closed-loop system, resulting in the flow of a current from the top electrode to the

Figure 5.7 (a) Schematic working principle of F-GO/PVDF TENG and (b) view of a single cycle showing four states at play in the working mechanism.

bottom electrode (**Figure 5.7a(ii)**). When it reaches an electrostatic equilibrium, there is no current flow in the circuit (**Figure 5.7a(iii)**). With the drop passing the Cu electrode, the redistributed charges will build a reversed potential and result in a current flow in the opposite direction (**Figure 5.7a(iv)**). When a new equilibrium has reached a cycle of electricity generation is finished. Based on this manner, the F-GO/PVDF TENG can generate an AC electrical output and the view of a single cycle, as shown in **Figure 5.7b**, corresponds to detailed four states of electrical transferred in the F-GO/PVDF TENG.

5.2.3. *Electrical output characteristics*

Aiming to characterize the TENG output performance with different triboelectric layers, a TENG device was placed in a wall of the water tank and water droplet system. The operating conditions of the TENG system were set at 50 μL per water droplet with a frequency of 2 Hz, a dropping height of 7.5 cm, and an inclination angle (α) of 30°. As seen in **Figure 5.8** the current and transferred charge increased after adding a GO nanosheet in PVDF. The output current changed from 5.1 μA with PVDF TENG to 10.8 μA and 16.4 μA with GO/PVDF TENG and F-GO/PVDF TENG; the transferred charge also increase from 17.2 nC to 25.1 nC and 33.2 nC, respectively. Simultaneously, the electrical output of the TENG using load resistances varying from 10 kΩ to 500 GΩ was analyzed and proposed in **Figure 5.9**. For all PVDF, GO/PVDF, and F-GO/PVDF-based TENG, the output power curves are rapidly increased at the beginning and reach the highest value at an external load resistance of 5 MΩ, then they gradually decrease. It is found that the highest power of F-GO/PVDF TENG is reached 0.14 mW, which is 7 times greater than PVDF TENG and 1.8 times higher than GO/PVDF TENG. This study indicated that the TENG output performance could be significantly improved by adding GO nanosheets functionalized in the PVDF membrane

Figure 5.8 (a) Current output and (b) transferred charge of the TENG using various triboelectric layer.

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Figure 5.9 Current and power with loading resistances ranging from 10 kΩ to 500 GΩ of (a) PVDF TENG, (b) GO/PVDF TENG, (c) F-GO/PVDF TENG.

To determine the optimal F-GO content in PVDF to obtain the best possible F-GO/PVDF TENG output performance, a series of F-GO/PVDF TENG with varied F-GO weights ratios were fabricated. The electrical output of the F-GO/PVDF TENG was analyzed under the same operating conditions and shown in **Figure 5.10** and **5.11**. As exhibited in **Figure 5.10a**, the values of the current of the F-GO/PVDF TENG were approximately 5.1, 6.2, 10.4, 16.4, 17.9, and 18.1 μA corresponding to F-GO weight ratios of 0, 0.1, 0.25, 0.5, 1.0, and 2.0 wt.%, respectively. Meanwhile, the voltage and transferred charge (**Figure 5.10b, c**) of the F-GO/PVDF TENG under different F-GO content in PVDF show the same trend as the output current. The output performance of F-GO/PVDF TENG dramatically increases as the content of F-GO improves from 0 wt.% to 1.0 wt.% and afterward remains constant as the content of F-GO exceeds 1.0 wt.%, implying that a small quantity of F-GO could have a significant impact on the triboelectric characterization of the membrane.

Figure 5.10 (a) Current, (b) voltage, (c) transferred charge of the F-GO/PVDF TENG fabricated with various F-GO content.

Moreover, the output power of F-GO/PVDF TENG with varying F-GO weight ratios depending on load resistance has been calculated as exhibited in **Figure 5.11**. It is evident that all the output power of these TENG increase rapidly at first when the load resistance is increased to 5 MΩ, and subsequently decreases as the load resistance continuously increases. Especially, the F-GO/PVDF-1 TENG demonstrated an excellent power output of 0.19 mW, which is around 9 times greater than PVDF TENG. Moreover, the output power of F-GO/PVDF-2 TENG has no obvious change compared to F-GO/PVDF-1 TENG. Accordingly, the addition of F-GO in PVDF has a notable enhancement on the TENG output power, which may be attributed to two main reasons: the increase of dielectric constant and polarization properties. The dielectric constant of F-GO/PVDF membranes gradually improves when the F-GO weight ratios increase as can be seen in **Figure 5.12**. Meanwhile, the polarization properties of F-GO/PVDF membranes, which represent by β phase content, show a significant improvement with the F-GO content is increased to 1.0 wt.%. However, the content of the β phase in the F-GO/PVDF membranes becomes saturated when the F-GO content is higher than 1.0 wt.%, which explains the minor change in TENG performance at a high level of F-GO in PVDF (**Figure 5.13**). As a result, it is possible to affirm that the optimal content of F-GO nanosheets in PVDF membrane is 1.0 wt.%, thus, F-GO/PVDF-1 TENG will be regarded solely for further energy generation research.

Figure 5.11 Output power of the F-GO/PVDF TENG fabricated with various F-GO content.

Figure 5.12 Dieclectric constant of different F-GO/PVDF membranes.

Figure 5.13 The β phase content of different F-GO/PVDF membranes.

5.2.4. Practicability in energy harvesting

As a potential source of electrical devices that converts water droplet energy into electrical energy, the energy harvesting capability of F-GO/PVDF-1 TENG under raindrops must be evaluated. The design of the TENG mounted on a rooftop as a raindrop energy gathering device is illustrated in **Figure 5.14**. Due to the possibility of miniaturization of the TENG devices, plenty of single F-GO/PVDF-1 TENG units could be parallelly connected forming a TENG system, which significantly increases the energy harvesting. In addition, rainwater was utilized to investigate the electrical output of the F-GO/PVDF-1 TENG. When using rainwater instead of DI water, the output current increases slightly, as illustrated in **Figure 5.15**. Rainwater, as we know, includes low concentrations of ions such as K^+, Na^+, Ca^{2+}, H^+, and others, which could increase the TENG output current[109]. As demonstrated in **Figure 5.16**, the power density was computed by using the equation $P = I^2 R / A$ (where A denotes the contact area when the droplet is fully spread out, 9.10^{-5} m^2). The maximum

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power density of F-GO/PVDF-1 TENG reaches the value of 2.08 mW/m^2 across a load resistance of 5 MΩ. Therefore, one water droplet could directly light up 30 LEDs without requiring any regulated circuit, as exhibited in **Figure 5.17**. A literature review of the energy harvesting performance of liquid-solid TENG based on hybrid membranes is displayed in **Table 5.1**. It can be noted that the F-GO/PVDF TENG has a high energy performance compared to other previous studies. Moreover, the TENG output is charged with various capacitors to investigate the charging speed and storage capacity (**Figure 5.18**). A 4.7 μF capacitor takes just 10 seconds to charge to 2.9 V, whereas a 10 μF capacitor takes 15 seconds to charge to 2.0 V. Importantly, after more than 4000 cycles of operation, the TENG's stability and endurance were demonstrated (**Figure 5.19**). This suggests that functionalized GO is a potential strategy to increase the triboelectric effect of PVDF membrane for superior efficiency TENGs and self-powered sensor devices.

Table 5.1. Comparative study of liquid-solid triboelectric nanogenerators based on hybrid membranes for energy harvesting.

Matrix	Material addition	Current (μA)	Voltage (V)	Power density (W/m^2)	Reference
PS	SIS	10.95	20.8	1.26	[110]
FEP	~	12	60	~	[111]
P(VDF-TrFE)	SiO$_2$	3.20	20	0.62	[95]
PVDF	F-GO nanosheets	18.1	16.5	2.08	This work

Figure 5.14 Application of F-GO/PVDF TENG as raindrop energy harvesting devices.

Figure 5.15 Current of F-GO/PVDF TENG with DI water and rainwater.

Figure 5.16 Analysis of current and power density as a function of resistance.

Lighting 30 LEDs by one droplet

Figure 5.17 LEDs lighting up by a water droplet.

Figure 5.18 Charging voltage curves for different capacitors.

Figure 5.19 Stability of F-GO/PVDF TENG for over 4000 cycles.

5.3. Chapter summary

In summary, a hybrid membrane acting as a triboelectric layer for energy harvesting based on liquid-solid TENG was proposed by incorporation of FOTS functionalized GO nanosheets and PVDF matrix. The polarization, hydrophobic properties, and dielectric constant of the F-GO/PVDF membrane were significantly enhanced, which was demonstrated by measuring the optical and electrical properties of the membrane. This indicated the F-GO/PVDF membrane has a superior negative triboelectric property, therefore playing a critical role in boosting the TENG output performance. Thus, a high-output performance F-GO/PVDF-1 TENG has been successfully achieved with a current of 18.1 µA and voltage of 16.5 V, which are 3.5 and 2.3 times higher than the corresponding values of the neat PVDF-TENG. Especially, the maximum TENG power density was obtained 2.08 W/m^2, which can light up directly 30 LEDs by one droplet without requiring any regulated circuit. As a result, this research proposes a potential, cost-effective technique for fabricating outstanding triboelectric materials by combining chemical functional optimization with surface microstructure assembly. Furthermore, its excellent stability and durability make the F-GO/PVDF TENG more appropriate for a wide range of energy harvesting and self-powered sensor.

CONCLUSION AND FUTURE WORKS

6.1. Conclusion

This thesis proposed three methods to enhance the tribo-polarity of the PVDF membrane to boost the output performance of the TENG.

1. In the first method, CFO nanoparticles and PVDF were employed to create a triboelectric composite membrane. Given that magnetic nanomaterial, anisotropy has a substantial influence on the interface polarizing of PVDF, the content of β phase in PVDF increased significantly from 51.2% of pure PVDF membrane to 77.7% of 5 wt% CFO nanoparticles in the PVDF matrix, which further increase the dielectric constant and negative charge of the membrane. As a consequence, the energy output of CFO/PVDF-5 TENG increased significantly with a voltage of 17.2 V, a current of 2.27 µA, and a power density of 90.3 mW/m^2, which is 2.4 times the performance of pure PVDF TENG. Finally, the proposal TENG hopes that its extraordinary stability and durability will provide additional views on hydrodynamic power generation in the future.

2. The second method proposes a high-performance LS-TENG reached from surface polarity tuning through epitaxial growth on the PVDF membrane. The PVDF surface functional is treated with SiNPs through chemical bonding and then grafted with negatively charged FOTS to form the FSiP membrane. The proposed membrane can induce fluorine-bearing silane chains and increase the interfacial polarization, leading to the outstanding hydrophobic property and dielectric constant. In consequence, the output power of FSiP-TENG demonstrates superior triboelectric performance with a current of 5.79 µA, a voltage of 28.3 V, and the highest power density of 420 mW/m^2. On the other hand, the FSiP-TENG-driven sensor system was shown a strong linear relationship, resulting in high sensitivity (0.144 µA/mL.s^{-1} with flow rate and -13.26 V/mol.L^{-1} with NaCl concentration) and minimal error detection. Moreover, by calculating the time interval between two cycles of output current, the flow rate of the stream could be determined regardless of the amplitude of the output result. Considering the excellent durability, stability, and water-resistant, the FSiP-

TENG can develop into a water energy harvesting device and a liquid self-powered sensor to be used in our daily life.

3. Finally, the method for combining two of the above strategies has been reported. The LS-TENG based on functionalized graphene oxide (F-GO) and PVDF composite membranes containing various F-GO concentrations were fabricated using the blade coating process. The surface of GO nanosheets was functionalized through covalent graft by using FOTS. As indicated in FE-SEM images, the miscibility of the F-GO containing fluorine group in PVDF was effectively improved, which created favorable conditions for PVDF crystallization and β phase configuration. Thus, the dielectric and polarization characteristics of the F-GO/PVDF membranes were greatly improved, eventuating in a rise in the output performance of F-GO/PVDF-based TENG. As a consequence, the F-GO/PVDF TENG generates 2.08 W/m^2 of output power from a single water droplet, which is 7 times more than PVDF TENG and 1.8 times higher than GO/PVDF TENG. It is proved the addition of functionalized GO nanosheets in PVDF is very effective for hydropower energy harvesting based on LS-TENG.

6.2. Future works

This research aims to improve the tribo-polarity of the PVDF membrane to be used in TENG devices. The result was shown the efficiency enhancement of tribo-polarity after applying some modification methodologies in PVDF. However, the study of this topic is not finished yet. Further study about the other fabrication methods, such as electrospinning, phase separation, and hydrothermal synthesis, should be applied to optimize the structure and characteristics of the membrane. Moreover, mass production should be investigated.

The output performance of TENG has been significantly improved after using the PVDF membrane with tribo-polarity enhancement, however, the performance still needs to be enhanced via modifying the working principle of TENG or applying corona pre-charging on the PVDF membrane surface. Moreover, the application of the TENG devices in practical application as a power source for electronic systems and self-powered systems would be very interesting in further fulfilling the integral meaningfulness of this study.

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