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Supplementary Information

Manipulating the triboelectric surface charge density of polymers by low-energy Helium irradiation/implantation

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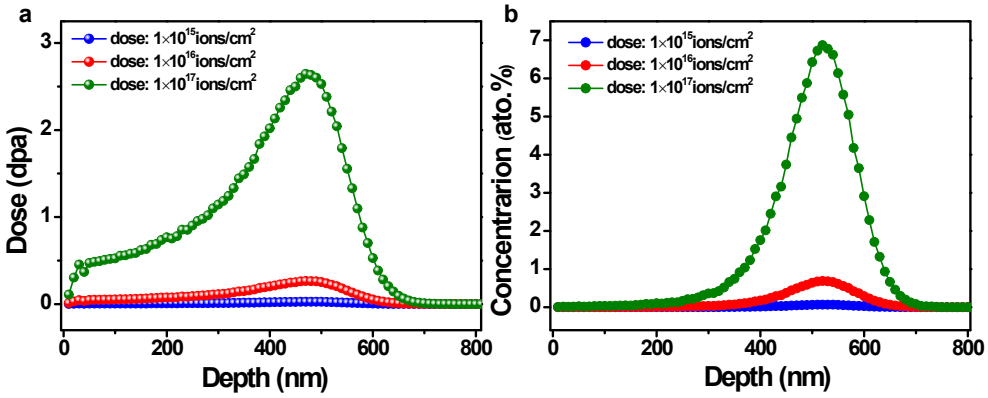
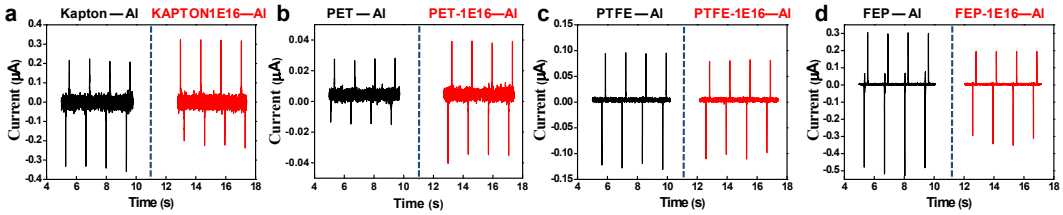
The details of Kapton model building and cascade simulation

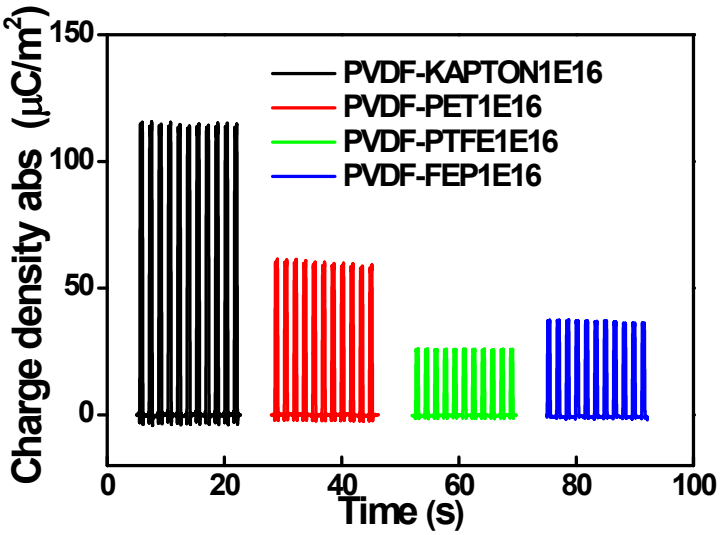
The simulation process is illustrated in Fig. 5a. Firstly, the single chain model of Kapton which consists of 4 repeating units terminated with hydrogen atoms is created by Material Studio and then fully relaxed by LAMMPS. All atoms are assigned zero charge initially and charge equilibration is executed by using electronegativity equalization method (EEM) to handle the electrostatic interactions among atoms every step until a precision of 10^{-6} *e* has reached. Conjugate gradient (CG) minimization method is used to relax atoms by iteratively adjusting its coordinates. The chemical structure of the polyimide repeating unit is presented in Fig. 4g. The hydrogen atoms are commonly chosen to be the chain ends so that the simulations represent the chemistry of bulk Kapton more realistically. [1] Secondly, the polyimide model is built with PACKMOL [2] by adding 200 single chains randomly into a box of 120 Å × 120 Å × 120 Å with molecular distance tolerance of 2 Å to get a reasonable initial configuration. In order to match the density of bulk Kapton with the value of 1.4 g/cm^3, the initial configuration is implemented into LAMMPS and compressed in NPT ensemble at 2.5 K with an external pressure until the box has reduced to 72 Å × 72 Å × 72 Å. Thirdly, the polyimide model is equilibrated in NVT ensemble at 300 K for 10 ps with a timestep of 0.1 fs. Finally, a carbon atom is created in the left-bottom corner of the box to be the PKA (primary knock-on atom), and launched along the space diagonal direction with a kinetic energy of 1 keV. Considering the majority in Kapton is carbon, it is reasonable to set a carbon atom be the primary PKA. In this collision cascade stage, the time step varies from 4×10^{-3} fs to 0.1 fs depending on the atomic velocities and force magnitude, avoiding atoms' velocities too large to track them in the beginning of the cascade. Periodic boundary conditions are applied in all three Cartesian directions throughout the simulation. The results are visualized by the Open Visualization Tool (OVITO), [3] and bonds are searched by setting pair-wise cutoff radii as Fig. 5a shows. A bond is checked to exist if two atoms within pair-wise cutoff radii listed in the criterion (Table 1).



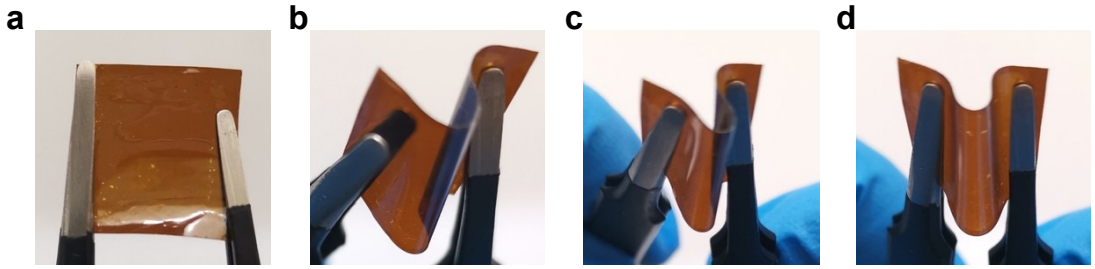
Supplementary Figure S1. **a**, Damage exposure (dpa) profile. **b**, He concentration with different irradiation doses according to SRIM.



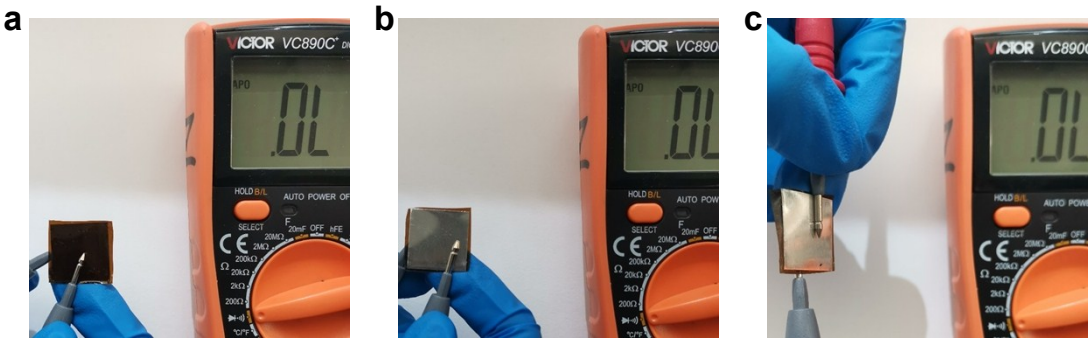
Supplementary Figure S2. The output currents from the contact electrification between different polymer film and Al foil. The effective contact areas for the TENG devices in are all kept to be 7 mm × 7 mm. The contact-separation type TENG devices has been applied for the measurement. The output currents of four different polymers (with and without irradiation) in contact with Al foil are presented : **a**, Kapton. **b**, PET. **c**, PTFE. **d**, FEP.



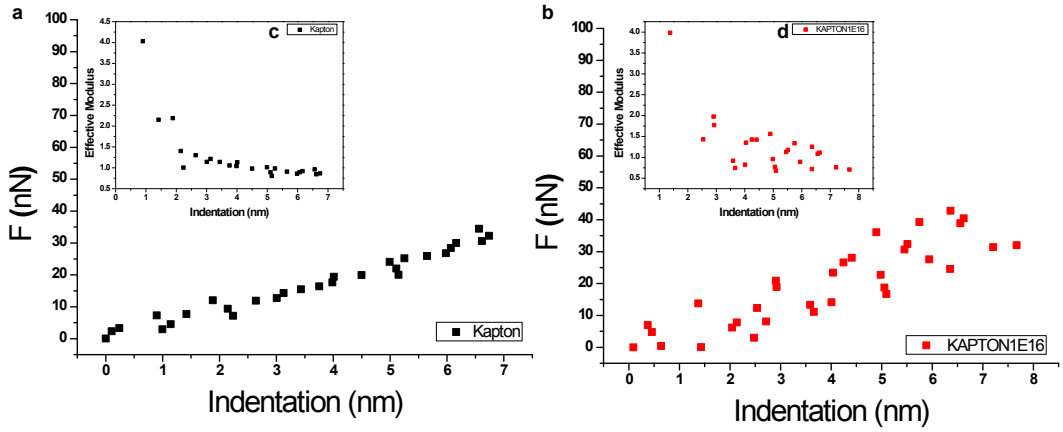
Supplementary Figure S3. The contact-separation type TENG devices are employed for the charge density abs of the Poly(vinylidene fluoride) (PVDF) film combine with four irradiated materials. The effective contact areas for the TENG devices in are all kept to be 49 mm^2.



Supplementary Figure S4. The flexibility of KAPTON1E16.



Supplementary Figure S5. The Al electrode is attached to the back of the polymer film and detect between the electrode and the polymer with two probes of the multimeter, showing no electrical signal.

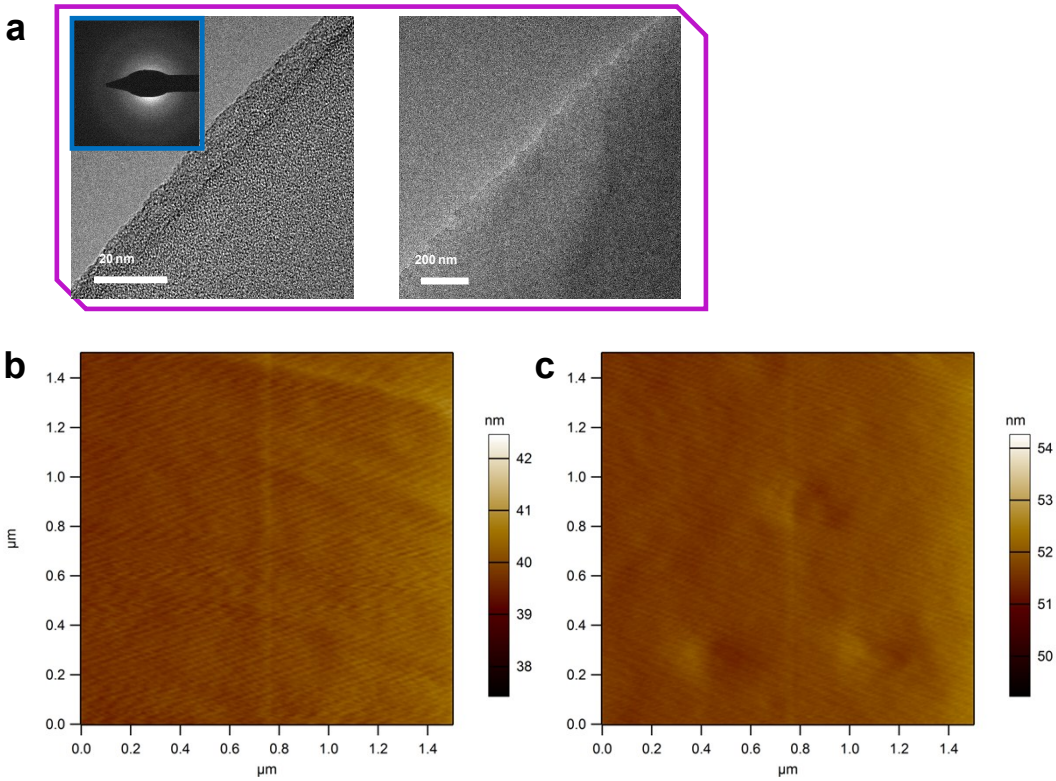


Supplementary Figure S6. The force-indentation curve for Kapton and KAPTON1E16 film: **a**, Kapton. **b**, KAPTON1E16. Inset: Young's modulus determined by fitting to the Hertz model, **c**, Kapton. **d**, KAPTON1E16.

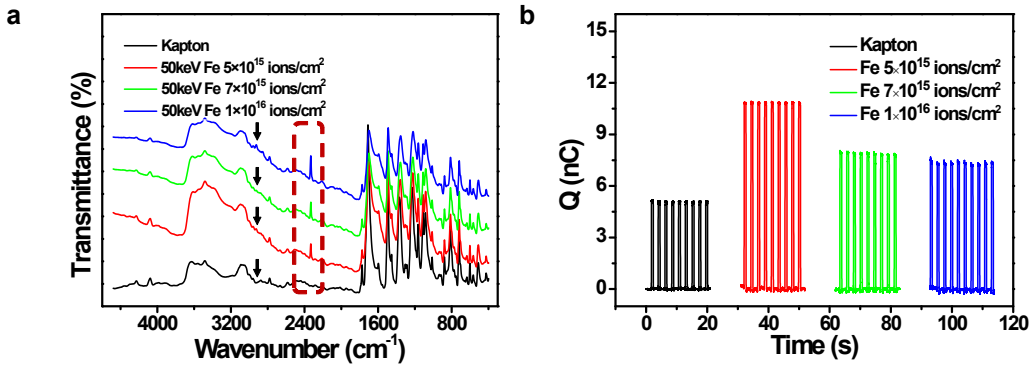
The indentation δ is calculated from : $\delta = |Z - Z_0| - |D - D_0|$ Here, Z and D are the piezo-displacement and the cantilever deflection, while Z_0 and D_0 are the piezo-displacement and the cantilever deflection at which the tip-surface contact occurs. The loading force F is determined from the spring constant of the AFM cantilever (2.8 N/m). Moreover, we have applied the Hertz model [4,5] to calculate the Young's modulus (E) of the sample based on the force data and the calculation equation is :

$$E = \frac{3(1 - v^2)\mathrm{F}}{4\sqrt{R}\delta^{1.5}}$$

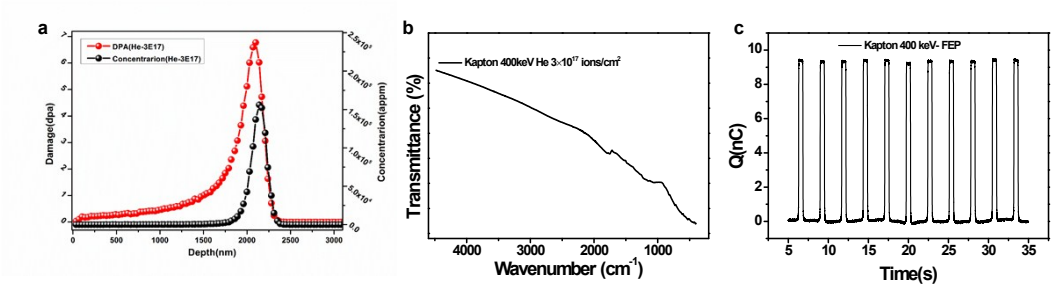
where R is the effective radius of the two bodies in contact, F is the applied force, δ is the indentation depth, and v is the Poisson ratio of the sample.



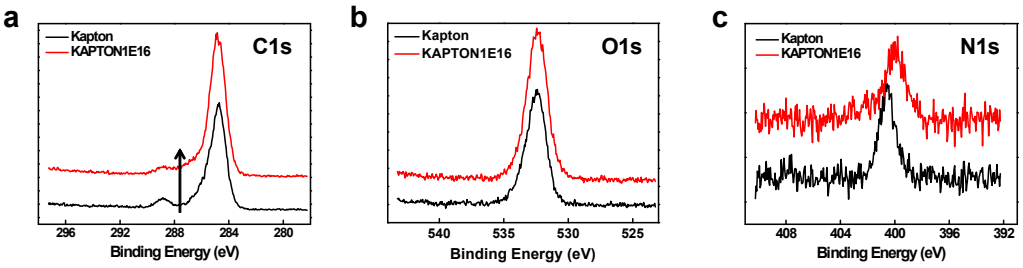
Supplementary Figure S7. a, The TEM and diffraction pattern of top part of the cross-section region of pristine Kapton film. No jagged region has been observed, which is different from irradiated sample. AFM image for the surface of the films: **b**, Kapton. **c**, KAPTON1E16.



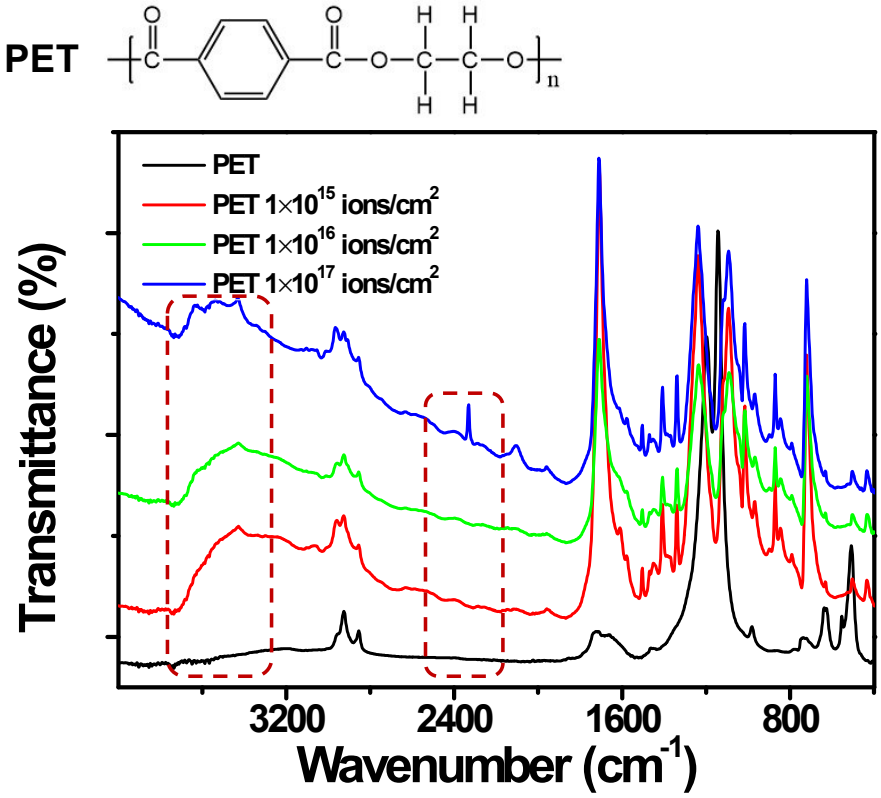
Supplementary Figure S8. The data of Kapton Fe in 50 keV. **a**, ATR-FTIR spectrum. **b**, The Q for Kapton Fe and FEP.



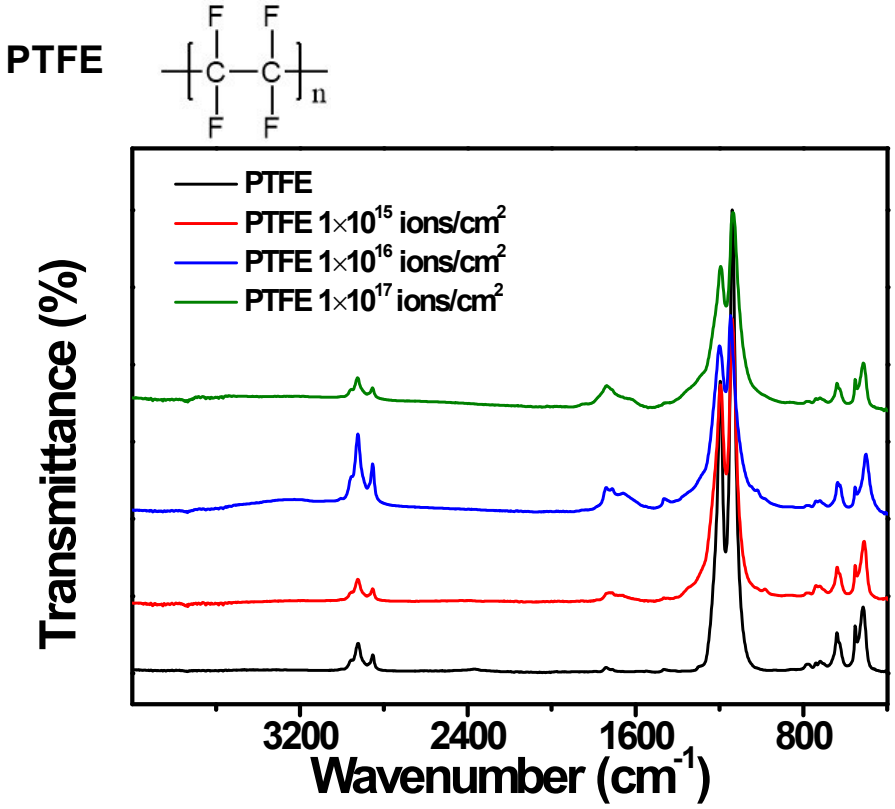
Supplementary Figure S9. The data of Kapton in 400 keV. **a**, The ion dose is 3×10^{17} ions/cm^2 and the DPA. **b**, ATR-FTIR spectrum. **c**, The Q for Kapton 3×10^{17} ions/cm^2 and FEP.



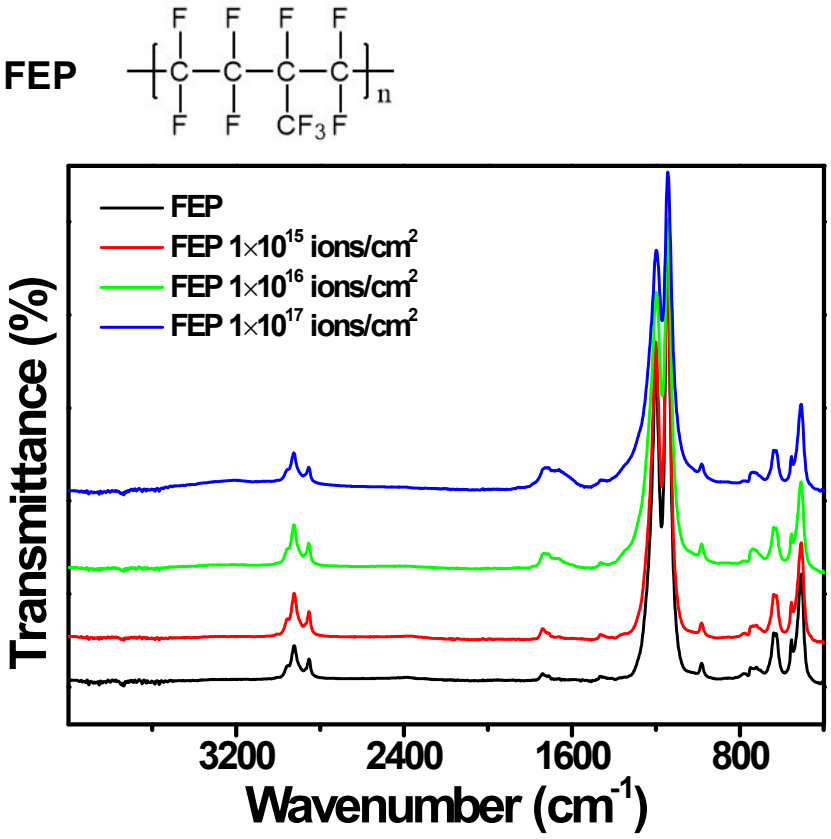
Supplementary Figure S10. X-ray photoelectron spectroscopy for Kapton and KAPTON1E16 sample: **a**, C1s. **b**, O1s. **c**, N1s.



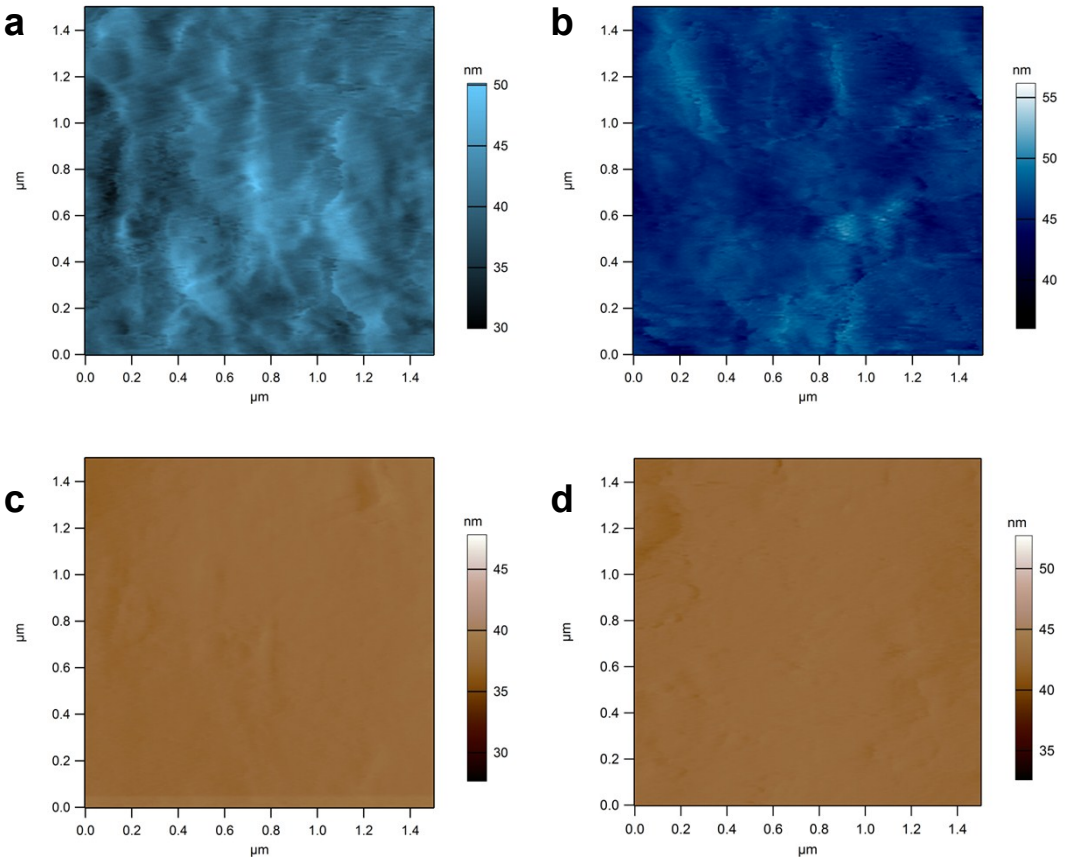
Supplementary Figure S11. ATR-FTIR spectrum of PET.



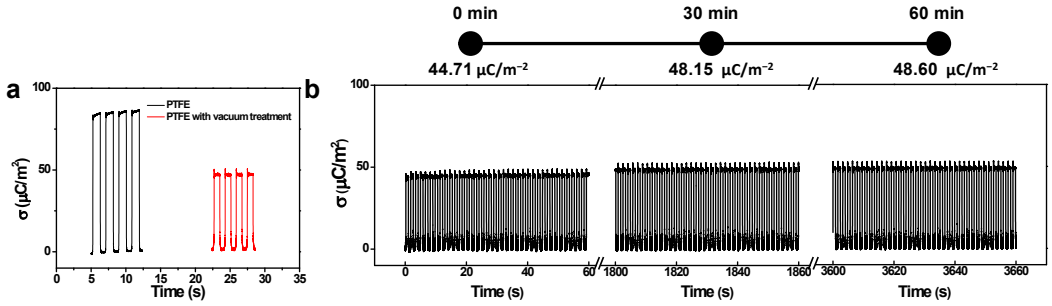
Supplementary Figure S12. ATR-FTIR spectrum of PTFE.



Supplementary Figure S13. ATR-FTIR spectrum of FEP.



Supplementary Figure S14. AFM image for the surface roughness of the films: **a**, PTFE. **b**, PTFE1E16. **c**, FEP. **d**, FEP1E16.



Supplementary Figure S15. The maximum transferred charge density (σ) of PTFE film during the contact electrification with FEP film: **a**, PTFE and PTFE with vacuum treatment. **b**, the cycle stability (from 0 min to 60 min) for PTFE after vacuum treatment. The contact-separation type TENG devices with a fixed contact area of 49 mm^2 are applied for the measurement.

Supplementary Table S1. Pair-wise cutoff radii for bonds among C, H, O, N (units: Å).

Pair-wise	Radius	Pair-wise	Radius
C-C	1.54	H-O	0.96
C-H	1.09	H-N	1.01
C-O	1.43	O-O	1.48
C-N	1.47	O-N	1.40
H-H	0.74	N-N	1.45

Supplementary Table S2. The details of irradiation experiments.

Sample	Fluence(ion/cm^2)	Irradiation time	the distance between the beam gun and the sample
Kapton	1×10^{14}	1min	11.5m
	1×10^{15}	10min	11.5m
	1×10^{16}	100min	11.5m
	1×10^{17}	400min	11.5m
PET	1×10^{15}	10min	11.5m
	1×10^{16}	100min	11.5m
	1×10^{17}	400min	11.5m
PTFE	1×10^{15}	1min	11.5m
	1×10^{16}	10min	11.5m
	1×10^{17}	400min	11.5m
FEP	1×10^{15}	10min	11.5m
	1×10^{16}	100min	11.5m
	1×10^{17}	400min	11.5m

Supplementary Table S3. The bond energy between each atom.

Bond	Length (Å)	Energy (kJ/mol)
C-C	1.54	348
C-H	1.09	413
C-O	1.43	360
C-N	1.47	308
H-H	0.74	436
H-O	0.96	366
H-N	1.01	391
O-O	1.48	145
O-N	1.40	201
N-N	1.45	170
C-F	1.41	347

The radius mentioned in table is also necessary. The radii mentioned in Supplementary Table 1 are the distances of different atomic pair wises. If the radii of different pair wises are less than the values listed in table, the corresponding bonds between different pair wises are considered to be formed. In order to make it clearly, we use the concept of Length to replace Radius. Universally, the bond energy is determined by bond length, i.e. $E=E(r)$. The interatomic potential used in this paper, i.e. Reactive force field[6,7] (abbr. ReaxFF), is an advanced potential in which the bonds between different atoms are not need to preset but checked and valid to be existed by calculating the distance of different atoms every step.

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