Multiscale surface modified magneto-mechano-triboelectric nanogenerator enabled by eco-friendly NaCl imprinting stamp for self-powered IoT applications†

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In this paper, we demonstrated a multiscale micro- and nano-structured magneto-mechano-triboelectric nanogenerator (MMTENG) enabled by a salt particle imprinting process to power an internet of thing (IoT) sensor. The fine salt particles were utilized to form a multiscale structure on a triboelectric polymer film by mechanical pressure via an eco-friendly, low-cost, and simple process, thereby reinforcing the contact triboelectrification and electrostatic induction. The surface modified MMTENG can generate an open-circuit peak-to-peak voltage of 851 V, a short-circuit current of 155 μA, and a maximum peak power of 10.3 mW under an AC magnetic field of 8 Oe. The energy device also presented output stability over 124 million operating cycles. Finally, the electricity of the surface enhanced MMTENG device was directly utilized to power an IoT temperature sensor with integration of an energy harvester, energy conversion circuit, and storage capacitor.

Introduction

The advent of the Fourth Industrial Revolution, characterized by extensive automation and connectivity, has brought many changes in various fields such as health care, environment, industry, and public safety. One of the core technologies is the collection of data through wireless sensor network (WSN) for Internet of Things (IoT) which rapidly transmit and receive enormous data in a real-time manner. In particular, it is essential to provide adequate electric power sources such as batteries and external energy lines to operate the IoT sensors. However, due to the limited methods for power supply into IoT systems, several problems such as location limitations and high maintenance costs must be resolved to expand the utilization of IoT devices in every place.

Energy harvesting is an appropriate solution to this problem in an eco-friendly and economical way to recycle the waste energy including heat, mechanical movement, and magnetic field. These energy sources can be converted into useful electric energy via a thermoelectric generator, piezoelectric generator, or triboelectric generator. In particular, magneto-mechano-electric (MME) generators have garnered interest as a power supply for IoT devices since they can continuously scavenge electric energy from the stray magnetic field generated by current flowing in electric cables in homes, factories, and infrastructures. Ryu et al. demonstrated a cantilever-structured MME generator using piezoelectric single crystals and magnetostrictive metals to achieve a mW-level output power from an alternating current (AC) magnetic field.

Triboelectric nanogenerators (TENGs) can inexpensively collect electricity from ambient mechanical energy sources (e.g., wind, human contact, and vibration), and this method is also suitable for application to magneto-mechano-triboelectric nanogenerators (MMTENGs). The triboelectric effect can be explained as a charge transfer process through contact electrification between two objects with different tribo-polarities. To improve the performance of TENGs, many subsequent studies have been conducted to increase the surface contact area of friction materials, which could have a crucial influence on contact-induced charges and frictional electrification. Diverse methods for modifying the surface morphology to a nano- or micro-scale have previously

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†Electronic supplementary information (ESI) available. See DOI: 10.1039/d1nr01336j

RSC Publication: Nanoscale 2021, 13, 8418-8424
been utilized to achieve enhanced triboelectricity, but most of them involved a toxic or costly fabrication process with chemicals, lithography, and vacuum equipment.37–40

In this paper, a high-performance MMTENG was demonstrated with a triboelectric multiscale (micro- and nano-) structured surface enabled by an eco-friendly, low-cost, and very simple salt particle imprinting process to develop a self-powered IoT system. The NaCl salt micro- and nano-particles were sprinkled on a perfluoroalkoxy (PFA) film and then high pressure was applied on the salt powder stamp to mechanically form a multiscale morphology in the polymer surface. The arithmetic mean roughness \( (R_a) \) of the imprinted film surface was \( \approx 22 \) times higher than the pristine film surface. The cantilever-type MMTENG was fabricated with the surface modified PFA and nylon films as the triboelectric pair materials. The salt-imprinted MMTENG can generate an open-circuit peak-to-peak voltage \( (V_{pp}) \), a short-circuit current, and peak power of up to 851 V, 155 μA, and 10.3 mW, respectively, under an AC magnetic field of 8 Oe induced by a Helmholtz coil. The device also generated stable output voltage signals over 124 million operating cycles. Finally, the electric energy of MMTENG was directly used to operate an IoT temperature sensor by integration of a triboelectric generator, energy conversion circuit, storage capacitor, and IoT sensor. With the energy harvesting, the IoT device can continuously measure ambient temperature and transmit the data into a server computer without an external electric source or battery.

Results and discussion

The schematic illustration in Fig. 1a shows the multiscale imprinting process to extend the surface contact area of the triboelectric polymer film enabled by salt stamp particles to improve the triboelectrification. The fabrication process is as follows: (i) The commercially available salt powder was crushed by a planetary mill at 150 rpm for 10 hours to minimize the particle size to a micro- and nano-scale (Fig. S1 in the ESI†). The minimized salt particles were then sprinkled on the surface of a PFA film (thickness of 100 μm), which had high electronegativity in the triboelectric series, to entirely cover the salt particles on the polymer surface.11 For imprinting the salt particles in the PFA, the film was placed inside a press machine with a mechanical pressure of 300 MPa at room temperature for 1 hour. (ii) The particle embedded PFA film was then put in water with sonication treatment at 40 °C for 30 minutes to dissolve all embedded salt. Since the strong electronegativity of NaCl in the triboelectric series could critically degrade the triboelectric harvesting performance, the salt component should be removed from the PFA surface. (iii) After drying the sample inside a dry oven with a temperature of 80 °C, we obtained the surface modified triboelectric film with micro- and nano-structures. The scanning electron microscopy (SEM) image presented in Fig. 1b shows the PFA surface with multiscale micro- and nano-morphology. The multiscale structures were uniformly formed on the observed whole area of the PFA film surface, as shown in Fig. S2 (see the ESI†). Compared with the image of a pristine flat sample (Fig. S3a in the ESI), the complicated structure on the target PFA film was successfully developed through an eco-friendly, simple, and cost-effective salt particle imprinting process. Therefore, we believe that the NaCl imprinting process could be easily utilized in various academic or industrial fields that require multiscale surface patterning. To confirm the size and shape of the multiscale structure, an Atomic Force Microscope (AFM) image of PFA was observed, as shown in Fig. 1c. The arithmetic mean roughness \( (R_a) \) of the imprinted film was 170 nm, whereas the \( R_v \) of the control polymer film was just 7.6 nm (Fig. S3b in the ESI†), thus showing significant enhancement of the triboelectric surface area by the salt imprinting process. Fig. 1d shows the surface element composition analysis by X-ray photoelectron spectroscopy (XPS) after forming the micro- and nano-structures on the PFA surface. Fluorine (F) atoms existed on the surface of the PFA due to the original components of the film, whereas Na and Cl components were not observed because salt particles were completely removed from the PFA surface.

The experimental setup was constructed for measuring the output performance of the MMTENG under an AC magnetic field induced by a Helmholtz coil, as shown in Fig. 1e. The Helmholtz coil had a dimension with inner diameter of 125 mm, outer diameter of 200 mm, and external width of 94.5 mm, and the clamping part of MMTENG device had a.
dimension of 25 × 35 × 60 mm³. To fabricate a cantilever-type MMTENG, an electropositive nylon film (width of 25 mm, length of 50 mm, and thickness of 25 μm) coated with Au on the backside was attached on a Ti substrate (width of 20 mm, length of 60 mm, and thickness of 300 μm) with an adhesive layer, and seven NdFeB magnets (total weight of 11 g) were located on the end of the cantilever to enable repetitive up and down motions by the AC magnetic field. On the above area of the nylon surface, the round shape PFA film (width of 60 mm) with backside Au-coated was placed as a negative triboelectric part (Fig. S4 in the ESI†). To generate maximum output performance of the MMTENG, the PFA film was placed above the nylon film of the cantilever part with an optimized gap distance of about 1.5 mm; as the gap distance was increased, the output of the MMTENG gradually improved until reaching a specific point.41 A stable and uniform AC magnetic field can be generated by the Helmholtz coil around the MMTENG device with simple oscillation of the amount of magnetic field by changing the input AC current. The continuous up and down vibration of the cantilever beam was induced by the magnet proof mass, where attractive and repulsive forces interact with the surrounding AC magnetic field.

The schematic diagrams in Fig. 2a and Fig. S6† present the operating mechanism of the MMTENG generator under an external AC magnetic field. Charge transfer does not occur in the initial state before the first contact of triboelectric materials (Fig. 2a-i). The cantilever is bending upward by the magnetic force exerted from the external magnetic field and magnets, causing contact and friction of the PFA and nylon films. Due to the difference in electron affinity, negative charges could move to the surface of PFA and positive charges could move to the surface of nylon (Fig. 2a-ii).11 The cantilever then bends in reversely to make a detached position, thus causing opposite polarities on the metal electrode layers of two triboelectric polymers (Fig. 2a-iii). An electron flow is generated by the potential difference between the PFA and nylon until both surfaces are completely separated, as shown in Fig. 2a-iv. When the gap distance of the two surfaces is decreased by the upward movement of the cantilever, thus reducing the dipole moment between the two triboelectric parts, the variation of the electric potential leads to electron flow from the electrode of the bottom nylon to the electrode of the top PFA film (Fig. 2a-v). As a result, the MMTENG can generate an AC-type electric output signals in the circuit by repeated vibrations of the cantilever structure.13,25

Fig. 2b shows finite element analysis (FEA) results obtained utilizing the COMSOL simulation program to compare the electrostatic potential values between multiscale modified and flat surfaces in the triboelectric operation. The theoretical voltage generation from the contact-type TENG is defined by eqn (1) below.13

\[
V = -\frac{Q}{\varepsilon_0} \left( \frac{d_{\text{nylon}}}{\varepsilon_{\text{nylon}}} + \frac{d_{\text{PTFE}}}{\varepsilon_{\text{PTFE}}} + x \right) + \frac{\sigma x}{\varepsilon_0} \quad (1)
\]

where \(V\) is the potential difference between two metal electrodes, \(Q\) is the transfer charge between two triboelectric layers, \(S\) is the area size of the effective surface, \(\varepsilon\) is the permittivity of PFA and nylon films, \(\varepsilon_0\) is the permittivity of free space, \(d\) is the thickness of the PFA and nylon films, \(x\) is the separated distance between the PFA and nylon, and \(\sigma\) is the triboelectric charge density. At the open-circuit state, there is no charge transfer (\(Q = 0\)) and therefore the open-circuit voltage (\(V_{\text{oc}}\)) is calculated by the following equation.16

\[
V_{\text{oc}} = \frac{\sigma \cdot x}{\varepsilon_0} \quad (2)
\]

With eqn (2), a maximum \(\sigma\) of 1 μC m⁻² was obtained from the flat PFA and nylon films employing the measured output voltage in the open-circuit condition from a real device, as shown in Fig. 3a. To draw the 2D model of the surface modified film in the simulation, we exploited the morphology information from the line profile of the AFM measurement, as presented in Fig. S7 (see the ESI†). The thickness of the PFA and nylon films was respectively set to 100 μm and 25 μm, and the gap distance between the two triboelectric films was set to 3 mm. Afterwards, the calculated triboelectric charge density \(\sigma\) of 1 μC m⁻² was input for the theoretical simulation to compare the calculated triboelectric potential between pristine and surface multi-structured films. The triboelectric potential was proportionally improved to the contact area, as shown in Fig. 2b-i and 2b-ii, since it could derive a higher amount of total electric charges on the electrificated surfaces.

We compared the output performance of MMTENGs between flat surface and multiscale structured films to confirm the effect of the micro- and nano-morphology formed by the salt imprinting process. Fig. 3a and b show open-circuit voltage and short-circuit current signals of flat and multi-structured MMTENG devices under an AC magnetic field of 8 Oe at
output current of MMTENG device, thus resulting in the non-stable output current signal in the Fig. 3b.

To verify the effect of surrounding conditions such as humidity, temperature, and contact angle for the MMTENG system, the output performance of harvesting device was measured with the various conditions as presented in Fig. S9 and S10.† Firstly, the ambient humidity was changed from ∼25% to ∼41% at room temperature of ∼25 °C during operation of MMTENG at AC magnetic field of 8 Oe. The output $V_{pp}$ of MMTENG was decreased from ∼850 V to 798 V as shown in Fig. S9.† Many research teams have reported the adverse effect of high humidity for the TENG performance, since the thin water layer by humidity on the positive and negative surfaces could derive the interaction of $\text{H}^+$ and $\text{OH}^-$ ions in the triboelectric layers, thus resulting in degradation of carrier charge generation during the operation.43 For the temperature, previous literature reported that the output voltage of TENG did not present noticeable change with the ambient temperature range of 20 °C to 60 °C.43 Lastly, the contact angle between top PFA film and bottom Nylon layer was changed from 0° to 20° during the MMTENG energy harvesting. The $V_{pp}$ was significantly decreased from ∼850 V to 248 V, respectively, as presented in Fig. S10.† The increased contact angle could cause the decreased triboelectric contact area during the operation, thus leading the performance degradation. The MMTENG system could be installed on the electric power transmission cables that inevitably generate stray AC magnetic field with specific frequency 50 Hz or 60 Hz. This condition is relatively stable to operate TENG device since the electric current is normally flowing through the electric power lines. Therefore, device structure and contact angle of triboelectric materials could be fixed by matching the resonance frequency. We believe that the biggest problem might be the alternation of ambient humidity during the long-term operation of MMTENG system. To avoid the effect of ambient humidity on the MMTENG device, an airtight packaging system must be introduced for the harvesting system to minimize the degradation of output performance by the increased humidity.

The output signals of the MMTENG with multiscale structure were measured in response to the different AC magnetic fields from 2 Oe to 8 Oe as shown in Fig. S11 (see the ESI†). The voltage and current output values were gradually improved with increment of the AC magnetic field due to the larger vibration displacement of MMTENG cantilever structure with the enhancement of AC magnetic field.41

Fig. 3c and d show graphs of the measured absolute peak voltage ($|\Delta V|$) and calculated peak power with external load resistances from 1 kΩ to 1 GΩ to compare the output performance of the MMTENGs before and after surface modification. The value of $|\Delta V|$ gradually increased and finally saturated with the change from low resistance to high resistance. To calculate the peak power, we adopted an equation that divides the square of $|\Delta V|$ by the load resistance ($P = V^2/R$, where $P$ is the power, $V$ is the output voltage, and $R$ is the resistance). The maximum peak power of the MMTENG with the salt stamp imprinted PFA was 10.3 mW at a resistance of 3 MΩ, which

117 Hz, which means that the MMTENG cantilever structure made 117 times up and down vibration movements per one second by external AC magnetic field, thus automatically enabling the 117 times gentle contact and separation motions between top PFA and bottom Nylon films in every second. The open-circuit peak-to-peak voltage ($V_{pp}$) and maximum short-circuit current ($I_{max}$) of the MMTENG using the modified film were 851 V and 155 μA, which were 44% and 50% increased values compared relative to the corresponding values of the pristine sample of 591 V and 103 μA. The salt multiscale imprinting process results in a noticeable improvement of the output voltage and current values for energy harvesting. Due to the uniform and stable output voltage wave form of MMTENG harvesting measured by a digital oscilloscope (WaveSurfer 44MX-A, Teledyne LeCroy), we believe that the speed of the contact and separation of triboelectric layers was well controlled by the repeated mechanical vibrations at resonance mode with uniform cantilever contact and separation motions. The measured current signal from MMTENG had relatively large fluctuation than the output voltage signal, since the source-meter (Keithley 2611A) equipment did not provide high-resolution time-domain analysis for AC-type electric transmission cables that inevitably generate stray AC magnetic field in Fig. S11.41

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published on 28 April 2021. Downloaded by Pukyong National University on 8/5/2021 1:24:08 AM.

Communication Nanoscale

was 2.3 times higher than the peak power of 4.4 mW for the pristine MMTENG at a resistance of 4 MΩ. The performance improvement for the surface multi-structured film may be reasonable by the larger triboelectric surface area and the stronger friction between two triboelectric contact materials. The output signal stability is a crucial feature for the triboelectric energy generators.44 Fig. 3e shows the results of the output durability test for the salt-pressed MMTENG with a voltage signal recorded over 124 million cycles under an AC magnetic field of 8 Oe at 117 Hz. The time-dependent \( V_{pp} \) graphs at the initial state (846 V), \(~1\) million cycles (830 V), and \(~124\) million cycles (803 V) are presented in the insets of Fig. 3e. We confirmed that mechanical abrasion of the polymer surface during the triboelectric harvesting could reduce the morphological complexity of the PFA film, as shown in Fig. S12 (ESI†). From the whole test period, the variation of the electric output voltage is less than 5% over 124 million cycles, which means that the MMTENG has remarkable durability compared to other triboelectric nanogenerators including previously reported MMTENG devices.24,36 This work may offer a scientific insight about the surface enlargement effect of novel NaCl particle imprinting on PFA film to achieve improved MMTENG performance by investigation of theoretical FEA as well as experimental energy harvesting demonstration.

Fig. 4a shows that the electric output of the surface modified MMTENG can directly turn on 100 blue light emitting diodes (LEDs) continuously without an external circuit and power source. The brightness of LED light was gradually increased with increment of AC magnetic field on the MMTENG device as shown in Fig. S13 and Video S1 (see the ESI†) since the MMTENG generated improved electric output under the higher AC magnetic field. To store the output energy from the MMTENG, we charged capacitors with capacitance of 10 μF, 47 μF, 100 μF, and 200 μF and recorded the charging curve until reaching a constant voltage of 3.7 V, as shown in Fig. 4b. The inset of Fig. 4b presents the circuit diagram of the capacitor charging system including the MMTENG device, a full bridge rectifier, and capacitors. The stored electric energy inside capacitor is defined by eqn (3) below.

\[
E = \frac{C \cdot V^2}{2}
\]

where \( C \) is the capacitance of the capacitor and \( V \) is the charged electric potential. We calculated the input energy per second from the MMTENG device into the capacitors by utilizing the capacitance and the charging time until reaching voltage of 3.7 V. Since the charging times for capacitances of 10 μF, 47 μF, 100 μF, and 200 μF were 7.1 s, 32.9 s, 69.2 s, and 146.4 s, respectively, the input energy values per second from the MMTENG into the capacitors were 19.3 μW, 19.6 μW, 19.8 μW, and 18.7 μW, respectively.

The schematic illustration Fig. 4c shows a practical application concept of a self-powered IoT temperature sensing system demonstrated by the salt imprinted MMTENG. (i) An IoT temperature sensor can be activated by electric energy from the MMTENG under an AC magnetic field of 8 Oe. (ii) and (iii) The powered IoT device can measure the ambient temperature and then transmit the temperature data into a server computer by a radio frequency (RF) communication. The conventional small-scale electronics are usually operated under direct current (DC) voltage of 5 V; the very high output voltage (normally several hundreds of V with AC signal) of the TENGs, however, was not appropriate to directly supply electricity to the small electronic devices. To activate the IoT temperature sensor, a commercially available power managing circuit was utilized to rectify the AC output of the MMTENG and convert it into a constant DC voltage to charge a storage capacitor. Fig. 4d shows the charging and discharging curve of the 1000 μF capacitor during the energy harvesting and sensor operation. The storage capacitor was charged up to 3.7 V within ~560 seconds, and discharged in sequence to continuously power the IoT temperature sensor. The charged voltage of the capacitor immediately dropped to 2.4 V for initial wake-up of the internal electronic system and recovered up to 3 V after 63.5 s by the input energy from the MMTENG. The inset of Fig. 4d shows captured images of the monitoring program on the server computer before and after receiving the temperature data from the IoT device. At the state of ‘Connect’, the temperature information of sensor was delivered to the computer via a RF signal. This demonstration, confirmed that...
the MMTENG could continuously supply sufficient electric power to an IoT device without an external power source or internal battery.

Conclusions

In summary, we modified the surface morphology of a triboelectric PFA film through an eco-friendly and simple salt particle imprinting process to form multiscale micro- and nanostructures on the polymer surface. With an AC magnetic field of 8 Oe, the salt imprinted MMTENG generated an open-circuit voltage of 851 V, a short-circuit current of 155 μA, and a peak power of 10.3 mW at the external resistance of 3 MΩ, far exceeding the values of the non-treated MMTENG device. This high performance of the MMTENG derived from the large surface area enhanced by the multiscale salt imprinting process and the multiscale surface morphology. The MMTENG showed output voltage degradation of less than 5% during ~124 million cycles under an AC magnetic field of 8 Oe, which is a remarkable cycle value compared to previously reported TENG devices. Finally, the multiscale surface modified MMTENG was utilized to turn on 100 blue LEDs and continuously drive an IoT temperature sensor system. This results verify the feasibility of the salt imprinted MMTENG for not only harvesting electricity from a weak AC magnetic field but also for various self-powered IoT applications. We are currently planning to investigate a hybrid-type energy harvester based on TENG and electromagnetic induction generator in the MME conversion to increase the output performance of MME harvesting system for various IoT applications.45-53

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The work at PKNU was supported by the NRF grant funded by the Korea government (MSIT) (No. 2019R1C1C1003765). The work at KIMS was supported by the Korea Institute of Materials Science (KIMS) internal R&D program (Grant No. PKN7560). The work at KMOU was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (No. 2017R1A2B4009832). The work at YU was supported by the National Research Foundation of Korea (grant number NRF-2019R1A2B5B0101070100).

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