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High performance direct current-generating triboelectric nanogenerators based on tribovoltaic p-n junction with ChCl-passivated CsFAMA perovskite

You-Sun Lee a,1, Sera Jeon a,1, Dabin Kim a, Dong-Min Lee a, Do-Hyung Kim b,∗ and Sang-Woo Kim a,c,d,∗

a School of Advanced Materials Science and Engineering, Sungkyunkwan University (SKKU), Suwon 16419, Republic of Korea
b New & Renewable Energy Laboratory, KEPCO Research Institute, Daejeon 34056, Republic of Korea
c SKKU Institute of Energy Science and Technology (SIEST), Sungkyunkwan University (SKKU), Suwon 16419, Republic of Korea
d SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University (SKKU), Suwon 16419, Republic of Korea

∗Corresponding authors. E-mail address: dhkim05@kepco.co.kr (D.-H. Kim), kimsw1@skku.edu (S.-W. Kim)
1These authors contributed equally to this work

Abstract
Herein, we develop direct current-generating triboelectric nanogenerators (DC-TENGs) based on the tribovoltaic p-n junction using n-type perovskite (CsFAMA) and p-type conductive polymer (PEDOT:PSS); CsFAMA based DC-TENG is shown to generate a high DC power output of about 2.1 µA cm⁻² (current) and 0.33 V (voltage). We also introduce
choline chloride (ChCl) to passivate the defects inside CsFAMA to improve the power-generating performance of DC-TENG by increasing triboelectric charge density, carrier mobility, and built-in potential, which are the key factors that determine device performance. Due to the synergetic effect of reduced defect sites (5.0×10^{10} \text{ cm}^{-3} \text{ to } 1.0×10^{10} \text{ cm}^{-3})

, enhanced electron mobilities (1.0×10^{-2} \text{ cm}^{2} \text{ V}^{-1} \text{ s}^{-1} \text{ to } 2.3×10^{-2} \text{ cm}^{2} \text{ V}^{-1} \text{ s}^{-1}), and modulated work function, the passivated CsFAMA-based DC-TENG generates an output current density of 11 \mu\text{A cm}^{-2} \text{ and an output voltage of 0.80 V. Our results are expected to contribute to the development of high-performance DC-TENGs by presenting a promising strategy that involves controlling the triboelectric semiconducting interface.

Keywords:
tribovoltaic effect, direct current triboelectric nanogenerator, dynamic p-n junction, passivation, perovskite

1. Introductions
Over the last decade, triboelectric nanogenerators (TENGs) have been extensively studied as promising mechanical energy harvesters for powering portable devices, wireless sensors, and implantable medical devices [1-4]. TENGs generate Maxwell displacement current through the coupling effect of contact electrification (CE) and electrostatic induction [5-7]. As a result, TENGs have poor battery charging efficiency due to their alternative current (AC) power output characteristic. Previous studies have attempted to achieve high power output in terms of materials by controlling surface charge density, permittivity, and surface potential [8-10]. However, the battery charge efficiency of TENG still remains low due to the high electrical impedance of the capacitive structure.
To overcome this limitation, direct current (DC)-generating TENGs have attracted substantial attention; in particular, they have been intensively investigated with an asymmetric device structure with a rectifying circuit and a discharge effect [11-13]. Although the above works generate DC electricity, these approaches have not provided real solutions for practical usage due to the bulky nature of the devices and their low energy conversion efficiency. Recent works have proposed semiconductor-based DC-TENGs that operate based on the “tribovoltaic effect”, which is similar to the photovoltaic effect but uses friction as the source energy instead of light [14-16]. Due to the characteristics of the semiconductor material, it has a low impedance (~ kΩ). Thus it is expected that DC-TENG generates power with high current (~ A/m²)[17]. AC-TENG inevitably has a large internal impedance (~100 M) due to its capacitive structure, generating power with low current and high voltage [18]. These DC-TENGs utilize the triboelectric charges themselves as mobile charges, and they are directly driven by the built-in electric field ($E_{bi}$) of the p-n junction or Schottky junction to generate DC output [17-19]. Nevertheless, there is still an issue with the low voltage output, which is determined by the built-in potential ($V_{bi}$). Although inserting insulating layers at the interface allows for improved voltage, the current drops drastically due to the reduced chance of electron tunneling between the interface [20].

In this paper, we demonstrate a p-n junction type DC-TENG operating through triple-cation n-type perovskite Cs$_{0.175}$FA$_{0.750}$MA$_{0.075}$Pb(I$_{0.880}$Br$_{0.120}$)$_3$ (CsFAMA) sliding over p-type conductive polymer. We also suggest a novel strategy with which to achieve simultaneous increases in voltage and current by employing a zwitterion ion ChCl as a passivation agent. We systematically investigate the effects of ChCl passivation on CsFAMA films in terms of electron mobility ($\mu_e$), trap density ($N_{trap}$), and Fermi levels ($E_F$), all of which make direct contributions to the transport of triboelectric charges and magnitude of $E_{bi}$. 
ChCl-mediated passivation has achieved remarkable improvements in voltage and current density by 140% and 420%, respectively.

2. Experimental section

2.1 Materials

Glass substrates with indium tin oxide (ITO) with a resistivity of 10 Ohm/sq. were purchased from AMG Tech. Lead (II) iodide (PbI$_2$, 99%), cesium iodide (CsI, 99.99%), and lead bromide (PbBr$_2$, 99%) were all purchased from Tokyo Chemical Industry. Formamidinium iodide (FAI, 98%) and methylammonium bromide (MABr, >99%) were purchased from Great Cell Solar. N,N-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.7%), and choline chloride (ChCl, 96%) were all purchased from Sigma-Aldrich. The poly-(3, 4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS VP AI 4083) was purchased (Clevios). All chemicals and reagents were used as received without further purification.

2.2 Fabrication of DC-TENGs

To fabricate the DC-TENGs, the ITO glass was cleaned with aqueous detergent, acetone, deionized water, and isopropyl alcohol (IPA) using ultrasonication for 10 min. After being dried in an oven at 60 °C for 12 h, the substrates were treated with ultraviolet (UV)-ozone for 30 min. The PEDOT:PSS was drop-casted and spin-coated (at 5000 rpm for 40 s) on clean ITO substrates as a p-type conductive layer and then annealed at 100 °C for 10 min in air. Our group followed a similar approach to that used for the mixed CsFAMA formulation, which reached efficiencies exceeding 20% for perovskite solar cells [21]. The n-type material solution of triple cation CsFAMA in mixed solvent DMF and DMSO was
prepared by dissolving PbI$_2$, PbBr$_2$, FAI, CsI, and MABr. Next, the CsFAMA solution (40 µL) was spin-coated onto the glass/ITO substrate at 500 rpm for 5 s and 4000 rpm for 45 s. At 30 s before the end of spin coating, chlorobenzene (0.2 mL) was dripped onto the substrate, which was subsequently heated at 100 °C for 10 min. The ChCl of the passivation material was dissolved in IPA (1 mg mL$^{-1}$) and spin-coated onto the CsFAMA film at 4000 rpm for 30 s, after which the films were heated at 100 °C for 10 min in a N$_2$ glove box (Fig. S12).

2.3 Characterization and measurement

The X-ray diffraction (XRD) was obtained by a RIGAKU D/MAX 2500 X-ray diffractometer with 2θ = 5~30° under Cu Kα radiation. Steady-state photoluminescence (PL) was obtained from a spectrofluorophotometer (SHIMADZU, RF-6000). The chemical composition and interaction of the CsFAMA films were confirmed using an X-ray photoelectron spectrometer (XPS, K-Alpha+, Thermo Fisher Scientific). The valence band maximum (VBM) values of the films were determined by UV photoelectron spectroscopy (UPS) (K-Alpha+, Thermo Fisher Scientific), and the conduction band minimum (CBM) values were calculated by adding the optical band gap ($E_g$) derived from the UV-Vis spectrophotometer (HP 8453, Hewlett Packard). To assess the characteristics of the DC-TENGs, the voltage and current were measured using Keithley 6514 and a sliding machine. The $N_{trap}$ and $\mu_e$ values of the n-type CsFAMA films with and without ChCl passivation were analyzed by the space charge limited current (SCLC) method using electron-only (ITO/C$_{60}$/CsFAMA/[6,6]-Phenyl-C$_{61}$-butyric acid methyl ester (PCBM)/Au) devices. The surface potential was measured by an amplitude-modulated Kelvin probe force microscope (KPFM) (Park Systems, XE-100) performed with a Pt/Cr-coated silicon tip. The potential axis was calibrated using highly oriented pyrolytic graphite (HOPG) as a reference material. In order to achieve the result of work function distribution and mapping using KPFM, the
working function value of the sample was obtained by measuring the contact potential difference between the HOPG and the AFM tip and the contact potential difference between the samples and the AFM tip, respectively [22].

3. Results and discussion

3.1 Direct current from dynamic triboelectric p-n junction

Tribovoltaic DC-TENG requires rectifying the p-n or Schottky junction, which can orient the carrier transport direction. In this work, n-type CsFAMA and p-type conductive polymer PEDOT:PSS are used to realize p-n junctions. Triple cation CsFAMA is employed as the n-type material due to its small exciton binding energy (< 50 meV), long carrier lifetime, and high $\mu_e$, all of which are also desirable features for n-type tribovoltaic materials [23,24]. On the other hand, PEDOT:PSS is known as a highly conductive organic semiconductor with hole-transporting characteristics. Fig. 1(a-c) describes the DC generation mechanism of the proposed device and its corresponding band structures. Fig. 1(a) demonstrates the state before contact occurs between PEDOT:PSS and CsFAMA. When the two materials contact, a charge transfer to reach thermodynamic equilibrium is achieved through the alignment of their $E_F$, which subsequently forms a p-n junction, as shown in Fig. 1(b). The electrons in the CsFAMA diffuse toward PEDOT:PSS, while the holes in the PEDOT:PSS diffuse toward the CsFAMA. As these mobile charges diffuse at the interface, there remains a depletion region consisting of immobile cations and anions, which form $V_{bi}$. Lastly, when CsFAMA slides on the PEDOT:PSS film, tribo-excitons (electron-hole pairs) are created at the interface, as shown in Fig. 1(c). These electron-hole pairs are separated and excited by friction-induced heat and $E_{bi}$. The excited electrons and holes are transported along the conduction band and the valence band, respectively, in the same direction as $E_{bi}$. This is how DC is generated from the p-n junction-based TENG by the tribovoltaic effect.
The current density \( (J_{\text{drift}}) \) generated by the tribovoltaic effect can be expressed as Eq. (1) [25]:

\[
J_{\text{drift}} = q_{\text{tri}} \mu E_{\text{bi}}
\]  

(1)

This relation implies that charges generated by friction \( (q_{\text{tri}}) \) are driven by \( E_{\text{bi}} \) and that the magnitude of such charge drift is related to the mobility \( (\mu) \) of materials. To elaborate, \( q_{\text{tri}} \) is a product of static CE between CsFAMA and PEDOT:PSS and dynamic friction generating tribo-exciton (electron-hole pair generation) at the interfaces. As a result, there are two sources of \( q_{\text{tri}} \): \( q_{\text{CE}} \) and \( q_{\text{tribo-exciton}} \), which can be expressed as Eq. (2):

\[
q_{\text{tri}} = q_{\text{CE}} + q_{\text{tribo-exciton}}
\]  

(2)

Specifically, when two different materials contact, the surface potential difference causes charge transfer to occur, which leaves \( q_{\text{CE}} \) on the surface. This phenomenon is called CE or triboelectrification, and it arises when the distance in between is a matter of angstroms and near enough to form atomic bonds [26]. The other source, \( q_{\text{tribo-exciton}} \), is generated by energy released as a result of bond breakage at the interface during the dynamic friction. This friction-induced heat energy dissociates the tribo-excitons at the interface. The other parameters, \( \mu \) and \( E_{\text{bi}} \), are highly dependent on the material property. \( \mu \) can be improved through defect engineering to avoid carrier scattering and eliminate electron-hole recombination sites. \( E_{\text{bi}} \) is formed at the space charge region and drives \( q_{\text{tri}} \) to flow in one orientation. \( V_{\text{bi}} \) is determined by the work function difference between n-type and p-type materials [26]. It is therefore desirable to obtain high \( \mu \) and the optimal work function to achieve effective DC generation.

On the other hand, CsFAMA film has several intrinsic defects that deteriorate its charge transport property and carrier lifetime, thus resulting in poor \( \mu \) and increased chances of electron-hole recombination [27,28]. For instance, Pb-I antisite (PbI) and Pb vacancy (V_{Pb}) are the intrinsic defects of CsFAMA, which exhibit positive and negative charges (Fig. S1).
These charged defects act as electron and hole traps restricting the transport of carriers. Therefore, removing those defects is one of the desired qualities to achieve high-performance DC generation. In this study, as shown in Fig. 1(d), ChCl is employed as a post-treatment chemical to realize defect-passivated CsFAMA. ChCl as a zwitterion is known for its ability to effectively passivate both positively- and negatively-charged defect sites [29-32]. It is thus expected that ChCl treatment will improve the $\mu_e$ and reduce the $N_{\text{trap}}$ of CsFAMA film. A five-time enhancement in current density is found to be achieved after ChCl passivation, as shown in Fig. 1(e). In addition, an increased number of $q_{\text{CE}}$ is generated during contact electrification between CsFAMA and PEDOT:PSS after ChCl treatment due to its quaternary amines with the strong tribo-positive property. Fig. 1(f) and Fig. 1(g) show the surface potentials of pristine CsFAMA and passivated CsFAMA measured before and after contact with PEDOT:PSS, respectively. The decreases in surface potential after contact are -29.0 mV for pristine CsFAMA and -277 mV for passivated CsFAMA. These results demonstrate the tribo-positive transition of CsFAMA after ChCl treatment.

3.2 Passivation of CsFAMA

Here, the effect of ChCl post-treatment is evaluated with a particular focus on defect passivation to reduce $N_{\text{trap}}$ and realize high $\mu_e$ for an elongated carrier lifetime and effective transport, as shown in Fig. 2(a). First, the optimal concentration of ChCl solution is determined from the crystallographic observation of CsFAMA films using XRD. ChCl was prepared in IPA at 0.1 mg/ml, 1 mg/ml, 3 mg/ml, and 10 mg/ml, and the CsFAMA films treated with each of these solutions are denoted as ChCl-0.1, ChCl-1, ChCl-3, and ChCl-10, respectively. The structures of the CsFAMA films have been characterized by XRD, as shown in Fig. 2(b). The main diffraction peaks at (110) and (220)—which are respectively
located at 14.1° and 28.4°—appear up to ChCl-1, whereas an unstable Lewis adduct phase forms when the concentration exceeds it, as is the case in both ChCl-3 and ChCl-10 [33].

The successful defect passivation of ChCl-treated CsFAMA is verified by XPS, as shown in Fig. 2(c) and Fig. S2. The binding energies of Pb 4 f\textsubscript{7/2} and 4 f\textsubscript{5/2} have shifted from 138.4 eV to 137.2 eV and from 143.2 eV to 143.1 eV, respectively, following ChCl treatment. These results show that the defects in CsFAMA can be successfully passivated by ChCl. Moreover, the decrease in core level electron binding energy implies an electron donation from Ch, which contributes to the increase of electron density around Pb atoms; as a result, the Pb\textsubscript{I} antisite and Pb clusters on the surface are also passivated [34,35]. The binding energy shift can also evidence the n-type transition of CsFAMA with a reduction of work function [36]. Overall, the XPS data demonstrates the selective passivation of the positively and negatively charged defects in CsFAMA. Consequently, it is expected that the \( N_{\text{trap}} \) will be reduced and \( \mu_e \) will be enhanced in ChCl-passivated CsFAMA films.

The steady-state PL spectra in Fig. 2(d) and Fig. S3 demonstrate the ChCl-mediated in-gap defect passivation. With increasing ChCl concentration, the PL intensities of the CsFAMA films remarkably rise up to ChCl-1, suggesting that ChCl is conducive to suppressing the non-radiative recombination and passivating the defects that act as charge trapping centers [37,38]. Specifically, the Pb\textsubscript{I} and Pb clusters—which are the typical surface defect sites creating deep trap levels—are passivated, as confirmed through XPS. At higher ChCl concentrations, the PL intensities start to diminish compared to ChCl-1, which is attributed to the formation of the unstable phase with low quantum yield. Further, the PL peak position is blue shifted from 762.9 nm in pristine to 761.2 nm in ChCl-1 after ChCl treatment, which suggests that ChCl effectively inactivates the defect states in the band gap. These results show that ChCl-1 is optimal for the passivation of the defect without change in CsFAMA crystals, and they are consistent with the XRD results.
The $\mu_e$ and $N_{\text{trap}}$ of each CsFAMA film are evaluated through SCLC measurement. Fig. 2(e) and Fig. S4 show the typical dark current-voltage (I-V) curves of electron-only devices. Electron-only devices are constructed by CsFAMA films sandwiched by $C_60$ and PCBM, which are electron-transporting layer materials [39,40]. The dark I-V curves can be divided into three regions: ohmic, trap-filled limit (TFL), and child regions. The low voltage level is the ohmic region in which the current increases linearly with the bias voltage. At the intermediate region, it transforms into the TFL region, and the current shows a sudden nonlinear increase with voltage, which is attributable to the trap states being completely filled by the injected carriers. $N_{\text{trap}}$ is calculated from the TFL voltage ($V_{\text{TFL}}$) using Eq. (3) [24]:

$$V_{\text{TFL}} = \frac{eN_{\text{trap}}L^2}{2\varepsilon\varepsilon_0}$$

(3)

where $V_{\text{TFL}}$ is the threshold voltage to begin the TFL region, $e$ is the elemental charge, $L$ is the thickness of the CsFAMA films (about 500 nm), $\varepsilon$ is the relative dielectric constant of the CsFAMA (28.8), and $\varepsilon_0$ is the vacuum permittivity. The $N_{\text{trap}}$ of CsFAMA films with different ChCl concentrations are shown in Fig. 2(f), and their exact values are listed in Table S1. The $N_{\text{trap}}$ values of pristine CsFAMA and ChC-1 CsFAMA are estimated to be $5.0 \times 10^{10}$ cm$^{-3}$ and $1.0 \times 10^{10}$ cm$^{-3}$ with $V_{\text{TFL}}$ of 0.39 V and 0.10 V, respectively. The $N_{\text{trap}}$ of ChCl-1 CsFAMA is reduced by 80% compared to that of the pristine CsFAMA, further evidencing the successful defect passivation by ChCl. It is found that the $N_{\text{trap}}$ increases up to ChCl-1 CsFAMA, while it begins to diminish at higher concentrations; this is consistent with the PL results. Moreover, the $\mu_e$ of CsFAMA films can be obtained using Mott-Gurney Eq. (4) [24]:

$$J_{\text{SCLC}} = \frac{9\varepsilon_0\varepsilon\mu V^2}{8L^3}$$

(4)

where $J$ is the current density, $\mu$ is the mobility of the charge carriers, and $V$ is the effective voltage. The $\mu_e$ values of CsFAMA are $2.3 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ and $1.0 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ for the pristine and ChCl-1 cases, respectively. The improved $\mu_e$ of CsFAMA after
passivation by ChCl implies an enhancement in the electron transport of ChCl-1 CsFAMA compared to that of the pristine CsFAMA. Overall, ChCl-1 CsFAMA is confirmed to have the lowest $N_{\text{trap}}$, the smallest recombination probability, and the highest $\mu_e$ by passivation effect, which are essential qualities for the development of high-performance DC-TENG, since the carriers are transported from the interfaces through the CsFAMA and PEDOT:PSS.

3.3 Development of tribovoltaic DC-TENGs based on ChCl-treated CsFAMA

While using the ChCl-treated CsFAMA as the DC-triboelectric material, the tribovoltaic DC generation is evaluated by DC-TENG output measurement, as shown in Fig. 3(a), Fig. 3(b), and Fig. S12. To investigate the effect of passivation with ChCl and determine the optimal ChCl amount to use in the surface passivation process, the DC-TENGs characteristics are measured according to various concentrations of ChCl. DC-TENGs using pristine CsFAMA, ChCl-0.1 CsFAMA, ChCl-1 CsFAMA, ChCl-3 CsFAMA, and ChCl-10 CsFAMA as n-type materials and PEDOT:PSS as counter p-type conductive materials are tested in the reciprocal friction mode at a speed of 50 mm/s and a traveling distance of 20 mm. The pristine CsFAMA generates 0.33 V whereas ChCl-0.1 CsFAMA and ChCl-1 CsFAMA output higher voltages of 0.41 V and 0.80 V, respectively. When the ChCl concentration exceeds ChCl-3, the voltage dramatically drops to 0.18 V for ChCl-3 and 0.02 V for ChCl-10. The current density of the pristine CsFAMA (2.1 µA cm$^{-2}$) is lower than those of ChCl-0.1 CsFAMA (5.8 µA cm$^{-2}$), ChCl-1 CsFAMA (11 µA cm$^{-2}$), ChCl-3 CsFAMA (4.0 µA cm$^{-2}$), and ChCl-10 CsFAMA (2.5 µA cm$^{-2}$). The voltage and current density both show their highest values at ChCl-1, after which they both gradually decrease. These results show that, in this research, the voltage of the presented DC-TENGs is dominantly determined by the workfunction difference between n-type CsFAMA and p-type conductive PEDOT:PSS. These results are attributed to the mechanism of DC generation wherein the electrons and
holes generated at the interfaces drift by $E_{bi}$ developed by the p-n junction as a driving force. The magnitude of $E_{bi}$ is highly related to the difference in the work function, so KPFM is conducted to investigate the work function of CsFAMA with different ChCl concentrations. Fig. 3(c) and Fig. S9 show the work function distributions and mapping results obtained using KPFM.

The work function of the CsFAMA with respect to PEDOT:PSS differs by 0.76 eV, 0.80 eV, 1.19 eV, 1.07 eV, and 0.92 eV for pristine, ChCl-0.1, ChCl-1, ChCl-3, and ChCl-10, respectively. All types of CsFAMA have smaller work functions than PEDOT:PSS. These results evidence the electron donation from CsFAMA to PEDOT:PSS during contact electrification. The $E_F$ increased with ChCl concentrations up to ChCl-1, which is attributed to the electron-donating property of choline, as it has been proven that each ChCl molecule can transfer 0.8 e to CsFAMA during passivation [29]. Regarding ChCl-3 CsFAMA and ChCl-10 CsFAMA, although they have a larger work function difference relative to PEDOT:PSS compared to ChCl-0.1 CsFAMA, their voltage generations are the smallest among the tested conditions. This is attributed to the fact that the formation of an unstable Lewis adduct phase results in an increase in $N_{trap}$ and a reduction in $\mu_e$. Moreover, ChCl molecules remain as they are without dissociating into Ch$^+$ and Cl$^-$ ions on the surface of the CsFAMA at high concentrations [29]. The deteriorations of output by ChCl-3 CsFAMA and ChCl-10 CsFAMA-based DC-TENGs also originate from the ChCl debris on CsFAMA, which cancels out the effect of $V_{bi}$ and hinders carrier transport. The tendencies of output performance with different concentrations of ChCl are remarkably consistent with their electronic properties ($N_{trap}$ and $\mu_e$), as discussed in Fig. 2.

UV-Vis and UPS measurements are conducted to obtain the electron energy band, as shown in Fig. 3(d). The UV-Vis and UPS measurements provide information on the $E_F$ and valence band and on the band gap values, respectively. The UV-Vis absorption spectra of the
CsFAMA films and the $T_{auc}$ plots used to analyze them to obtain the band gap values are shown in Fig. S5 and Fig. S6, respectively. Pristine CsFAMA, ChCl-0.1 CsFAMA, and ChCl-1 CsFAMA all have bandgaps around 1.61-1.62 eV, while ChCl-3 CsFAMA and ChCl-10 CsFAMA each have a band gap of about 1.59 eV. The band gap reduction indicates the emergence of the Lewis adduct phase for ChCl-3 CsFAMA and ChCl-10 CsFAMA, as shown in Fig. 2(b). In fact, the band gap of CsFAMA slightly increases by about 0.003 eV from pristine CsFAMA to ChCl-1 CsFAMA, which is consistent with the PL shift. The plots of UPS in Fig. S7 provide the VBM and $E_F$ of the CsFAMA films. The results are combined to yield the band diagrams of CsFAMA films and PEDOT:PSS, as shown in Fig. S10. The changes in the $E_F$ of CsFAMA films are consistent with the work functions measured by KPFM.

The band diagrams of the p-n junction in Fig. 3(e) provide an understanding of the DC output characteristics of the designed TENGs. The passivation by ChCl strengthens $V_{bi}$ at the PEDOT:PSS/CsFAMA-based p-n junction. Specifically, $V_{bi}$ increases from 0.76 eV to 1.19 eV, which thus intensifies the driving force of the tribovoltaic effect. In other words, the electrons and holes generated by friction are under a stronger electric field, thus causing them to drift faster in ChCl-1 CsFAMA-based DC-TENG than the pristine CsFAMA-based counterpart. The working speed-dependent DC-TENG performance is tested with the aim of investigating the friction-induced tribovoltaic effect. The higher speed entails greater friction energy; therefore, it should generate increased populations of $q_{tribo\text{-}exciton}$ and more chances for the excitation of electrons and holes by friction energy. In this scheme, it is expected that the DC-TENG working at a higher speed generates a larger output. The ChCl-1 CsFAMA based DC-TENG is examined at speeds of 25 mm/s, 50 mm/s, 75 mm/s, and 100 mm/s, and it outputs the current densities of 3.5 $\mu A\ cm^{-2}$, 11 $\mu A\ cm^{-2}$, 15 $\mu A\ cm^{-2}$, and 18 $\mu A\ cm^{-2}$, respectively, as shown in Fig. 3(f). A notable finding is that the output behavior is
proportional to the working speed, which further supports the friction-induced tribovoltaic effect. In this examination, the only distinguishing factor of each condition is the $q_{\text{tribo-exciton}}$ generated with different working speeds, while $\mu_e$ and $E_{bi}$ remain constant, since they are material-dependent physical quantities [41]. This therefore demonstrates that the higher speed or larger friction energy creates more numbers of $q_{\text{tribo-exciton}}$, thus resulting in greater tribovoltaic current density, according to Eq. (1). In addition, the power output of DC-TENG is analyzed in a function of load resistance to evaluate its internal resistance. It is found that the power density is maximized to $18 \mu\text{W cm}^{-2}$ at $1 \text{M}\Omega$ as an external load resistance, as can be seen in Fig. 3(g).

### 3.4 DC-TENGs with different heterojunctions

The DC generation of other junction types is investigated by using the NiO$_x$ and TiO$_2$ to form a p-n junction and a n-n junction with PEDOT:PSS. NiO$_x$ and TiO$_2$ are widely used as hole- and electron-transporting materials in photovoltaic devices. Fig. 4(a) and Fig. 4(b) present the design of two DC-TENGs and their corresponding band structures. ChCl-1 CsFAMA prepared in 1 cm$^2$ is slid along the surface of NiO$_x$ or TiO$_2$ to test their DC generation. Fig. 4(c) and Fig. 4(d) show the band diagrams of NiO$_x$-CsFAMA and TiO$_2$-CsFAMA after friction. The p-type conductive NiO$_x$ and n-type CsFAMA form a p-n junction similar to that in PEDOT:PSS-CsFAMA; however, NiO$_x$ has a larger work function than PEDOT:PSS. This difference forms the larger $V_{bi}$, which results in steeper band bending for the NiO$_x$-CsFAMA-based p-n junction. Therefore, as shown in Fig. 4(e), the friction between NiO$_x$-CsFAMA generates 0.85 V, which is a slightly higher value compared to the PEDOT:PSS-based one. In the case of TiO$_2$-CsFAMA, it forms a n-n junction, since TiO$_2$ is also an n-type conductive material, like CsFAMA. The n-n junction demonstrated in Fig. 4(d) indicates that it is energetically favorable for all the carriers to transport toward CsFAMA. In
other words, the electron and hole flow in directions that cancel out each other’s effects, thus causing TiO$_2$-CsFAMA based DC-TENG to generate poor DC output (Fig. 4(f)). Overall, the results with various counter materials indicate the significance of material choices in building an appropriate band alignment to design high-performance DC-TENGs.

4. Conclusions

In conclusion, we have demonstrated p-n junction-type tribovoltaic DC-TENGs through the friction between n-type CsFAMA and p-type conductive PEDOT:PSS. The results of this study show that the ChCl passivation of the pristine CsFAMA has led to an 80% reduction of the electron trapping defects, a 130% improvement in the $\mu_e$, and an increase in $V_{bi}$ at the interface from 0.76 eV to 1.19 eV. The ChCl-passivated CsFAMA-based DC-TENG has generated an output current density of 11 $\mu$A cm$^{-2}$ and an output voltage of 0.80 V. It is worth noting that improvements in voltage and current are simultaneously achieved; specifically, a five-time enhancement in current generation is achieved with the aid of material modification, which in our case is chemical treatment. Our results present directions for realizing high-performance DC-TENGs with a promising strategy by controlling triboelectric interfaces.

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Reference


Figure captions

**Fig. 1.** Working principles of p-n junction-based DC-TENG. Schematics and energy band diagrams of PEDOT:PSS-CsFAMA-based DC-TENG (a) before and (b) after contact, and (c) during friction. (d) Device structure of PEDOT:PSS-CsFAMA-based DC-TENG and atomic structures of ChCl and CsFAMA. (e) Current output of DC-TENGs with pristine and passivated CsFAMA. Surface potential of (f) pristine CsFAMA and (g) ChCl-passivated CsFAMA before and after friction with PEDOT:PSS.

**Fig. 2.** Effect of ChCl passivation. (a) Schematic illustrations of pristine and passivated CsFAMA films. (b) XRD spectra of CSFAMA films modified with different concentrations of ChCl. (c) XPS characterizations of Pb element on pristine and ChCl-1 CsFAMA. (d) PL of
pristine and ChCl-1 CSFAMA. (e) SCLC plots of pristine and ChCl-1 CsFAMA based on electron-only devices. (f) $\mu_c$ and $N_{\text{trap}}$ of CsFAMA with different concentrations of ChCl.

**Fig. 3.** Output performances of DC-TENGs based on CsFAMA with different ChCl concentrations. (a) Voltage output and (b) current output. (c) Surface potential of CsFAMA with different ChCl concentrations. (d) Energy band diagrams of PEDOT:PSS, pristine, and ChCl-1 CsFAMA from UV-Vis and UPS measurements (e) Energy band diagrams of PEDOT:PSS-pristine CsFAMA and PEDOT:PSS-ChCl-1 CsFAMA. (f) Output performance of ChCl-1 CsFAMA-based DC-TENG at different working speeds. (g) Current density and power density of ChCl-1 CsFAMA-based DC-TENG as a function of external load.

**Fig. 4.** DC-TENGs with different heterojunctions. Device structures of (a) NiO$_x$-CsFAMA and (b) TiO$_2$-CsFAMA-based DC-TENGs and their energy band diagrams before contact. Energy band diagrams of (c) p-n junction formed by NiO$_x$-ChCl-1 and (d) n-n junction formed by TiO$_2$-ChCl-1. Voltage output of (e) NiO$_x$-CsFAMA and (f) TiO$_2$-CsFAMA-based DC-TENGs.
Figure 1
Figure 2
Figure 3
Figure 4
Biographies

You-Sun Lee is currently a Ph.D. course student supervised by Prof. Sang-Woo Kim at School of Advanced Materials Science & Engineering, Sungkyunkwan University. Her current research interests include the triboelectric energy harvesting and high-performance perovskite solar cells for their applications.

Sera Jeon is currently a Ph.D. candidate under the supervision of Prof. Sang-Woo Kim at the School of Advanced Materials Science and Engineering at Sungkyunkwan University (SKKU). Her main research interests are focused on triboelectric and piezoelectric energy harvesting in the aspect of materials with theoretical (simulations based on density functional theory and molecular dynamics) and experimental approaches.

Dabin Kim is a Ph.D. student under the supervision of Prof. Sang-Woo Kim at the School of Advanced Materials Science and Engineering at Sungkyunkwan University (SKKU). Her current research interests include the triboelectric and piezoelectric energy harvesting for its environmental/biomedical applications.
**Dong-Min Lee** is a Ph.D. student under the supervision of Prof. Sang-Woo Kim at School of Advanced Materials Science and Engineering, Sungkyunkwan University (SKKU). His current research interests are the material design and characterization for bioresorbable energy harvesting devices to produce clinical benefits in the diagnostic, therapeutic, rehabilitation purposes.

**Dr. Do-Hyung Kim** is a principal researcher at KEPCO Research Institute. He received his Ph.D. degree in Materials Science and Engineering from the Gwangju Institute of Science and Technology, South Korea in 2005. His recent research interest is focused on high-performance perovskite solar cells and their application including large-area, semi-transparent, and building integrated photovoltaics.

**Prof. Sang-Woo Kim** is an SKKU Distinguished Professor at Sungkyunkwan University (SKKU), Korea. He is currently the director of two government-funded research centers of the Triboelectric Energy Harvesting Research Center (Leader Research) and the National Core Materials Research Center supported by NRF of Korea. His recent research interest is focused on triboelectric/piezoelectric nanogenerators for powering body-implatable and wearable electronics, self-powered sensors, and 2D materials for energy harvesting. Prof. Kim has published over 300 research papers with the H-index of 83. He is currently serving as an Associate Editor of *Nano Energy* and an Executive Board Member of *Advanced Electronic Materials*. 
CRediT author statement

**You-Sun Lee:** Conceptualization, Data Curation, Methodology, Investigation, Visualization, Writing-review & editing.  **Sera Jeon:** Conceptualization, Data Curation, Methodology, Investigation, Visualization, Writing - original draft, Writing-review & editing.  **Dabin Kim:** Investigation, Methodology, Writing – review and editing.  **Dong-Min Lee:** Visualization.  **Do-Hyung Kim:** Formal analysis, Resources, Supervision, Methodology.  **Sang-Woo Kim:** Conceptualization, Supervision, Writing - review & editing, Funding acquisition.

Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical Abstract

We demonstrate the improved direct current (DC) output performance of the triboelectric nanogenerators (TENGs) based on a dynamic p-n junction with passivation treatment. Output
performance of DC-TENGs can be significantly enhanced by the electrical property change of friction materials such as triboelectric charge density, carrier mobility, and built-in potential. We experimentally observed that perovskite-based DC-TENGs can simultaneously improve voltage and current through triboelectric material modification by passivation.

**Highlights**

- This paper offers an intriguing approach to improve output performance of tribovoltaic DC-TENGs by controlling key factors.
- Passivation of CsFAMA realizes the optimization of triboelectric charge density, carrier mobility, and work function.
- The passivated CsFAMA generates DC with five-time larger current density.
- Our results pave a way to realize high-performance DC-TENGs as a promising strategy to control triboelectric interfaces.