

RARE EARTH OXIDE DIELECTRICS FOR FLEXIBLE TRIBOELECTRIC NANOGENERATOR

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Abstract

Rare earth oxides (REO) are well known in catalysts, glass-related industries, and permanent magnets manufacturing for almost 70%, according to the mature industry. This work proposes the new developments of REO as the emergence for mechanical energy harvesting (MEH) technology. The binary-system of REO or R_2O_3 , including La_2O_3 , Sm_2O_3 and Nd_2O_3 , are used as dielectric materials to incorporate polydimethylsiloxane (PDMS) for fabricating flexible triboelectric nanogenerators (TENG), one of MEH devices. The change in REO's amount was studied at 0.5, 2.5, 5, and 10 wt%. Upon applying mechanical force in vertical direction, the PDMS/ R_2O_3 TENG can convert mechanical energy into electricity for the best value of ~66 V and ~93 μA with power density of about ~62 $\mu W \cdot cm^{-2}$. The PDMS/ La_2O_3 can be used to fully charge the 0.22 and 0.33 μF capacitor within 3 seconds and power up over 100 LEDs directly. Moreover, the influence of triboelectric polarity and dielectricity on the triboelectric output performance is scientifically discussed by following the percolation point with air breakdown limitation's theory. The researcher believes that the knowledge of this work will be inexhaustible useful to develop a group of REO in broad applications of MEH electronics in future.

Keywords: Rare earth oxide; Triboelectric nanogenerators; Polydimethylsiloxane; Composites

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Introduction

Rare earth (RE) elements are known as a group of 17 elements in periodic table that has been discovered in the earth's crust (Kingkam *et al.*, 2022; Rattanaphra *et al.*, 2022; Chai *et al.*, 2023). In Thailand, RE elements are found in the phosphate minerals monazite and xenotime (Kingkam *et al.*, 2022; Rattanaphra *et al.*, 2022). Among several compounds containing RE, RE oxides (REO) become more important in catalysts, glass-related industries, and permanent magnets manufacturing for almost 70%, regarding the mature industry (Li *et al.*, 2021). In near future, REO will gain higher and higher important as future electronic materials, following in magnetism, optics, power electronics, data storage, and energy conversion devices (Coll *et al.*, 2019; Li *et al.*, 2021). This work proposes the new developments of REO as the emergence of mechanical energy harvesting (MEH) devices to open the opportunity for linking RE resources with burgeoning electrical energy supply technology.

Over the years, the wearable and flexible electronics industry has had a high growth rate and achieves highly developed in response to the convenience of living in modern century (Sharma *et al.*, 2022; Vaghasiya *et al.*, 2023). The growth in that kind of industry has resulted in designing small electronic components including the category of energy harvesting equipment (Ali *et al.*, 2023). Relying on avoiding environmental dependence, the MEH devices for transforming mechanical energy sources into electricity have been subsequently developed providing a chance for replacing the recharged battery usage. One of the interesting MEH devices for this decade is the triboelectric nanogenerator (TENG), which attains extraordinary growth as evidenced from 3 publications in 2012 to 1406 documents in 2023. The TENG immensely offers significant scaleup with potential towards commercialization due to its high output, simple structure, various device designs of using a wide choice of material with cost-effectiveness (Choi *et al.*, 2023; Ra *et al.*, 2023). For achieving high triboelectric output, efficient surface charge generation and effective charge transfer are necessary. Introduction of dielectric materials has been reported to increase the surface charge density. The TENG's output performance is directly proportional to its relative permittivity, confirming in term of both theoretical and experimental way (Kim *et al.*, 2016; Kim *et al.*, 2021; Suo *et al.*, 2023). Previously, various metal oxides have been gradually discovered for fabricating the triboelectric layer for TENG due to their excellent dielectric properties (Kim *et al.*, 2017). Pu *et al.*

experimentally found that the open circuit voltage (V_{OC}) and short circuit current (I_{SC}) of the TENG could be reached 300 V and 10 μ A by adding ZnO (Pu *et al.*, 2020). Other metal oxides dielectrics, including Al_2O_3 (Bai *et al.*, 2020), MnO_2 (Zhang *et al.*, 2022), Ti_2NbO_7 (Sriphan *et al.*, 2023), TiO_2 (Jian *et al.*, 2020) and its nanostructure forms (Maluangnont *et al.*, 2022; Maluangnont *et al.*, 2023), were also utilized as micro/nano capacitors proving ability to improve both dielectric permittivity and output efficiency of the TENG. REO are one of interested dielectric materials that have attracted more attention especially in the field of the high k dielectrics (Li *et al.*, 2021; Li *et al.*, 2023; Zhao *et al.*, 2023) and pseudo-capacitors (Paravannoor *et al.*, 2020; Muthuselvi *et al.*, 2021), thanks to its suitable dielectric constant and excellently physical and chemical stability. Up to now, a series of binary rare-earth oxide dielectrics such as CeO_2 , La_2O_3 , Sm_2O_3 , Ta_2O_5 , etc., have been investigated (Charoonsuk *et al.*, 2018; Kolodiaznyi *et al.*, 2019; Xue *et al.*, 2000). Even though many researchers have reported inexhaustible potential of REO through investigation within broad applications, the development in field of MEH, especially TENG, still not discovered and reported. However, using solid phase of REO cannot be able for fabricating as flexible triboelectric layer, utilizing polymer matrix is necessary. It is well known that materials used for TENG have been grouped according to their ability to repel or receive electrons, called the Triboelectric Series. Polydimethylsiloxane (PDMS), which contains high electron affinity, is a good choice for using in this case (Zhang and Olin, 2020). Even though there are several publications that contain many attempts for developing PDMS's output performance (Katragadda *et al.*, 2023; Liu *et al.*, 2023; Luo *et al.*, 2023), there is still plenty of room to develop its electrical output to meet those requirements with scientific knowledge.

In this work, utilizing REO as a new kind application of flexible TENG is proposed. Herein, the REO-based composite TENG is fabricated by combining PDMS matrix with three different types of REO (R_2O_3); where R is lanthanum (La), samarium (Sm) and neodymium (Nd) as dielectric fillers. The effect of types as well as their loading content on the dielectric properties and electrical output are studied. The phase purity and crystal structure of materials can be confirmed. The Synchrotron X-ray tomographic microscopy (SR-XTM) showed favorable distribution of R_2O_3 within the PDMS matrix that is important for explaining the

well distribution of fillers at optimum condition. Based on experimental results, matching amount of dielectric filler at percolation point is found to be a dominant role to generate the highest electrical output including V_{OC} , I_{SC} and maximum output power (P_{max}). A scientific discussion of mechanism is also provided in-depth. The practical applications are designed further and tested showing its potential capability for being developed as small power supply to operate small electronic components and provide potential way in the field of MEH technology in future.

Experimental Procedure

Materials

The rare earth element sources including lanthanum (La), samarium (Sm) and neodymium (Nd) in form of ions source in ethylenediaminetetraacetic acid (EDTA) solution was received from the Thailand Institute of Nuclear Technology (TINT). Oxalic acid ($C_2H_2O_4 \cdot 2H_2O$, 99.5%, AR/ACS, Loba Chemie PVT. Ltd.), was used as precipitating agent. 22,000 $g \cdot mol^{-1}$ molecular weight of PDMS (Sylgard 184, Down Corning Co. Ltd.) was purchased from Ellsworth Adhesive Thailand.

Rare earth oxide (REO) powders preparation

The La, Sm and Nd ion sources were originally from natural minerals, e.g., monazite. After decomposition and purification using ion-exchanging, a large amount of La, Sm and Nd source in EDTA solution was obtained (Kingkam *et al.*, 2022). The stock solution of 10 %w/v of oxalic acid was prepared for use as precipitant. 10% w/v oxalic acid was dropped in 20 $mL \cdot min^{-1}$ rate into the rare earth-EDTA solution simultaneously with continuous stirring under 400 rpm. The white precipitates were formed at pH around 4. Vacuum pump was used for filtering to separate the precipitates from supernatant solution and used distilled water for washing several times until the pH became neutral. The obtained precipitates were dried at 110°C for 6 h in oven before grinding and calcination at 900°C for 3 h to get R_2O_3 powder. All the types of REO were prepared with this similar method. The synthetic procedure is shown schematically in Figure 1(a). The calcined powders were sieved to collect the uniform size particles and kept within closed plastic bottles. The powder characterization was investigated to confirm the single phase before use in the next section. The characterization will be discussed later.

PDMS/ R_2O_3 composite films preparation

In this work, the PDMS/ R_2O_3 was prepared by simple method of casting. The experimental step is summarized according to Figure 1(b). Firstly, the PDMS and curing agent were prepared in the ratio of 10:1 wt%. The R_2O_3 oxide solid powders were loaded into the viscous PDMS and gently stirred by hand for 5 minutes to prevent the occurrence of air bubbles. Then, the prepared curing agent was added slowly simultaneously with stir before pouring it into the plastic petri dish and placed in an oven at 60°C for 4 h. Examples of PDMS/ R_2O_3 composite films including La_2O_3 , Sm_2O_3 and Nd_2O_3 are illustrated in Figure 1(c).

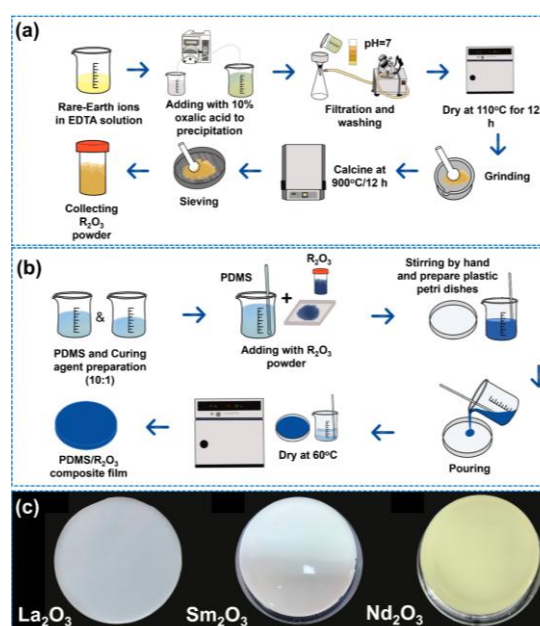


Figure 1. Schematic diagram of REO (R_2O_3 , where $R = La, Sm$ and Nd)'s precipitation (a) and PDMS/ R_2O_3 composite films fabrication (b), with the examples of the obtained composite film taken by digital camera (c)

PDMS/ R_2O_3 composites TENG fabrication

The TENG device was fabricated within an acrylic structural frame for holding triboelectric materials during applying force for performance testing. Its structure was separated into two sides. Each side is composed of triboelectric materials attached to electrode tape on one side of them. Herein, the two sets of material pair were built for TENG to find the real-suitable choice of material pair for PDMS/ R_2O_3 . The set no. 1 is fabricated by using PDMS/ R_2O_3 paired with Al tape. Meanwhile,

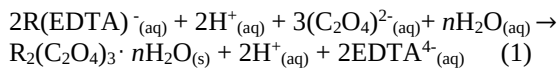
set no. 2 is composed of PDMS/R₂O₃ paired with PTFE. The structural model and operating mechanism are explained later in the part of electrical output measurement. The connection wires were attached to the electrodes of each side. The size of all triboelectric layers and electrodes was fixed at the same 3×3 cm² dimension.

Material characterizations and electrical output measurement

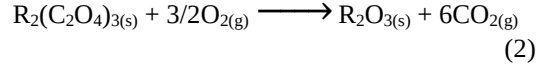
Infrared spectroscopy (IR, Shimadzu IRTracer-100) and X-ray diffractometer (XRD, Rigaku Smartlab) were used for identifying the chemical bonds and crystal structure of all powders and composite films. Scanning electron microscope (SEM, FEI QUANTA 250) and energy dispersive x-ray spectroscopy (EDS) was brought to see morphology of materials and elemental identification. X-ray tomographic microscopy using Synchrotron radiation (SR-XTM) was performed for imaging inside materials by creation the 3D virtualization to survey the distribution of filler phase in composites. In the session of electrical properties and electrical output, the LCR meter (Agilent E4980A) was operated for the dielectric properties' investigation. Digital oscilloscope (DSO-X 2012A Keysight) and digital multimeter (DM3058E model) is performed to examine the output signal waveforms, including V_{OC} and I_{SC} .

Results and Discussion

In this work, the sources of mixed rare earth were prepared from Thai monazite. According to the experimental part, the dissolved rare earth ions in EDTA was obtained from ion exchange extraction and purification process of mixed rare earth ores (Rattanaphra, 2012). The inductively coupled plasma - optical emission spectrometry (ICP-OES) was used to determine the rare earth source concentration, which was found to be around ~98% for all. The pH of rare earth solution in EDTA was about 8. Therefore, oxalic acid is the precipitating agent to separate the rare earth intermediate compound by precipitation before calcination. After oxalic acid was dropped gently into the La-EDTA solution with the constant rate, the rare earth acetate (R₂(C₂O₄)₃; where R is La, Sm and Nd, was formed. The acetate form was transformed into REO by calcination at 900°C/4h in air. The chemical reaction is shown according to chemical equation (1) and (2).



900°C/3h



The XRD pattern of the three oxides forms of rare earth minerals, including La₂O₃, Sm₂O₃ and Nd₂O₃, is illustrated in Figure 2, which can confirm their single phase. All the XRD peaks for La₂O₃, Sm₂O₃ and Nd₂O₃ correspond well with the standard data JCPDS number 05-0602, 42-1464 and 03-065-6792. The crystal structure and lattice parameters were determined and found consistent with hexagonal structure ($a = b = 0.1635(6)$ Å, $c = 0.9390(8)$ Å), orthorhombic structure ($a = 0.2017(6)$ Å, $b = 0.1800(4)$ Å, $c = 0.1954(3)$ Å), and hexagonal crystal structure ($a = b = 0.1634(4)$ Å, $c = 0.1073(5)$ Å) for La₂O₃, Sm₂O₃ and Nd₂O₃, respectively. After confirming the phase of REO, the composite films were prepared. The various condition of loading amounts is study from 0.5-10 wt%.

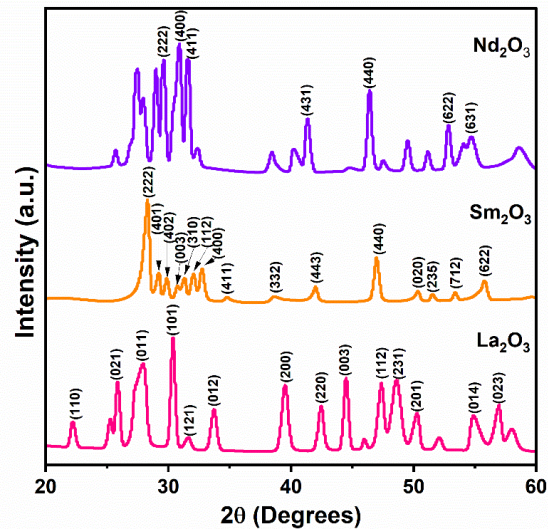
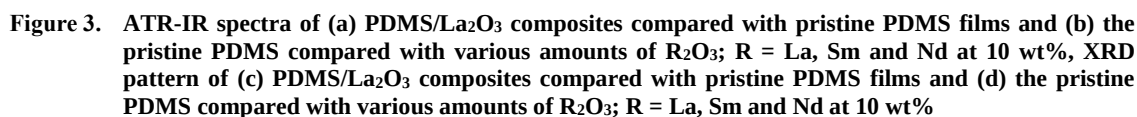


Figure 2. XRD pattern of (a) Nd₂O₃ powder (b) Sm₂O₃ powder and (c) La₂O₃ powder

ATR- IR spectrum within the 4,000-400 cm⁻¹ region for the PDMS-based composites was recorded as shown in Figure 3(a) and b. All the composite samples illustrate the IR peaks that corresponded to the IR pattern of the PDMS structure. The transmittance peak in the wavenumber of about 2970 cm⁻¹ corresponds to the stretching vibration of the C-H within Si-CH₃ group (ν_{as} -CH). The peak at around 1440 cm⁻¹ is observed from the -Si-CH₂CH₂ bending vibration (δ_{as} - Si-CH₂CH₂). At 1260 cm⁻¹, the CH₃ bending vibration

In this work, the effect of the types follows by amount of REO on the electrical output performance is studied. In the part of characterization, XRD results of PDMS/La₂O₃ with various composition of La₂O₃ in 0.5, 2.5 and 10 wt% are illustrated representatively in Figure 3(c). At low concentration of La₂O₃ for 0.5%, the XRD pattern of oxide could not be observed. After the percentage of La₂O₃ was increased to 2.5 wt%, the new diffraction peaks appear at 48.7°, which represents the (112) plane of La₂O₃. Meanwhile, a clear diffraction pattern of La₂O₃ at 27.5, 39.0 and 48.2° can be found by adding at 10wt%, representing the planes of (011), (200) and (112), respectively. Meanwhile, the broad peak of PDMS also existed. This result can therefore confirm the composites between PDMS and La₂O₃. As can be seen in Figure 3(d), loading 10% of all types for REO (La₂O₃, Sm₂O₃ and Nd₂O₃) into PDMS showed evidence of the oxide's crystalline phase, meanwhile, the amorphous characteristics of PDMS phase still existed, confirming the composing of R₂O₃ with PDMS in the PDMS/R₂O₃ composites. The composite between PDMS/R₂O₃ was successfully prepared with facile method in this work.



It is well known that the composite material's properties, especially electrical properties, dominantly depend on the dispersion ability of filler particles. Achieving the suitable distance and connection between each particle or preventing in agglomeration conditions becomes a crucial role. To achieve this goal, other than characterization, the challenge of having the well particle distribution needs to be addressed. Herein, the distribution of filler particles insight PDMS matrix was investigated with SR-XTM technique. Using X-ray imaging, the different absorption ability of the different phases in composite is useful to provide several contrasts of images, giving a hundred frames (from 0° to 180°) of pictures to be virtualized. Finally, the 3D images were simulated by Octopus software for demonstrating internal dispersibility. The 3D visualization images of the PDMS/La₂O₃ at various content at 0.5, 2.5 and 10wt% are representatively as illustrated in Figure 4(a-c), where the La₂O₃ dispersive phase is indicated separately by pink dots and the PDMS matrix phase is indexed by blue painting. The mixed phase between PDMS and La₂O₃ in composites is also shown. SR-XTM results clearly identify that the La₂O₃ filler was not only presented on the matrix's surface but could also be incorporated in the interior of PDMS. The increasing amount of filler phase shows directly proportional to the dispersion region indicated by pink dots. However, the distribution of filler particles inside the PDMS matrix is still nice for 0.5 and 2.5wt%. At 10 wt% the densely incorporated filler was found covering most of the PDMS area with some agglomeration. The SRXTM results for PDMS/Sm₂O₃ and PDMS/Nd₂O₃ with various condition for 0.5, 2.5 and 5 wt% is in accordance with the trend of SRXTM result for PDMS/La₂O₃. The agglomeration would directly affect the electrical output performance in the final device. This point will be discussed later in the part of output performance.

The dielectric properties as a function of frequency in the 20 Hz to 1 MHz period for the pristine PDMS and the composite set PDMS/R₂O₃, where R = La, Sm and Nd, was investigated. The results of dielectric permittivity (ϵ_r) and dielectric loss ($\tan \delta$) are illustrated in Figure 5(a-d). At the low frequency at 20-50 Hz, the pristine PDMS exhibited the lowest ϵ_r around ~ 7.5 and was not

dependent with frequency. The ϵ_r of PDMS was insignificantly changed by increasing of frequency. At the same frequency range, adding dielectric REO of La₂O₃, Sm₂O₃ and Nd₂O₃ at the same concentration of 2.5 wt%, the ϵ_r was increased in order of PDMS / La₂O₃ > PDMS/Nd₂O₃ > PDMS/Sm₂O₃, as shown in Figure 5(a). Upon increasing of frequency, the ϵ_r of the PDMS/R₂O₃ composites was found to be decreased because of the polarization contribution at low frequency. All the four types of polarization, i.e., space charge, dipolar, ionic, and electronic contribute to permittivity at low frequency. They will basically diminish at high frequencies, providing high dielectric loss, especially in space charges (Batra *et al.*, 2019). Since PDMS/La₂O₃ shows the highest ϵ_r by comparison within the same frequency and loaded concentration, the dielectric results of PDMS/La₂O₃ with various concentration are illustrated representatively in Figure 5(b). It can be seen that the amounts of La₂O₃ directly effect on the dielectric results especially the ϵ_r . The ϵ_r could be increased as increasing amounts of La₂O₃ for 0.5, 2.5 and 5 wt%. Loading at 2.5 wt% could exhibit maximum value of ϵ_r of about ~ 16 . After adding higher to 10 wt%, the ϵ_r was dropped significantly. These results show consistent with the electrical output performance of TENG that will be discussed later. For all dielectric materials, the $\tan \delta$ is occurred normally by meaning of the energy dissipation's proportion to the energy that stored by polarization under the electric field (Batra *et al.*, 2019). Low loss $\tan \delta$ is the target of dielectric materials for using since high loss comes to waste heat generation during operation. The $\tan \delta$ of all samples; pristine PDMS and PDMS/R₂O₃-based composites, shows insignificant difference. Figure 5(c) and d displays the variation of $\tan \delta$ with various frequency of the PDMS and PDMS/R₂O₃ composites, demonstrating the frequency dependent in materials. As increasing frequency, the $\tan \delta$ also increased. This was found due to dielectric leakage owing to the increase in electrical conductivity at high frequency. This significant behavior shows in good agree well with the behavior in other ceramic-polymer composites (Batra *et al.*, 2019).

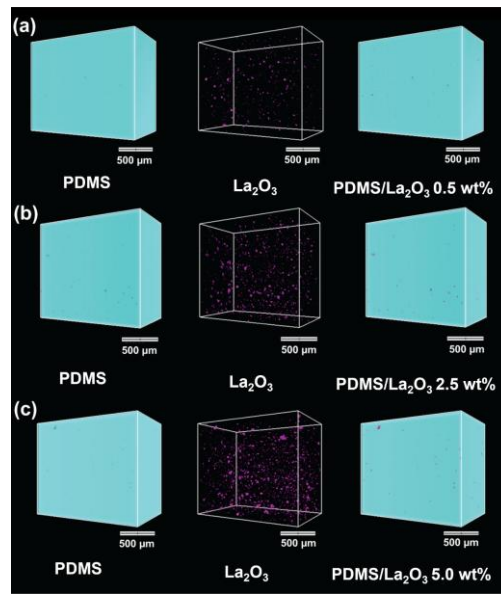


Figure 4. 3D virtualization images by SRXTM techniques of PDMS/La₂O₃ composite films at different amounts of loaded La₂O₃ at (a) 0.5wt% (b) 2.5wt% and (c) 5wt%

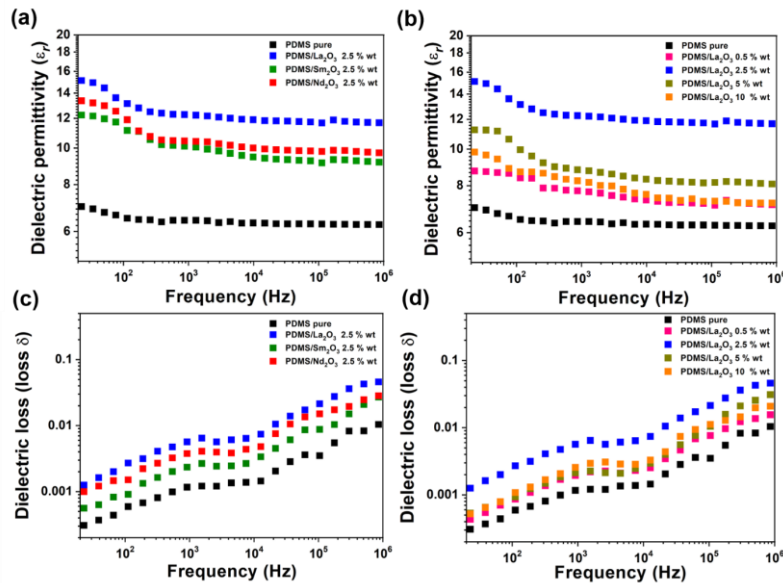


Figure 5. The dielectric permittivity and dielectric loss of PDMS/La₂O₃ composite films at different types, (a) and (b), with the dielectric permittivity and dielectric loss of different amount of La₂O₃, (c) and (d)

To fabricate the TENG devices for examination the output performance, selecting suitable materials pair is important. The triboelectric series is basically considered as reference to select proper materials. The possibility to estimate the negatively or positively charged side can be predicted at the beginning from the list of electron acceptor and donor ability according to

triboelectric series. In 2017, there was a report of adding the oxide materials into the list in triboelectric series for the time using experimental proves (Kim *et al.*, 2017). Most dielectric oxide *i.e.*, TiO₂, SiO₂, HfO₂, Al₂O₃ and Ta₂O₅, *etc.*, shown high potential to be positively charged. Therefore, even the PDMS, which normally prefers to be negative charges by gaining electron, still exhibits

as the matrix, the incorporating of R_2O_3 might probably be on the surface and turns the ability from accepting to donating. Herein, two categories of TENG, metal-to-dielectric and dielectric-to-dielectric structural TENG were used. The schematic diagram of its structure is presented in Figure 6(a) and b. In Figure 6(a), the metal-to-dielectric TENG is composed of one dielectric friction layer and two metal layers of Metal 1 (M1) and metal 2 (M2). The M1 is positioned at the bottom of dielectric layer (DL1) as electrode while M2 contains the two duties of friction layer and electrode itself. The M2's total charges, therefore, have two parts of the triboelectric charges ($S \cdot \sigma$) accumulated on surface and the transferred charges between the two electrodes of M2 and M1 ($-Q$). The total charge amounts on M2 are $S\sigma - Q$, as schematically illustrated in Figure 6(a). In the metal-to-dielectric TENG. The DL was used as tribo-negative materials attached with Al electrode, meanwhile, the Al tape was used as tribo-positive materials as well as electrode. The Al-tape on both sides, top and bottom, were connected to the conductive wires.

The TENG operates by combining contact electrification and electrostatic induction between Al and PDMS/ R_2O_3 material pair (Al-PDMS/ R_2O_3), resulting in the transfer of charge between the Al and PDMS/ R_2O_3 triboelectric layers. The tribo-charging process readily induces opposite charges on its electrodes. Releasing the two surfaces generates a positive voltage peak. Compressing the copper electrode again results in the loss of the previously obtained stable state, generating voltage pulses in the opposite direction. This back-and-forth motion process is repeated, generating continuous voltage pulses. The voltage will generally relate with the accumulated charges (Q) and the distance between two layers as a function of motion time; $x(t)$. Here is called the V-Q-x relationship, which is the model operation when connection with a load resistance (R). The TENG's output power (P) depends on the V_{OC} and I_{SC} . The V_{OC} is influenced by the load resistance. According to the Kirchhoff's law, the equation can be express as equation (3) (Jurado *et al.*, 2019);

$$R \frac{dQ}{dt} = -\frac{1}{C(x)}Q + V_{OC(x)} = -\frac{1}{C}Q + V_{OC} \quad (3)$$

where V_{OC} denotes the potential energy generated between two contact sides and C is the capacitance, which is $C = \frac{\epsilon_0 S}{d_0 + x(t)}$ (Kim *et al.*, 2023). The d_0 is the effective thickness or sum of the dielectric layer's thickness divided by its permittivity, $\frac{d_1}{\epsilon_{r1}}$. The ϵ_0 and ϵ_r is the permittivity

in vacuum and in dielectric layer, and S is the electrode area (Kim *et al.*, 2023). It can be understood from this equation that if the ϵ_r of dielectric materials is high, a high voltage and current of TENG can proportionally be generated. The increase in capacitance can evidently attributed to the increase in the ϵ_r , which results from the incorporating R_2O_3 in PDMS matrix. The V_{OC} and I_{SC} also related to the surface charge density (σ) that the σ further depends on the dielectric material's properties (Jurado *et al.*, 2019). For metal-to-dielectric TENG, voltage between the two electrodes can be depicted as follows, where S denotes the area of the metals which is larger in several orders than that of their effective x ($d_1 + x(t)$).

$$V = E_1 d_1 + E_{air} x = -\frac{Q}{S\epsilon_0} \left(\frac{d_1}{\epsilon_{r1}} + x(t) \right) + \frac{\sigma x(t)}{\epsilon_0} \quad (4)$$

In the dielectric-to-dielectric TENG with a vertical contact-separation method, the two metal films, M1 and M2, serve as electrodes attaching with the dielectric layers of its side that is different from metal-to-dielectric TENG. As depicted in Figure 6(b), two dielectric materials, PDMS/ R_2O_3 and PTFE, are attached with Al metal electrode on its side, and when it comes into contact, the triboelectrification takes place, resulting in the formation of friction charges, $+\sigma$ and $-\sigma$ on the PDMS/ R_2O_3 and PTFE layer's surface. During separation at increasing $x(t)$, which can be varied under the mechanical force agitation, a potential difference ($+V$ and $-V$) arises. The same amounts of opposite charges, as defined by Q , then continuously transfer through electrode to the load.

With the above model of dielectric-to-dielectric TENG, the V-Q-x relationship can be derived based on electrodynamics, including another one of DL layers ($d_1 + d_2 + x$). The voltage can be given by

$$V = E_1 d_1 + E_2 d_2 + E_{air} x = -\frac{Q}{S\epsilon_0} \left(\frac{d_1}{\epsilon_{r1}} + \frac{d_2}{\epsilon_{r2}} + x(t) \right) + \frac{\sigma x(t)}{\epsilon_0} \quad (5)$$

The V-Q-x relationship for both types of TENG can be summarized as equation (6) that is basically used for the contact-mode TENG to calculate its output property.

$$V = -\frac{Q}{S\epsilon_0} (d_0 + x(t)) + \frac{\sigma x(t)}{\epsilon_0} \quad (6)$$

In terms of experiment, the electrical output is measured by the two cases of the open-circuit (OC)

and short-circuit (SC) conditions. The OC condition is utilized for voltage measurement or V_{OC} where there is no charge transfer ($Q = 0$). Therefore, the V_{OC} is normally equal to $\frac{\sigma x(t)}{\epsilon_0}$. The SC condition is used for current measurement or I_{SC} . At this

condition, the potential difference is zero ($V = 0$). Therefore, the I_{SC} equation is given by,

$$I_{SC} = \frac{dQ_{SC}}{dt} = \frac{S\sigma d_0}{(d_0 + x(t))^2} \frac{dx}{dt} = \frac{S\sigma d_0 v(t)}{(d_0 + x(t))^2} \quad (7)$$

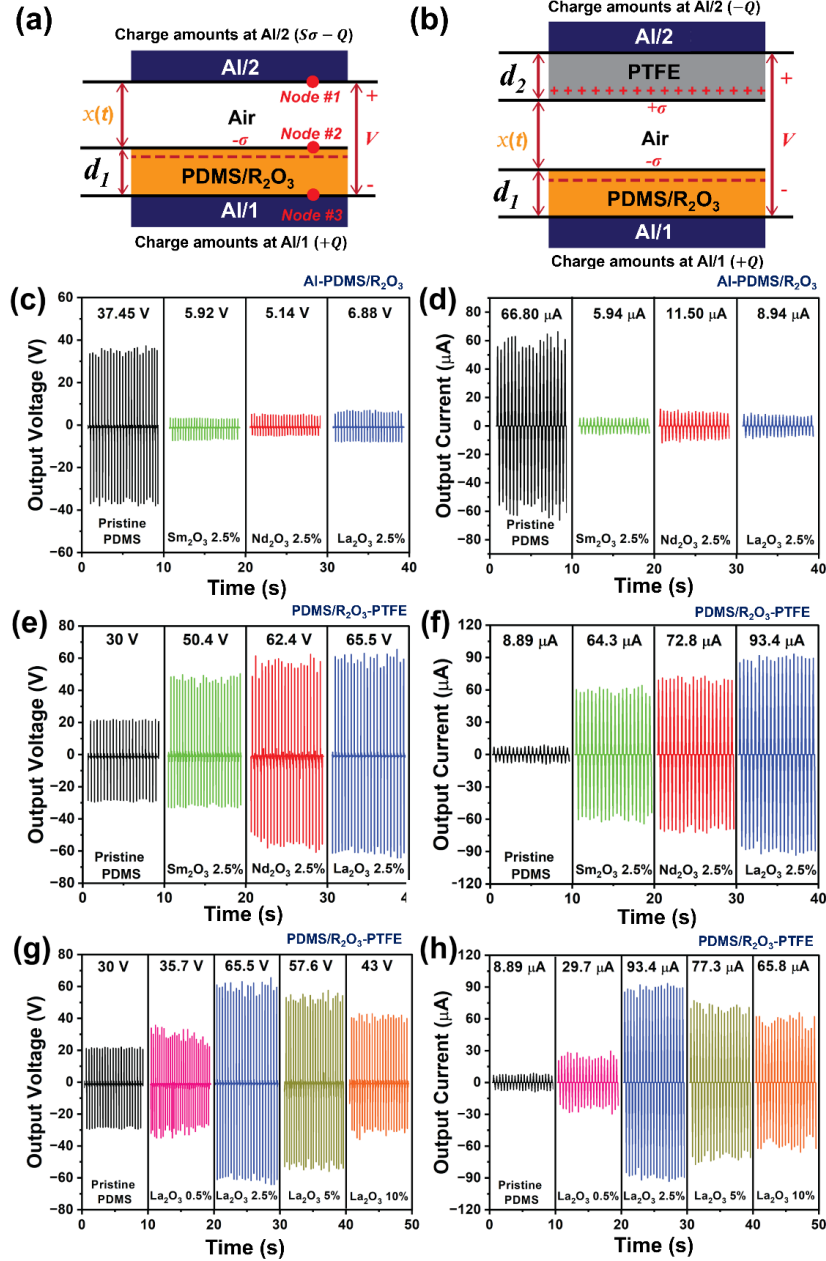


Figure 6. (a) metal-to-dielectric and (b) dielectric-to-dielectric model structure for the TENG devices, (c) V_{OC} and (d) I_{SC} for the PDMS/R₂O₃ at various types of R₂O₃ by hitting with the Al plate (Al- PDMS/R₂O₃ system), comparing to (e) V_{OC} and (f) I_{SC} hitting with the PTFE (PDMS/R₂O₃-PTFE systems), and (g) V_{OC} and (h) I_{SC} of PDMS/R₂O₃-PTFE systems by various condition of La₂O₃ addition

In experiment of this work, to confirm the positivity and negativity of the materials in TENG, the electrical output performance of PDMS/R₂O₃ and Al TENG was tested comparing to the PDMS/R₂O₃ and PTFE pair. The PDMS/R₂O₃ and Al TENG lies in the metal-to-dielectric mode while the PDMS/R₂O₃ and PTFE pair lies in the dielectric-to-dielectric mode TENG. Figure 6(c) and d shows the V_{OC} and I_{SC} for the pristine PDMS film and the PDMS filled with various types of REO compounds (PDMS/R₂O₃), including PDMS/La₂O₃, PDMS/Sm₂O₃ and PDMS/Nd₂O₃, contacting with the Al tape pair. Meanwhile, Figure 6(e) and Figure 6(f) illustrate the results of electrical output signal when the TENG consisted of PDMS/R₂O₃ system paired with PTFE. Notably, the 2.5 wt% of La₂O₃, Sm₂O₃ and Nd₂O₃ was representatively selected for testing. It can be clearly seen from the results that the PDMS/R₂O₃ paired with PTFE can generate output efficiency higher than the producing from PDMS/R₂O₃ paired with Al, at the same condition. The V_{OC} and I_{SC} output signal generated from the PDMS loading with La₂O₃, Sm₂O₃ and Nd₂O₃ films, when brought to contact with Al tape, are less than the pristine PDMS. These results can be evidence that additional R₂O₃ in this work made the PDMS to be more positive causing the nearest electronegativity between them (Al and PDMS/R₂O₃). Friction with Al, therefore, diminishes the output performance of the PDMS/R₂O₃ composite films. The result shows good agreement with the report from Y.J. Kim and co-workers. They found the positive charges on metal oxide compounds providing new triboelectric series that post the dielectric oxides in the top of positive materials (Kim *et al.*, 2017). This result indicates that the triboelectric polarity is a more dominant factor than the relative permittivity by affecting the PDMS/R₂O₃ TENG's electrical output. However, after completing measurement V_{OC} and I_{SC} in PDMS/R₂O₃-PTFE systems in similar concentration of 2.5 wt% of REO loading, PDMS/La₂O₃ could provide the highest of electrical output for ~65.5 V and ~93.4 μ A. Consequently, PDMS/La₂O₃-PTFE was selected for showing the effect of loading amount on the TENG's electrical output, as shown in Figure 6(g) and Figure 6(h). The V_{OC} and I_{SC} illustrate a tendency to increase with increasing of La₂O₃ amount from 0.5 and 2.5 wt% and tend to decrease with increasing La₂O₃ further at 5 and 10 wt% because of its agglomeration. Both V_{OC} and I_{SC} showed a general tendency to increase as the relative permittivity increases.

Figure 7(a) illustrates the normal working mechanism of PDMS/R₂O₃-PTFE TENG under a vertical pressing load. According to the device

structure, the materials A (Mat A) denotes PTFE while the materials B (Mat B) means the PDMS/R₂O₃ films. At the initial state (i), there is no contact between two friction materials, resulting in no charge transfer. Electricity does not exist at this state. When the top plate, PTFE, is pressed by apply force within vertical direction. The two friction materials contact each other inducing the triboelectrification occurrence. At this state, electrons transfer from PDMS/R₂O₃ film's surface to the PTFE. By following the propose of quantum mechanical transition (QMT) (Zou *et al.*, 2020) and the electron-cloud potential-well (ECPW) (Xu *et al.*, 2018) model to explain the triboelectrification in terms of inorganic non-metallic materials TENG. In the case of semiconductors and insulators, the materials contain their own energy gap. The different highest occupied energy level and the individual electron clouds of both remain separated. The containing potential barrier protects electron from free escaping. During the contacting process, triboelectrification can shorten the distance of potential barrier bringing the atoms to be close to each other. The Fermi levels must be aligned, causing the energy bands to bend and overlap, allowing the electrons to flow from the low-to-high electronegativity materials. This electron transfer mechanism is mainly from the surface energy states that would not occur if the work functions and electronegativity of two materials are equal. Herein, the triboelectrification causes the electron flowing from PDMS/R₂O₃ to PTFE leaving positive and negative charges on its surface. However, the originally neutralized charges still maintain as long as both materials still contact during state (ii). Once the applied force is removed at state (iii), the two materials are separated, the imbalance charges on each side will induce the opposite charge occurrence on its electrode. Electrostatic induction occurs. The electric potential difference is established as a driving force for pushing electrons from the negative-to-positive material through the electrode. The existing electric potential difference diminishes until reaching the equilibrium at state (iv). During contacting-separating working, the electric output, including V_{OC} and I_{SC} are measured. Then, upon applying force again at state (v), the triboelectrification and electrostatic induction will repeat. The charge flowing in the opposite direction is induced to complete the cycle of contact-separation. The alternative current is obtained.

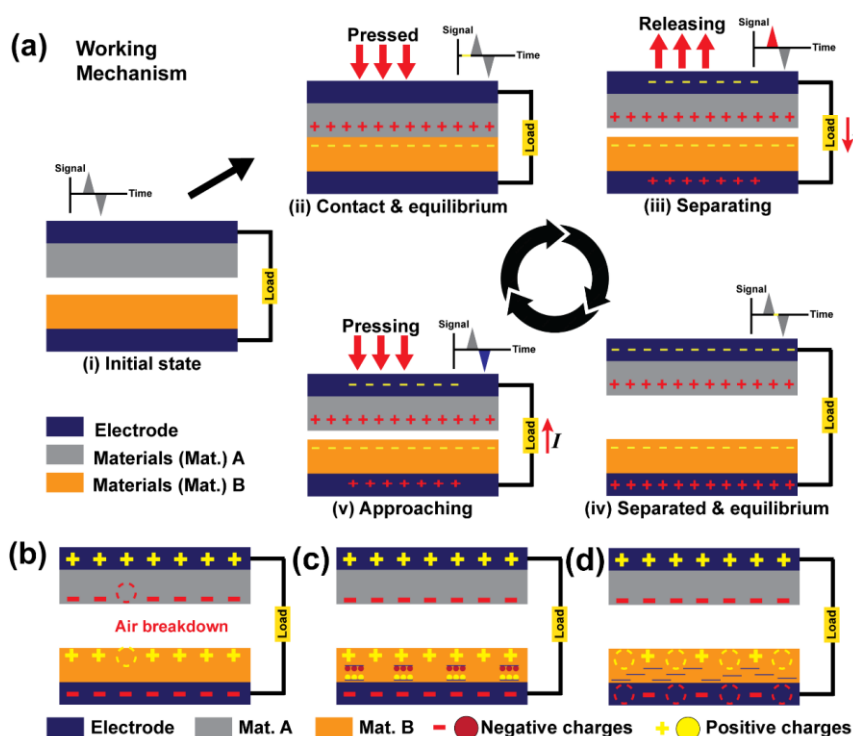


Figure 7. (a) Working principle of the PDMS/R₂O₃ composite TENG with (b) the air breakdown condition

After considering the V_{OC} and I_{SC} of the PDMS/R₂O₃ composite TENG with various amounts of R₂O₃ from 0.5-10 wt%, loading at 2.5 wt% shows the maximum value. This can be well explained by the percolation theory that only one condition can provide the best properties of materials. Herein, one of predominant explanations upon reaching the percolation point is the suitable interaction and connection between matrix and filler's particle and particles itself, belonging to the particle distribution. Even changing the particle distribution, a little, the particle-matrix interaction and particle-particle connection are a nontrivial matter. As we know, the particle distance in polymer/particle composite is determined by the particle content so that it is difficult to know the interparticle distance by random distributing. The most effective way to investigate the particle distribution in this work is using the SR-XTM that the 2.5wt% shows the nice distribution. Meanwhile, adding La₂O₃ at 5 wt% shows some areas of agglomeration. The results show consistent with the V_{OC} and I_{SC} results. The percolation threshold not only explains in terms of filler particle distribution but also explains in terms of air breakdown limitation in accordance with the Paschen's law (Liu *et al.*, 2022). Many researchers have invested in great strategies of increasing triboelectrification. Nevertheless, with the increase of the triboelectric

charge density (TECD) on the dielectric film's surface, the AC output signal of TENG is confined by effect of air breakdown (Wang *et al.*, 2014; Zhang *et al.*, 2020). The number of charges from electrostatic induction is not equal to the charges created by triboelectrification. Moreover, the generated charges on surface can also cause atmospheric ionization by attracting the opposite charges in atmosphere resulting in the charge loss (Wang *et al.*, 2014; Zhang *et al.*, 2020), as illustrated in Figure 7(b). Therefore, the electrostatic induced charges are generally smaller than the triboelectric charges because they can be released by air breakdown before being completely induced in external circuit. Thus, the air breakdown effect always limits the charge output (Zi *et al.*, 2017). The incorporation of dielectric R₂O₃ in friction materials can trap electrons from air breakdown discharging similar to the microcapacitor behavior to prevent the losing of charges and enhance higher TECD. Loading the appropriate amount of dielectric R₂O₃ at percolation point makes the air breakdown limitation that can also maximize the charge trapping ability, resulting in highest electrical output according to Figure 7(c). Exceeding this percolation point would result in the recombination of triboelectric and inductive charges due to the densely pack of the charges reducing the distance between the surface charges

and electrode (Figure 7d). The TECD and electrical output would be sharply dropped. This air breakdown limitation at percolation is also mentioned and discussed in literature (Charoonsuk *et al.*, 2021; Yi *et al.*, 2021; Satpute *et al.*, 2023; Ukasi *et al.*, 2024).

Before the practical application was tested. The instantaneous output power (P) was investigated indirectly by connecting the PDMS/La₂O₃ TENG with electrical circuit that contains the load resistance (R). The V was measured directly using oscilloscope by changing the R from 1000 Ω to 10 M Ω with achieving I from $V = I \times R$. Finally, the P of each R was then calculated using $P = V \times I$. Once the internal and external resistance is matched, the maximum output power (P_{max}) will be obtained. According to the result in Figure 8(a-c), the P_{max} of about ~213, ~13 and ~557 μ W for Al-PDMS, Al-PDMS/La₂O₃ and PDMS/La₂O₃-PTFE show in the same trend with V_{OC} and I_{SC} . After adding La₂O₃ into PDMS matrix, the PTFE could be the appropriate material pair for

providing high output efficiency. As the wide application of TENG for MEH devices mostly depend on its power density. Herein, the power density is found to be ~62 μ W·cm⁻² for PDMS/La₂O₃-PTFE with loading La₂O₃ at optimum condition of 2.5 wt%. Figure 8(d) and e illustrate the electronic circuit connection with rectifier to convert AC to DC signal waveform of suitable use for application and the result of V_{DC} and I_{DC} . It was found that the PDMS/La₂O₃ could provide V_{DC} and I_{DC} of ~49 V and ~21 μ A, which was enough to fast and fully charge the 0.22 and 0.33 μ F capacitors within 3 seconds as shown in Figure 8(f). The charged-discharged cycles were stable for both 0.22 and 0.33 μ F capacitors according to Figure 8(g). Finally, using the PDMS/La₂O₃ TENG could directly drive the brightness 113 LEDs as clearly illustrated in Figure 8(h) and Figure 8(i). Therefore, the benefit of PDMS/La₂O₃ for practical application could be confirmed.

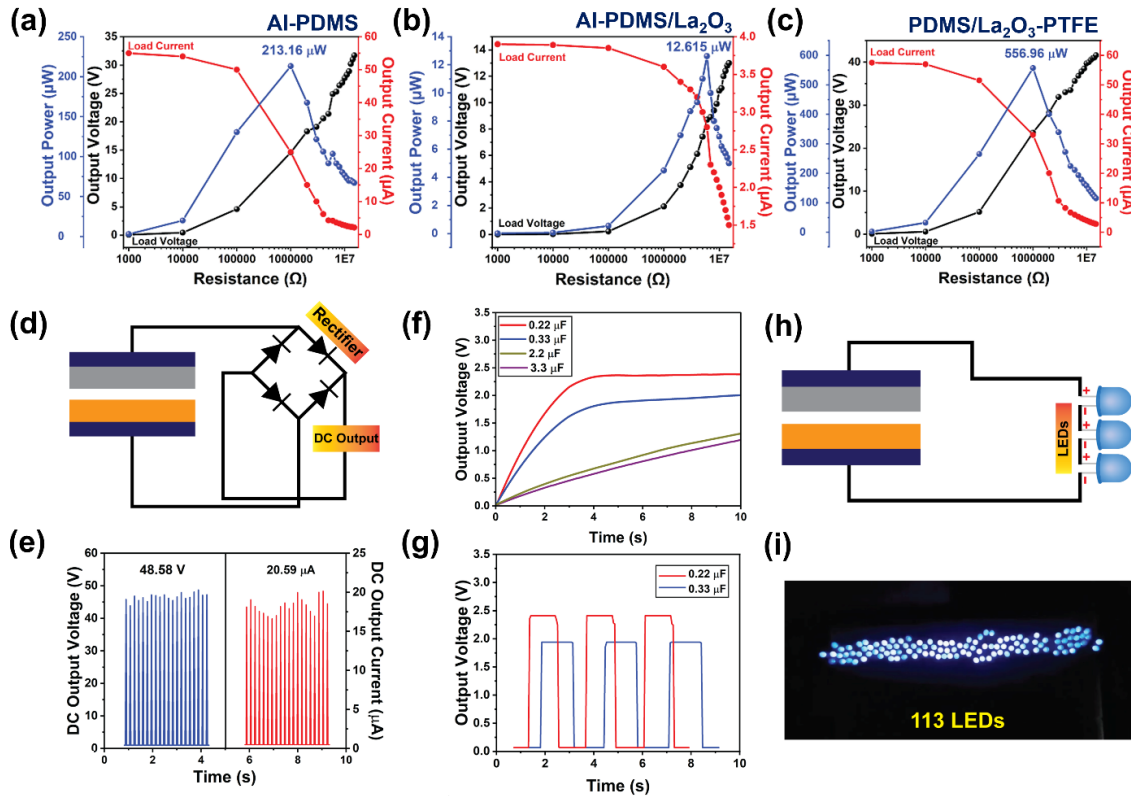


Figure 8. Instantaneous output power with various load resistance of the pristine PDMS paired with Al (a), PDMS/R₂O₃ composite paired with Al (b) and PDMS/La₂O₃ composite paired with PTFE (c), electrical circuit for DC signal measurement (d) with V_{DC} and I_{DC} (e), result of charging capacitors (f), charge-discharged cycle (g), circuit for driving LED directly (h) and the bright 113 LEDs (i) driving by PDMS/La₂O₃ at optimum condition

Conclusions

This work successfully developed REO materials for standing in new application of flexible TENG by incorporating in PDMS polymer. The highest electrical output of REO-based TENG comes up with highest dielectric permittivity containing by adding appropriate choice of REO with exact amount. By comparing between Al and PTFE films for being suitable choice of triboelectric materials pair, PTFE is found to be suitable. Adding REO to PDMS turns the PDMS-based composite to be positive triboelectric side, indicating that the triboelectric polarity in triboelectric series is a dominant factor for achieving highly efficient electrical output. The critical amount of the loaded content is evidently occurred, explained by the rule of percolation threshold. Once the percolation point is attained, the huge chain polarization at the interface, internetwork connection among fillers, and the air breakdown limitation is derived. Finally, loading 2.5wt% of La_2O_3 into PDMS film could generate the highest V_{OC} , I_{SC} and P_{max} for ~66 V, ~93 μA , and ~62 $\mu\text{W}\cdot\text{cm}^{-2}$, demonstrating fully charging ability of 0.22 and 0.33 μF together with 100 LEDs lighting. The scientific discovering with in-depth discussion in this research can be the great opportunity for providing knowledge together with developing the new application of REO in fields of MEH and self-powered sensing industrial technology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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