

Supplementary Materials

Hydrogen-bond-cross-linked PVA/MXene films for durable triboelectric nanogenerators and gesture sensing

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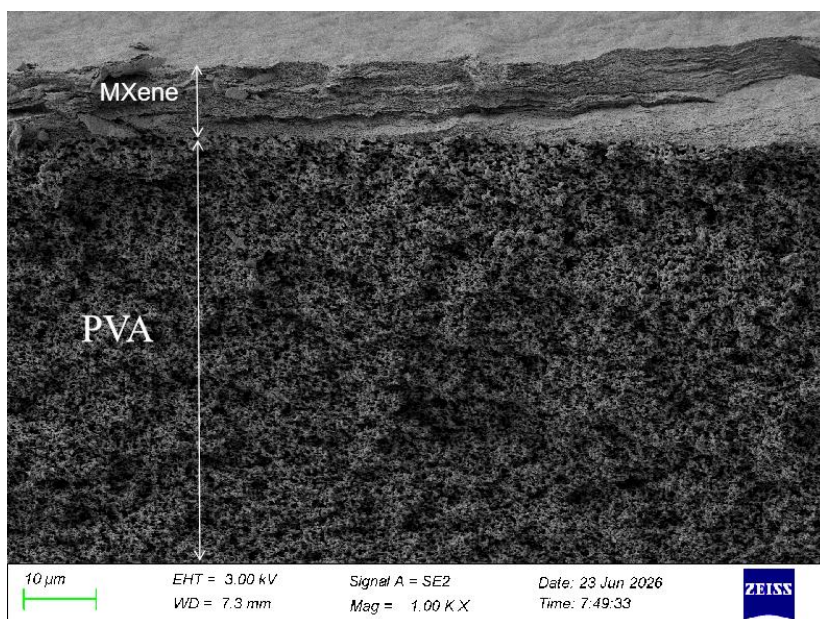


Figure S1. Cross-sectional scanning electron microscopy (SEM) of the PVA/MXene composite film. The newly acquired high-magnification cross-section image reveals the PVA-coated layer uniformly covering the multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film, confirming coating continuity and interfacial integrity.

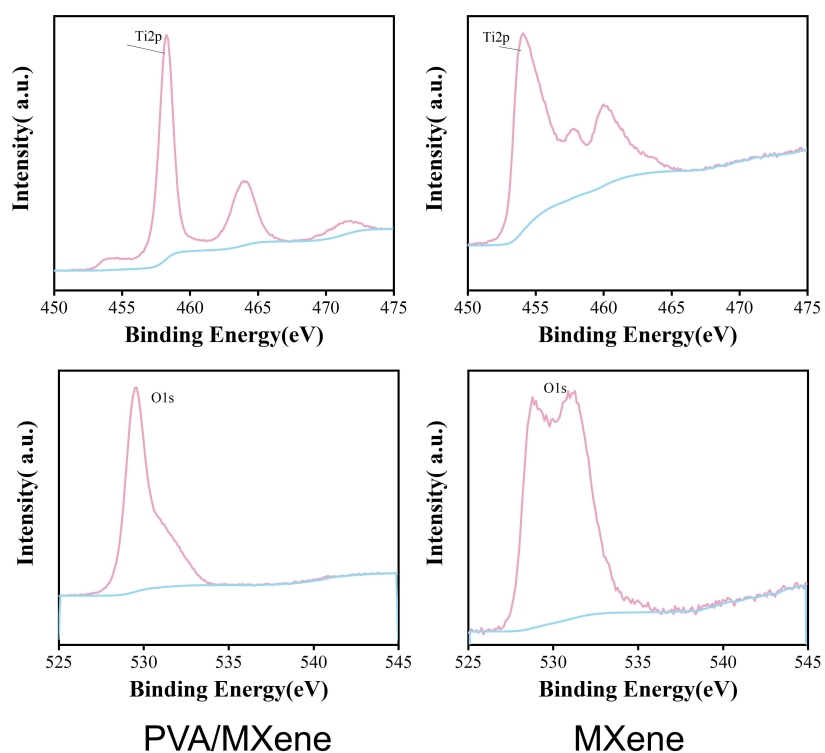


Figure S2. XPS evidence for MXene oxidation suppression. High-resolution Ti 2p, and O 1s core-level spectra of the bare MXene and PVA/MXene films illustrate that PVA coating preserves the Ti–C

component and limits Ti–O growth under ambient exposure, supporting the accelerated-oxidation result in Figure 3B–E.

Comparative analysis of high-resolution XPS Ti 2p and O 1s spectra of two batches of oxidized MXene samples reveals that the sample corresponding to the right-side spectra undergoes much severer oxidation degradation than the left-side counterpart. In Ti 2p spectra, the right sample exhibits an intense, broad Ti^{4+} characteristic peak assigned to TiO_2 oxide phase within the high binding energy range of 460–470 eV, whose signal intensity is comparable to that of intrinsic Ti-C peak; by contrast, only a trivial weak hump is observed at the identical region for the left sample, indicating negligible formation of TiO_2 . The O 1s spectra provide further supportive evidence: the right sample delivers a stronger and broader main peak at ~530 eV originating from lattice oxygen of TiO_2 , corresponding to a drastically increased proportion of oxide species. These XPS results collectively demonstrate that the left MXene sample retains the intrinsic Ti-C skeleton far more effectively and possesses superior oxidation resistance.

Table S1. Machine-learning feature set and model hyperparameters. The six time/frequency-domain features are extracted from each 1-kHz sampled voltage signal before PCA dimensionality reduction.

Domain	Feature	Symbol / definition
Time	Peak-to-peak amplitude	$V_{pp} = \max(V) - \min(V)$
Time	Root-mean-square	$RMS = \sqrt{\text{mean}(V^2)}$
Time	Zero-crossing rate	ZCR = number of sign changes / signal length
Time	Waveform length	$WL = \sum V_i - V_{i-1} $
Time	Signal entropy	Shannon entropy of the normalized amplitude histogram
Frequency	Dominant FFT magnitude	Magnitude of the peak in the single-sided amplitude spectrum

Model settings: SVM with RBF kernel; C and γ determined by grid search; stratified 5-fold cross-validation; PCA retaining 95% variance reduces the 6-D feature vector to 2 principal components. Training/test split within each fold is 80/20.

Table S2. XPS core-level binding energies (eV) of the pristine MXene film, obtained from Shirley-background Voigt deconvolution.

Core level	Component	Binding energy (eV)
Ti 2p	Ti–C	454.6
Ti 2p	Ti–O / Ti–O _x	458.3
C 1s	C–C / C=C	284.6
C 1s	C–O	286.0
C 1s	C=O	288.0
O 1s	Ti–O	530.0
O 1s	C–O / OH	532.0

Table S3. COMSOL Multiphysics parameters for the bending-stress simulation shown in Figure 3A.

Item	Value / setting
Geometry	MXene film: 5 cm × 1 cm × 10 μm; PVA coating: 5 cm × 1 cm × 220 μm
Elastic modulus (MXene)	E _{MXene} ≈ 300 GPa
Elastic modulus (PVA)	E _{PVA} ≈ 2 GPa
Poisson ratio	ν ≈ 0.3 (both layers)
Mesh	Free tetrahedral; max element size 0.5 mm; local refinement to 0.05 mm at interface
Boundary conditions	Bottom face fixed; top face under uniformly distributed normal pressure 25 N, cyclic contact–separation
Key output	Bare MXene peak stress ≈ 2.0 × 10 ⁸ Pa; with PVA coating < 5.0 × 10 ⁷ Pa

Table S4. Commercial capacitor specifications used for energy harvesting. Capacitance, type, rated voltage, and tolerance for the devices charged in Figure 5I–J.

Nominal capacitance (μF)	Type	Rated voltage (V)	Tolerance (%)
2.2	Commercial MLCC	10	$\pm 10\%$
4.7	Commercial MLCC	10	$\pm 10\%$
10	Commercial MLCC	10	$\pm 10\%$

Table S5. Performance comparison with recently reported PVA-based / MXene-based TENGs. Summary of fabrication strategy, output voltage, peak power density, ML recognition accuracy, and representative application. Values are taken from the cited references under the authors' reported test conditions.

Work / Ref.	Material strategy	Voc (V)	Peak power density	Recognition	Application
This work	PVA surface-coated MXene film	50	$6 \mu\text{W}/\text{cm}^2$ ($0.06 \text{ W}/\text{m}^2$)	93% (6 gestures, SVM)	Durable TENG + gesture HMI
$\text{Ti}_3\text{CNT}_x/\text{PVA}$ nanofiber [7]	Electrospun $\text{Ti}_3\text{CNT}_x/\text{PVA}$ nanofiber membrane	—	$5.5 \text{ W}/\text{m}^2$ ($550 \mu\text{W}/\text{cm}^2$)	96.36% (MLP)	Human–computer interaction
PVA/g- C_3N_4 [33]	PVA/g- C_3N_4 /PDMS bulk composite	353.3	—	—	Energy harvesting
h-BN composite [34]	h-BN composite film	198.6	$7.86 \text{ W}/\text{m}^2$ ($786 \mu\text{W}/\text{cm}^2$)	Handwriting (ML)	Energy harvesting + ML recognition
$\text{Ti}_3\text{C}_2\text{T}_x$ dual-electrode [35]	2D $\text{Ti}_3\text{C}_2\text{T}_x$ -MXene superstructures /	120	$5.66 \text{ W}/\text{m}^2$ ($566 \mu\text{W}/\text{cm}^2$)	—	Self-powered electronics
Silane-PVA/MXene hydrogel [36]	Silane-modified PVA/MXene hydrogel	190–212	—	—	Flexible TENG

PVA/MXene/PAA-Hanji [37]	Multifunctional PVA/MXene/PAA textile	—	102.2 $\mu\text{W}\cdot\text{cm}^{-3}$	—	Energy harvesting + EMI shielding
Masked TENG [38]	Masked triboelectric nanogenerator	—	—	88.7% (letters)	Intelligent PPE
Triple-network hydrogel [39]	Triple-network hydrogel-based TENG	326.89	368.3 $\mu\text{W}/\text{cm}^2$	—	Motion detection / SHM

Note: The present device deliberately trades peak power for durability and oxidation resistance via the surface-coating architecture. Direct cross-comparison of absolute voltage/power is complicated by different contact areas, forces, frequencies, and load resistances.

Table S6. Per-fold SVM classification metrics. Accuracy, precision, recall, and F1-score for each of the five stratified validation folds, together with the overall mean $\pm$ standard deviation. The dataset comprises six hand gestures with a total of 45 signal records sampled at 1 kHz under 1 Hz contact actuation.

Fold	Accuracy (%)	Precision (%)	Recall (%)	F1-score (%)
Fold 1	88.89	94.44	88.89	88.89
Fold 2	88.89	81.48	88.89	84.44
Fold 3	88.89	94.44	88.89	88.89
Fold 4	100.00	100.00	100.00	100.00
Fold 5	100.00	100.00	100.00	100.00
Mean $\pm$ SD	93.33 $\pm$ 6.09	94.07 $\pm$ 7.57	93.33 $\pm$ 6.09	92.44 $\pm$ 7.13

Supplementary Note 1

Quantitative FTIR and XPS analysis

FTIR quantitative analysis.

The O–H stretching region was deconvoluted into a free –OH component (higher wavenumber, narrower) and a hydrogen-bonded –OH component (lower wavenumber, broader). Compared with MXene, the PVA/MXene composite shows a redshift of the O–H stretching band from $\approx 3270\text{ cm}^{-1}$ to $\approx 3240\text{ cm}^{-1}$ together with band broadening, which is characteristic of strengthened interfacial hydrogen bonding. The integrated area ratio of H-bonded to free –OH ($A_{\text{H-bond}} / A_{\text{free}}$) increases upon PVA coating, consistent with the enhanced interfacial H-bonding reported for PVA/MXene systems [36]; the deconvoluted profile is shown in Figure 2C.

XPS quantitative analysis.

High-resolution XPS core-level spectra were deconvoluted with a Shirley background and Voigt line shapes. The fitted peak positions are summarized in Table S2.

The relative area ratios (Ti–C/Ti–O, C–C/C–O/C=O, and Ti–O/C–O–OH) quantify the surface-termination evolution after PVA coating and confirm reduced oxidative conversion of Ti–C to Ti–O, in agreement with the suppressed oxidation reported for PVA-encapsulated MXene electrodes [35,36].

Supplementary Note 2

Mechanism and evidence for PVA suppression of MXene oxidation

$\text{Ti}_3\text{C}_2\text{T}_x$ MXene degrades in ambient air because H_2O and O_2 intercalate between the layers and oxidize Ti–C bonds to Ti–O_x, accompanied by a loss of electrical conductivity. The main manuscript therefore reports an accelerated oxidation test (60 °C circulating-air oven) in which bare and PVA-coated MXene films were monitored by a four-probe conductivity measurement every 20 h (Figure 3B, C, and E). After 160 h the bare film showed visible cracking and retained only $\sim 20\%$ of its initial conductivity, whereas the PVA/MXene film remained largely intact except for slight edge warping and retained $\sim 50\%$ of its conductivity. This difference is consistent with XPS (Figure 2G–L), where the Ti–C component is preserved and Ti–O growth is limited after coating, confirming that the PVA layer reduces oxidative attack on MXene.

The protective effect is attributed to two cooperative mechanisms. First, hydrogen bonds between PVA hydroxyl groups and MXene surface terminations (–F, –O, –OH) anchor the PVA coating tightly to the MXene surface, creating a dense physical barrier that slows $\text{H}_2\text{O}/\text{O}_2$ diffusion. Second, the flexible PVA layer accommodates mechanical deformation and prevents crack propagation that would otherwise expose fresh MXene surfaces to air. Long-term ambient stability of PVA-encapsulated MXene has been independently demonstrated, with retained conductivity/structural integrity over weeks at room temperature [35–37]; this corroborates the accelerated-test conclusion drawn above and indicates that the PVA/MXene film sustains high conductivity under ambient storage.

Supplementary Note 3

Specific capacitance from CV and GCD curves

The PVA/MXene interfacial specific capacitance was calculated from the galvanostatic charge–discharge (GCD) curve using $C = (I/m) \cdot \Delta t / \Delta V$, where I/m is the specific discharge current. Because the supplied GCD curve is reported at $1 \text{ mA} \cdot \text{g}^{-1}$ (mass-normalized), the absolute active mass m is not required to obtain the specific capacitance. With a discharge time $\Delta t \approx 2200 \text{ s}$ and a voltage window $\Delta V \approx 0.75 \text{ V}$, $C \approx (1 \text{ mA} \cdot \text{g}^{-1})(2200 \text{ s}) / 0.75 \text{ V} \approx 2.9 \text{ F} \cdot \text{g}^{-1}$ (quoted as $\approx 3 \text{ F} \cdot \text{g}^{-1}$). The rectangular CV shape and symmetric GCD profile together indicate pseudo-capacitive charge storage dominated by Ti–O redox and reversible polarization of PVA hydroxyl groups.

For the cyclic voltammetry (CV) curves, specific capacitance can alternatively be calculated as $C = \int I \, dV / (v \cdot m \cdot \Delta V)$, where v is the scan rate and the integral is the enclosed area. Because the CV y-axis in the supplied image is labelled in current units, the active mass must be known to convert to $\text{F} \cdot \text{g}^{-1}$; we therefore report the GCD-based estimate as the primary value. The rectangular CV shape and symmetric GCD profile together indicate pseudo-capacitive charge storage dominated by Ti–O redox and reversible polarization of PVA hydroxyl groups.