

Cite this: *Nanoscale*, 2026, **18**, 16855

Conformal TiO₂ nanolayers on electrospun PVDF fibers *via* spatial atomic layer deposition for enhanced triboelectric charge generation

Thi Thuong Nguyen,^{†a} Quang Tan Nguyen,^{†b} Ting-Han Lin,^c
Ming-Chung Wu,^d Nguyen Xuan Duong,^e Dinh Nam Nguyen,^a
Hung-Anh Tran Vu,^a Viet Huong Nguyen^{†*a} and Duy Linh Vu^{†*a}

Direct-current triboelectric nanogenerators (DC-TENGs) based on metal–semiconductor interfaces provide an effective strategy to eliminate external rectification circuits and enhance energy conversion efficiency; however, precise interfacial regulation and multifunctional integration remain challenging. Herein, we report a conformal TiO₂-coated electrospun PVDF fiber membrane fabricated *via* spatial atomic layer deposition (SALD) to construct a Schottky junction engineered DC-TENG. Unlike conventional polymer blending or surface modification approaches, SALD enables scalable, low-temperature, and thickness-controlled oxide deposition on three-dimensional fibrous membranes while preserving their porous architecture. The TiO₂ nanolayer acts as an interfacial semiconductor regulator that enhances charge trapping, interfacial polarization, and asymmetric carrier transport at the Al/TiO₂/PVDF interface. The optimized device delivers a peak current of 521 μA and a maximum power density of 40.7 $\mu\text{W cm}^{-2}$, representing a 108% enhancement compared with pristine PVDF. The TiO₂/PVDF-TENG output enables direct capacitor charging without external rectifiers, storing up to 2100 μJ in a 1000 μF capacitor. Moreover, stable operation over 6000 contact–separation cycles at 100% relative humidity demonstrates excellent moisture tolerance. The device also exhibits a humidity-dependent linear current response, enabling self-powered environmental sensing. This work highlights SALD-enabled nanoscale oxide interface engineering as an effective and scalable strategy for developing humidity-resilient DC-TENGs with integrated energy-harvesting and sensing functions.

Received 14th March 2026,
Accepted 8th July 2026

DOI: 10.1039/d6nr01028h

rsc.li/nanoscale

1. Introduction

Triboelectric nanogenerators (TENGs) have attracted sustained interest as a mechanically driven power source for distributed sensing, wearable electronics, and other low-power systems.^{1–3} TENGs generally operate through the coupling of contact electrification and electrostatic induction. When two materials

with different electron affinities or triboelectric polarities come into contact, interfacial charge transfer occurs. Therefore, the TENG output is strongly affected by surface charge density, dielectric polarization, charge retention, and carrier transport.^{4–6} From a polymer-science perspective, TENGs are particularly appealing because their performance can be tuned through polymer chemistry, surface functionality, morphology, and processing route. Electroactive polymers, porous membranes, and fibrous assemblies provide large interfacial areas and mechanically compliant contact surfaces, which are advantageous for contact electrification and long-term cycling.^{7–9} However, a persistent limitation of most conventional TENG architectures is that the electrical output is inherently alternating current (AC).^{10–14} Although AC-TENGs can exhibit high open-circuit voltages, their practical use commonly requires rectification and power-management circuits to obtain usable direct current (DC) for charging capacitors and driving electronics. These additional components increase circuit complexity, occupy space, and introduce conversion losses, which can become significant when the mechanical

^aFaculty of Materials Science and Engineering, Phenikaa School of Engineering, Phenikaa University, Hanoi 12116, Vietnam.

E-mail: linh.vuduy@phenikaa-uni.edu.vn, huong.nguyenviet@phenikaa-uni.edu.vn

^bCenter for Environmental Intelligence, VinUniversity, Hanoi 100000, Vietnam

^cCenter for Sustainability and Energy Technologies, Chang Gung University, Taoyuan 333323, Taiwan

^dDepartment of Chemical and Materials Engineering, College of Engineering, Chang Gung University, Taoyuan 333323, Taiwan

^eDivision of Neonatology, Department of Pediatrics, Chang Gung Memorial Hospital, Linkou, Taoyuan 333423, Taiwan

^fFaculty of Electronics and Telecommunications, VNU University of Engineering and Technology, Vietnam National University, Hanoi 12116, Vietnam

[†]These authors have equal contributions.

input is weak, intermittent, or when miniaturization is required.^{15,16}

In response, direct-current triboelectric nanogenerators (DC-TENGs) have emerged as an important development because they can deliver unidirectional output without an external rectifier. In practical energy-harvesting modules, native DC output simplifies power-conditioning, reduces diode-related losses, and can improve effective charging efficiency for storage elements.^{17,18} Therein, environmental stability is critical issue for TENGs, especially under elevated relative humidity (RH). Moisture can screen surface charges, increase surface/bulk conductivity, and accelerate charge relaxation, often resulting in reduced output.^{7,19,20} In DC-TENGs, humidity can be even more disruptive because directional output frequently depends on a carefully established interfacial barrier and a controlled conduction pathway. To ensure reliable TENG operation under moisture-rich environments, tribo-layers must sustain high charge density even in the presence of adsorbed water. Rather than treating water solely as a source of charge dissipation, its strong polarity and hydrogen-bonding capability can be exploited to promote interfacial charge transfer.^{21–23} Moisture-assisted output enhancement has been reported in several tribo-layer material, such as graphene oxide,^{20,24} polyelectrolytes,²⁵ carbon film,²⁶ and cellulose.²⁷

Poly(vinylidene fluoride) (PVDF) is a widely used polymer in triboelectric devices due to its strong electronegativity, chemical resistance, and mechanical robustness. Compared with many inorganic triboelectric materials, PVDF offers superior flexibility, lightweight characteristics, and processability, making it particularly suitable for flexible and wearable TENG applications. In addition, PVDF can be processed into fiber membranes by electrospinning, providing a high specific surface area, interconnected porosity, and compliant contact interfaces.^{28–33} These structural attributes can increase effective triboelectric contact area and improve mechanical adaptability during repeated contact-separation.^{34–36} Nevertheless, PVDF alone provides limited control over the interfacial energy needed to sustain directional charge extraction in DC-TENG operation.^{37–39} Accordingly, an effective strategy is to introduce a functional interlayer that modifies surface electronic/chemical states to support directional charge transport.

Ultrathin metal-oxide overlayers are attractive for DC-TENGs because they offer tunable surface states, an enhanced dielectric response, and barrier-like charge transport when paired with suitable electrodes.^{40–42} TiO₂ is particularly appealing due to its chemical stability and semiconductor electronic structure, which can modulate interfacial charge transfer and enable barrier-regulated charge extraction—an important prerequisite for sustaining unidirectional current output.^{34,43,44} Moreover, TiO₂ readily interacts with water and hydroxyl species; with proper engineering, these surface interactions can help regulate humidity-assisted conduction pathways instead of promoting uncontrolled leakage.^{45–48} For electrospun PVDF fiber membranes, however, performance is highly sensitive to coating uniformity and thickness control. As a 3D

porous fiber network, PVDF requires a conformal overlayer that uniformly wraps individual fibers and penetrates through the membrane depth; pinholes or nonuniform growth can create localized leakage and inconsistent barrier behavior, degrading reproducibility and DC stability at high relative humidity.

Atomic layer deposition (ALD) is widely recognized for delivering conformal, angstrom-level thickness control through self-limiting surface reactions, making it effective for modifying polymeric and porous substrates. Its conventional implementation, however, is commonly vacuum-based and time-sequenced in batch reactors, which limits throughput and complicates scale-up for large-area, flexible polymer membranes.^{49–51} In contrast, spatial ALD (SALD) segregates precursors in space rather than time, enabling continuous coating at substantially higher growth rates and throughput.^{52,53} Importantly, SALD can often operate at atmospheric pressure, eliminating the need for vacuum pumping and pressure-control cycles; this simplifies reactor design and process integration while reducing system complexity and maintenance. These features rapid deposition and a more straightforward, pressure-independent hardware concept, make SALD particularly attractive for temperature- and morphology-sensitive fiber membranes, while still preserving the key ALD advantages of conformality and precise thickness control when the process is properly optimized.^{54–56}

Herein, we report a humidity-resilient DC-TENG based on an electrospun PVDF fiber membrane conformally functionalized with a TiO₂ nanolayer deposited by SALD. SALD enables a uniform, controllable TiO₂ overlayer throughout the fiber network, thereby establishing a robust interface for unidirectional charge extraction. The resulting DC-TENG is evaluated under elevated RH to assess output stability and the persistence of DC current characteristics under moisture exposure. Overall, this study demonstrates that SALD-based oxide functionalization is a scalable route for engineering polymer nanofiber interfaces toward high-performance DC triboelectric energy harvesting, direct energy storage, and self-powered humidity sensing, particularly for wearable, outdoor, and distributed sensor applications operating under humid conditions.

2. Materials and methods

2.1 Material

Polyvinylidene fluoride (PVDF, M.W. ~ 534 000), polyvinylpyrrolidone (PVP, M.W. ~ 350 000), and titanium tetrachloride (TiCl₄, 99.9%) were obtained from Sigma-Aldrich (USA). *N,N*-Dimethylformamide (DMF, 99%), acetone (97%), ethyl alcohol (97%) were supplied from Guangdong Guanghua Sci-Tech (China).

2.2 Preparation of porous PVDF fiber membrane

The porous PVDF fiber membranes were prepared *via* electrospinning (Fig. 1). PVDF was dissolved in a mixed solvent of DMF and acetone (2 : 1, v/v) to form a 10 wt% polymer solution

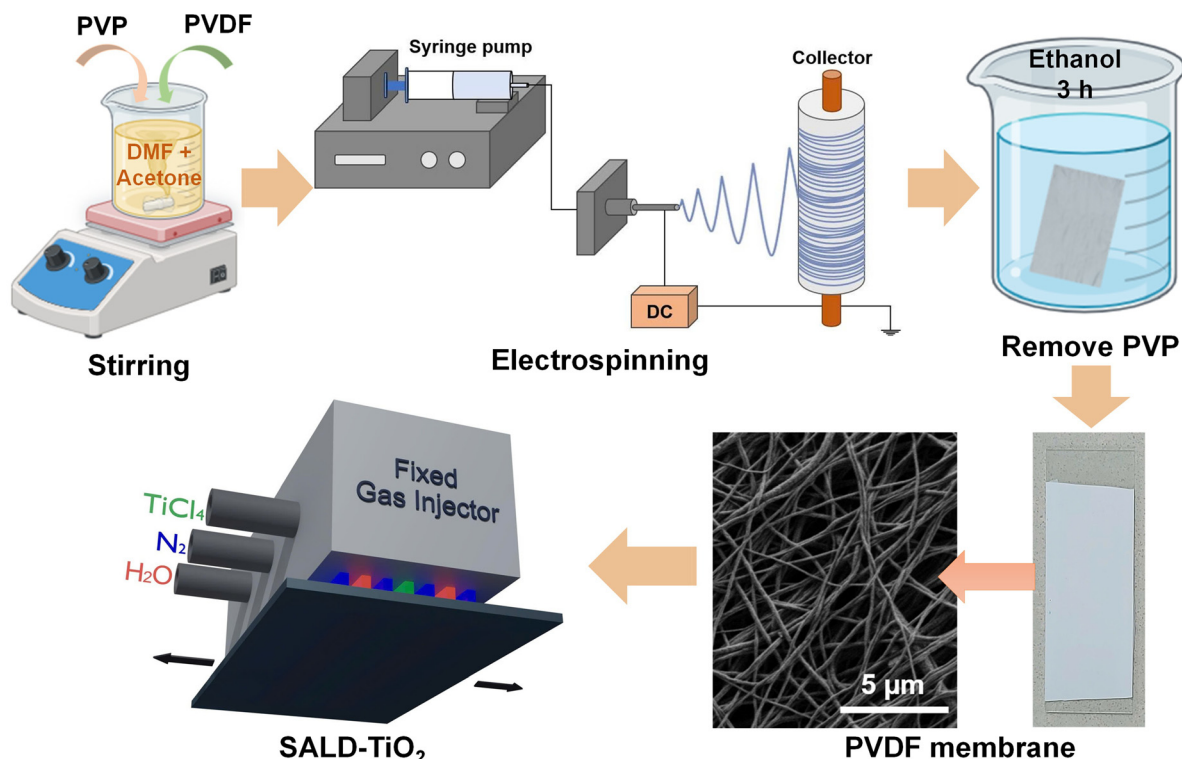


Fig. 1 Schematic illustration of the fabrication process for PVDF porous fiber membrane and SALD deposition of conformal TiO₂ nanolayers on the PVDF porous fiber membrane.

under continuous stirring until a homogeneous solution was obtained. Subsequently, PVP was incorporated as a sacrificial polymer at a PVDF : PVP mass ratio of 2 : 1. The precursor solution was loaded into a syringe with a metallic needle and electrospun using a laboratory-scale setup equipped with a DC high-voltage power supply. Fibers were collected over a 4 h spinning period to obtain free-standing membranes. The as-spun membranes were dried at 60 °C overnight to eliminate residual solvents. To generate porosity, the membranes were immersed in ethanol for 2 h to selectively remove the PVP phase, followed by thorough rinsing with deionized water. Finally, the porous PVDF fiber membranes were dried in an oven at 70 °C to subsequent processing or characterization.

2.3 Preparation of TiO₂/PVDF fiber membrane

A home-built atmospheric-pressure spatial ALD (AP-SALD) system was operated at a constant substrate temperature of 100 °C (Fig. 1) to deposit TiO₂ onto the PVDF fiber membrane. TiCl₄ and H₂O precursors were alternately pulsed over the substrate, with inert gas channels separating the streams, and nitrogen served as the carrier and purge gas to ensure uniform deposition. This process yielded a highly conformal, ultrathin TiO₂ layer with precisely controlled thickness while preserving the membrane's intrinsic porous fibrous morphology. Detailed information on the AP-SALD reactor configuration and film-growth optimization is provided in the SI. The parameters used to optimize film growth are presented in Fig. S1, SI. TiO₂/

Table 1 Sample nomenclature and SALD deposition conditions for TiO₂-coated PVDF fiber membranes

Sample ID	TiO ₂ SALD (cycles)	TiO ₂ thickness (nm)	Deposition temperature (°C)
PVDF	0	0	—
S1-TiO ₂ /PVDF	8	1	100
S5-TiO ₂ /PVDF	40	5	100
S10-TiO ₂ /PVDF	80	10	100
S15-TiO ₂ /PVDF	120	15	100
S20-TiO ₂ /PVDF	160	20	100

PVDF samples with different TiO₂ thicknesses were obtained, as summarized in Table 1.

2.4 Characterization and measurements

The surface morphology and elemental distribution of the fiber membranes were examined by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM/EDX; Apreo 2S Hi-Vac, Thermo Fisher Scientific). The chemical structure of the membranes was analyzed by Fourier transform infrared spectroscopy (Varian 640-IR FTIR spectrometer, Varian). The TENG devices were tested in vertical contact-separation mode using a programmable mechanical actuator. The applied force was fixed at 10 N and the working frequency was maintained at 1.5 Hz. The effective electrode contact area was 1.5 × 1.5 cm². The current and voltage

outputs were recorded using a digital electrometer (DMM6500, Keithley). For humidity-dependent measurements, the devices were conditioned and measured under controlled RH conditions. The saturated-humidity stability test was performed after conditioning the device at 100% RH. Detailed procedures and additional characterization data, including water uptake, *I*-*V* characteristics, and conductivity measurements, are provided in the SI.

3. Results and discussion

3.1 Membrane characteristics

SEM analysis was conducted to investigate the surface morphology and fiber characteristics of the electrospun membranes. As shown in Fig. S2a and b, the PVDF/PVP membrane exhibits a homogeneous, randomly oriented fibrous network with smooth fiber surfaces and no observable bead defects, indicating stable jet formation and optimized electrospinning parameters. The uniform morphology confirms the successful fabrication of continuous nanofibers with good structural integrity. The corresponding diameter distribution (Fig. S2c) follows an approximately normal distribution, with an average fiber diameter of 244.6 nm, suggesting relatively consistent fiber formation. After the removal of PVP, distinct morphological changes are observed in the PVDF membrane (Fig. S2d and e). The fibers display a wrinkled surface texture and slight structural collapse, which can be attributed to the extraction of the sacrificial PVP component. This post-treatment process induces pore generation and localized shrinkage along the fiber axis, leading to surface roughening and partial densification of the polymer matrix. Consequently, the average fiber diameter decreases to approximately 221.7 nm, as shown in Fig. S2f. The reduction in diameter is primarily associated with the dissolution of PVP and the subsequent contraction of the remaining PVDF framework.

Fig. 2 presents the SEM images of pristine PVDF and TiO₂-coated PVDF fiber membranes with TiO₂ thicknesses ranging

from 1 to 20 nm. Upon TiO₂ deposition *via* SALD, progressive surface modification is observed as the coating thickness increases. At low TiO₂ thicknesses (approximately 1–10 nm), the presence of TiO₂ is evident from the slightly roughened fiber surfaces and subtle increases in fiber diameter (Fig. 2b–d). However, at this stage, the coating does not form a clearly continuous film. The TiO₂ layer appears as discrete or partially coalesced domains conformally attached to the fiber surface, preserving the original fibrous morphology without blocking the inter-fiber pores. The porous architecture of the membrane remains essentially unchanged. When the TiO₂ thickness reaches 15–20 nm (Fig. 2e and f), a distinct and continuous TiO₂ shell becomes clearly visible around each fiber. The fibers exhibit a more uniform and denser outer layer, indicating the formation of a well-developed conformal coating. The encapsulation of the PVDF fibers by TiO₂ is significantly more pronounced at these higher thicknesses, resulting in a smoother and more homogeneous inorganic shell. Despite the thicker coating, the overall three-dimensional porous network is maintained, and no fiber agglomeration or structural collapse is observed.

To confirm the successful deposition of TiO₂ onto the PVDF fibers, EDX and FTIR analyses were conducted. Fig. 3a presents EDX spectra of pristine PVDF and TiO₂/PVDF fiber membranes with systematically varied TiO₂ thickness. The pristine PVDF membrane exhibits characteristic signals of C, F consistent with the chemical structure of the $-(\text{CH}_2-\text{CF}_2)-$ repeating unit. Moreover, O component is observed, which can be attributed to the PVP, indicating that a small amount of PVP is still retained within the porous fiber matrix. As expected, no Ti signal is detected in the pristine polymer. Upon SALD deposition, a Ti peak emerges and progressively intensifies with increasing cycle number, as clearly resolved in the magnified spectra (Fig. 3b), confirming the successful and thickness-dependent growth of TiO₂ on the PVDF fiber surface. Quantitative elemental analysis further substantiates this evolution (Table 2). The Ti content increases monotonically from 0 wt% (PVDF) to 0.1, 0.3, 0.5, 1.1, and 1.2 wt% for

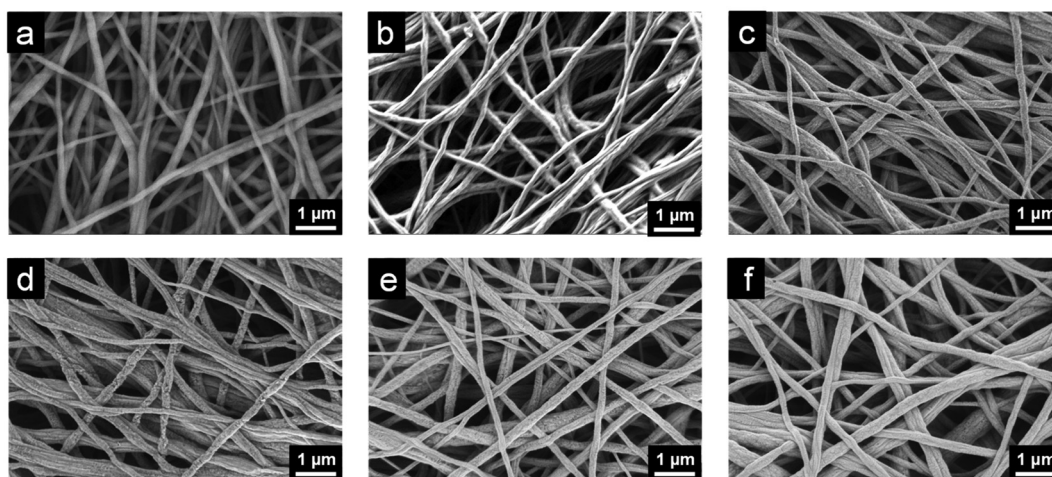


Fig. 2 SEM image of TiO₂/PVDF fiber membranes with varying TiO₂ thicknesses (a) 0 nm, (b) 1 nm, (c) 5 nm, (d) 10 nm, (e) 15 nm and (f) 20 nm.

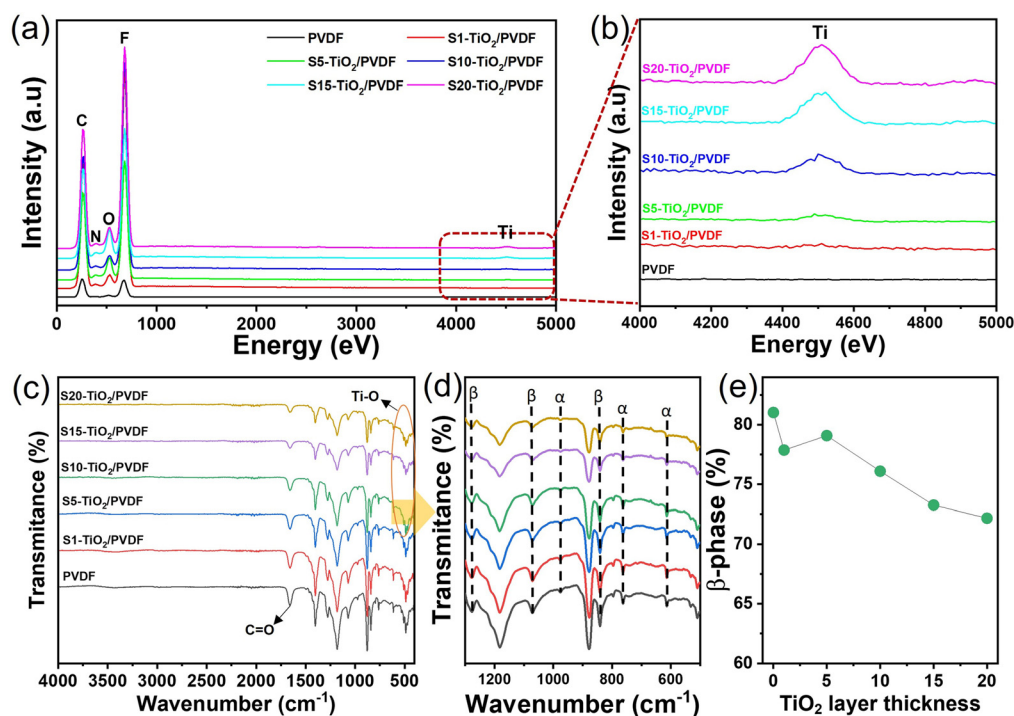


Fig. 3 (a) and (b) EDX spectra; (c) and (d) FTIR spectra and (e) β -phase content pristine PVDF and TiO₂-coated PVDF fiber membranes with increasing TiO₂ thickness.

Table 2 Elemental composition of pristine PVDF and TiO₂-coated PVDF fiber membranes with increasing TiO₂ thickness

Sample ID	Element				
	C (wt%)	N (wt%)	O (wt%)	F (wt%)	Ti (wt%)
PVDF	44.0	2.2	6.1	47.7	0.0
S1-TiO ₂ /PVDF	39.1	2.2	6.8	51.8	0.1
S5-TiO ₂ /PVDF	35.6	2.2	9.8	52.1	0.3
S10-TiO ₂ /PVDF	32.7	2.4	4.5	59.8	0.5
S15-TiO ₂ /PVDF	32.0	2.4	6.6	57.9	1.1
S20-TiO ₂ /PVDF	30.8	2.4	12.5	53.1	1.2

S1-, S5-, S10-, S15-, and S20-TiO₂/PVDF, respectively, evidencing the precise controllability of the ALD process.

The chemical interaction and crystalline phase evolution were further probed by FTIR spectroscopy (Fig. 3c, d and Fig. S3, SI). Pristine PVDF exhibits the typical vibrational fingerprints of α - and β -phases, including absorption bands at 612, 763, 974 cm⁻¹ (α -phase) and 840, 1070, 1280 cm⁻¹ (β -phase).^{57–59} After TiO₂ deposition, additional absorption features appear in the low-wavenumber region (450–550 cm⁻¹), which are assigned to Ti–O and Ti–O–Ti stretching vibrations. The intensity of these bands increases progressively with TiO₂ thickness, corroborating the EDX results and confirming the formation of an inorganic oxide network on the fiber surface. In parallel, the β -phase fraction decreases modestly with thickness (from 81.0% at 0 nm to 72.1% at 20 nm) (Fig. 3e), consistent with interfacial competition between early-stage inorganic

nucleation that can locally polarize/organize near-surface PVDF segments and a thicker, mechanically rigid oxide shell that increasingly constrains segmental mobility and dipole reorientation, thereby reducing the electroactive β -phase contribution. The multimodal evidence demonstrates thickness controlled ALD TiO₂ growth on electrospun PVDF, progressing from sub-percolated early deposits (≤ 10 nm) to a continuous conformal shell (15–20 nm) without sacrificing porous fibrous scaffold. This architecture is expected to increase surface wettability and enhanced structural robustness while maintaining high accessible surface area and mass-transport pathways crucial for membrane functionality.

3.2 Working principles

Fig. 4 and Fig. S4 (SI) elucidates the operating mechanism and electrical characteristics of the TiO₂/PVDF-TENG, which functions in a contact-separation mode and delivers a DC output through Schottky junction engineering. Prior to electrical measurements, the TiO₂/PVDF-TENG was conditioned in a saturated-humidity atmosphere (100% RH) to maximize moisture uptake within the fiber membrane. With this humidity-enhanced conduction pathway, the TiO₂ semiconductor interlayer further introduces an intrinsic energy-band asymmetry at the interface, which guides carrier motion and suppresses backward charge flow during the contact-separation cycle.^{42,60}

As depicted in Fig. 4a(i), the device remains electrically neutral in the initial state, with no contact and no net potential difference across the Al/TiO₂/PVDF/Cu interface. Once mechanical contact is established (Fig. 4a(ii)), triboelectrifica-

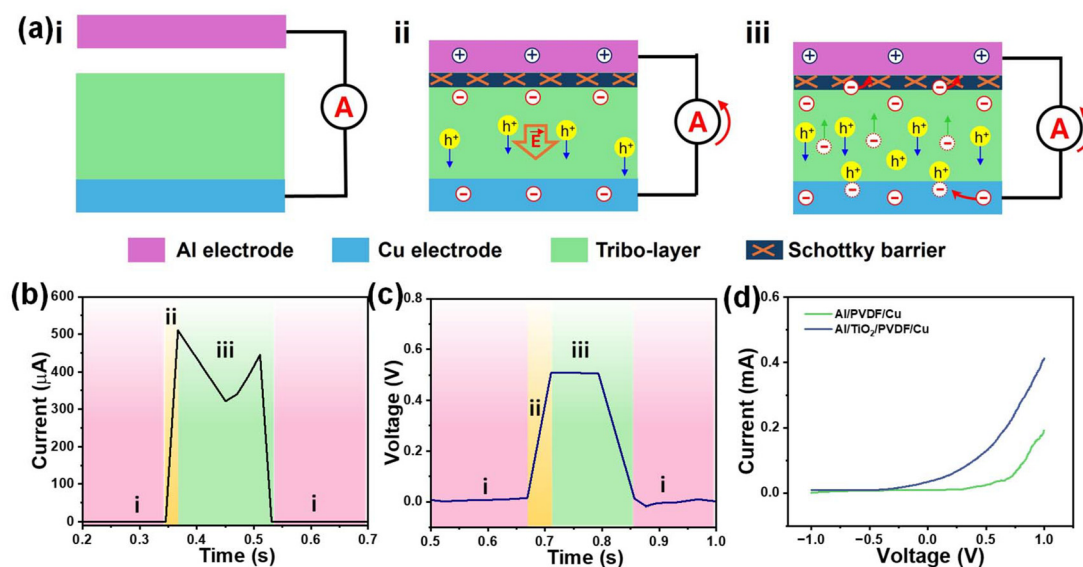


Fig. 4 (a) Working principle of the TiO₂/PVDF-TENG, (b) current and (c) voltage cycle of TiO₂/PVDF-TENG, (d) *I*-*V* characteristic curves of PVDF and TiO₂/PVDF membrane with Al-Cu electrode.

tion occurs due to differences in electron affinity and work function between Al and the TiO₂/PVDF membrane. Surface charge transfer generates negatively charged species on one side and positive charges on the other, creating a strong interfacial electrostatic field. Simultaneously, the Al/TiO₂ interface forms a Schottky junction owing to the mismatch in work function between the metal and the semiconductor TiO₂. This results in band bending within the semiconductor and the formation of a depletion region adjacent to the interface. The built-in electric field established across this region restricts carrier back-diffusion and imposes asymmetric carrier transport conditions. Unlike conventional dielectric-based TENGs, where charge flow is governed solely by electrostatic induction, the present system couples triboelectric potential with semiconductor junction physics.^{17,21,61} Under increased mechanical compression (Fig. 4a(iii)), the triboelectric potential effectively modulates the Schottky barrier height and narrows the depletion width. When the electrostatic excitation energy exceeds the interfacial barrier, electrons are driven across the junction toward the Al electrode, while holes drift toward the Cu electrode.^{62,63} The built-in electric field ensures preferential carrier flow in one direction, thereby converting the transient triboelectric potential into a continuous unidirectional current. This interfacial barrier modulation mechanism is consistent with reported DC-TENG architectures that exploit metal-semiconductor contacts to achieve intrinsic rectification. An equivalent circuit model of the TiO₂/PVDF-TENG is provided in Fig. S5, SI.

The time-dependent current and voltage responses (Fig. 4b and c) further validate this mechanism. During the contact stage (ii), a rapid increase in current and voltage corresponds to the formation of tribo-induced potential and initial carrier injection. In stage (iii), a stable current and voltage are

observed, indicating sustained carrier transport across the Schottky barrier under maintained external force. Upon release (stage i), the current rapidly decays to zero, completing a single operational cycle.

The interfacial rectifying effect is quantitatively evidenced by the *I*-*V* characteristics shown in Fig. 4d. Both Al/PVDF/Cu and Al/TiO₂/PVDF/Cu devices exhibit nonlinear and asymmetric *I*-*V* curves, indicative of Schottky-type contacts by using thermionic emission theory for metal-semiconductor junctions.^{64,65} For a Schottky diode under forward bias, the current density *J* is governed by:

$$J = J_s \left[\exp\left(\frac{qV}{nkT}\right) - 1 \right] \quad (1)$$

where *J_s* is the saturation current density, *q* is the elementary charge, *V* is the applied voltage, *n* is the ideality factor, *k* is Boltzmann's constant, *T* is absolute temperature.

The saturation current density is defined as:

$$J_s = A^* T^2 \exp\left(-\frac{q\Phi_B}{kT}\right) \quad (2)$$

where *A*^{*} is the Richardson constant and Φ_B is the Schottky barrier height.

From the semi-logarithmic forward-bias region of the *I*-*V* curve, the ideality factor can be extracted from the slope:

$$n = \frac{q}{kT} \left(\frac{dV}{d(\ln I)} \right) \quad (3)$$

A lower *J_s* and higher Φ_B correspond to stronger rectifying behavior and reduced reverse leakage current. The experimentally observed enhancement in rectification ratio from 18.6 (Al/PVDF/Cu) to 45.6 (Al/TiO₂/PVDF/Cu) indicates a sub-

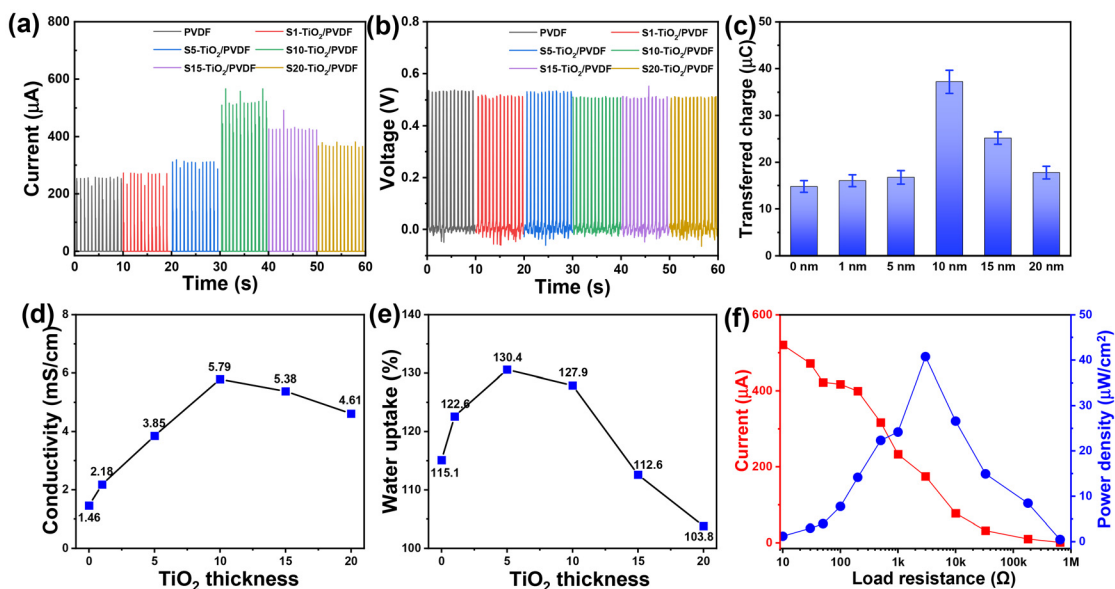


Fig. 5 (a) Current, (b) voltage and (c) transfer charge of different TiO₂/PVDF-TENG; (d) conductivity and (e) water uptake of TiO₂/PVDF-TENG with the varying TiO₂ thicknesses; (f) current and power density under external load resistance of the S10-TiO₂/PVDF-TENG.

stantial reduction in reverse saturation current and an increase in effective barrier height after TiO₂ incorporation.

The rectification ratio (RR) calculated with the range of -1 V to 1 V is expressed by:

$$RR = \frac{|I(1\text{ V})|}{|I(-1\text{ V})|} \quad (4)$$

The 2.5-fold increase in rectification ratio indicates significantly enhanced transport asymmetry, confirming the formation of a stronger Schottky barrier at the Al/TiO₂ interface. This result confirms the Schottky-regulated asymmetric carrier transport in the TiO₂/PVDF-TENG.

3.3 Electrical performance

Fig. 5 comprehensively summarizes the thickness-dependent electrical performance of the TiO₂/PVDF-TENG and reveals a clear relationship between TiO₂ thickness and device output. As shown in Fig. 5a and b, the output voltage remains relatively stable at approximately 0.52 V regardless of TiO₂ thickness, indicating that the overall triboelectric potential difference between the electrodes is largely preserved. In contrast, the output current exhibits a pronounced thickness dependence. The peak current increases from 251 μA for pristine PVDF to a maximum of 521 μA at 10 nm TiO₂, corresponding to a 108% enhancement, and subsequently decreases as the TiO₂ thickness increases to 15 and 20 nm. This trend is consistent with the transferred charge behavior (Fig. 5c), where the maximum charge increases significantly from 14.8 μC for PVDF-TENG to 37.2 μC for S10-TiO₂/PVDF-TENG, followed by a decline at higher thicknesses. These results confirm that 10 nm represents an optimal TiO₂ thickness for maximizing charge generation and transport.

The observed enhancement can be attributed to the synergistic effect of Schottky junction formation and interfacial polarization. At low TiO₂ thicknesses, the oxide layer is not sufficiently continuous to fully regulate the metal-semiconductor interface, resulting in limited improvement in charge extraction. With increasing thickness up to 10 nm, the TiO₂ layer becomes more effective in establishing an interfacial semiconductor pathway with the Al electrode. This strengthens Schottky-type transport asymmetry, enhances interfacial dipole polarization, and provides additional charge-trapping sites.^{42,66} These effects promote carrier separation and directional charge extraction during contact-separation cycles, leading to the maximum current and transferred charge for the S10-TiO₂/PVDF-TENG. However, when the TiO₂ layer becomes excessively thick (≥ 15 nm), the oxide layer introduces a larger transport resistance across the Al/TiO₂/PVDF interface. The thicker TiO₂ shell increases the carrier transport distance and reduces the efficiency of electron exchange between the triboelectric interface and the electrode. Consequently, the current output decreases at larger TiO₂ thicknesses despite the relatively stable voltage.

Fig. 5d and e further elucidate the underlying factors governing this behavior. The conductivity increases markedly from 1.46 mS cm^{-1} for PVDF membrane to 5.79 mS cm^{-1} for S10-TiO₂/PVDF membrane, before decreasing at higher thicknesses. Similarly, water uptake initially increases due to the hydrophilic nature of TiO₂ and surface hydroxyl groups, reaching 130.4% at 5 nm and remaining high at 10 nm. Moisture adsorption enhances dielectric polarization and surface charge stabilization, contributing to improved triboelectric performance. These results indicate that moderate TiO₂ coating improves conductivity and moisture-assisted charge transport, whereas excessive coating increases transport resis-

tance and limits moisture diffusion, leading to reduced output.

Fig. 5f demonstrates the load-dependent output characteristics of the optimized S10-TiO₂/PVDF-TENG. As load resistance increases from 10 Ω to 650 k Ω , the output current decreases from 521 μ A to 1.3 μ A. The TENG power density (P) was calculated using the following equation:

$$P = \frac{I^2 R}{A} \quad (5)$$

where I is output current across the load resistance R and A is contact area (1.5×1.5 cm²). The power density initially increases, reaching a maximum power density of 40.7 μ W cm⁻² at a load resistance of 3 k Ω , then subsequently declines at higher load resistances. A comparative analysis with previously reported Schottky junction-driven DC-TENG systems (Table 3) further highlights the advantages of the TiO₂/PVDF architecture developed in this work. While earlier devices based on PVDF-PAN and PPy-TiO₂ systems exhibited relatively

low power densities and cellulose-based structures achieved 6.6 μ W cm⁻², the present TiO₂/PVDF-TENG delivers a substantially higher power density of 40.7 μ W cm⁻². Even compared with advanced semiconductor-integrated, the current device demonstrates superior output performance. Beyond performance metrics, the use of scalable electrospinning and low-temperature ALD processes, together with inexpensive and abundant electrode materials (Cu and Al), provides a cost-effective and manufacturable route toward high-performance DC-TENGs.

Regarding energy harvesting applications, Fig. 6 demonstrates the scalability, energy storage capability, and operational stability of the optimized S10-TiO₂/PVDF-TENG. As shown in Fig. 6a, the output voltage increases linearly with the number of cells connected in series, rising from 0.52 V for a single cell to 0.91 V for two cells and reaching 1.74 V for four cells. This nearly proportional voltage scaling confirms effective series integration without significant internal loss, reflecting stable DC output behavior and low interfacial resistance. The ability to enhance voltage through simple series connection highlights the modular and scalable nature of the device architecture. The capacitor charging characteristics (Fig. 6b and c) further demonstrate direct DC energy storage capability without the need for an external rectifier. For a single cell, capacitors of 220 μ F, 470 μ F, and 1000 μ F exhibit rapid voltage increases followed by saturation behavior. Smaller capacitances reach saturation more quickly due to reduced charging time. For instance, the 220 μ F capacitor reaches 0.48 V within 20 s, whereas the 1000 μ F capacitor requires approximately 50 s. When four cells are connected in series, the charging rate and final voltage increase significantly; notably, a 1000 μ F capacitor attains 1.4 V within 150 s.

Table 3 Literature comparison of Schottky junction-driven DC-TENG system

Electrode	Material	Voltage (V)	Current (μ A)	Power density (μ W cm ⁻²)	Ref.
Al-Au	PVDF-PANI	3.2	15	0.003	8
Al-Au	PPy-TiO ₂	0.84	570	6.2	67
Al-Cu	Cellulose	0.5	2720	6.6	21
Al-Al	MoS ₂ , N-Si	5.1	112	13	68
Cu-Al	PVDF-TiO ₂ , SiO ₂	1.79	720	27.3	42
Cu-Al	TiO ₂ /PVDF	0.52	522	40.7	This work

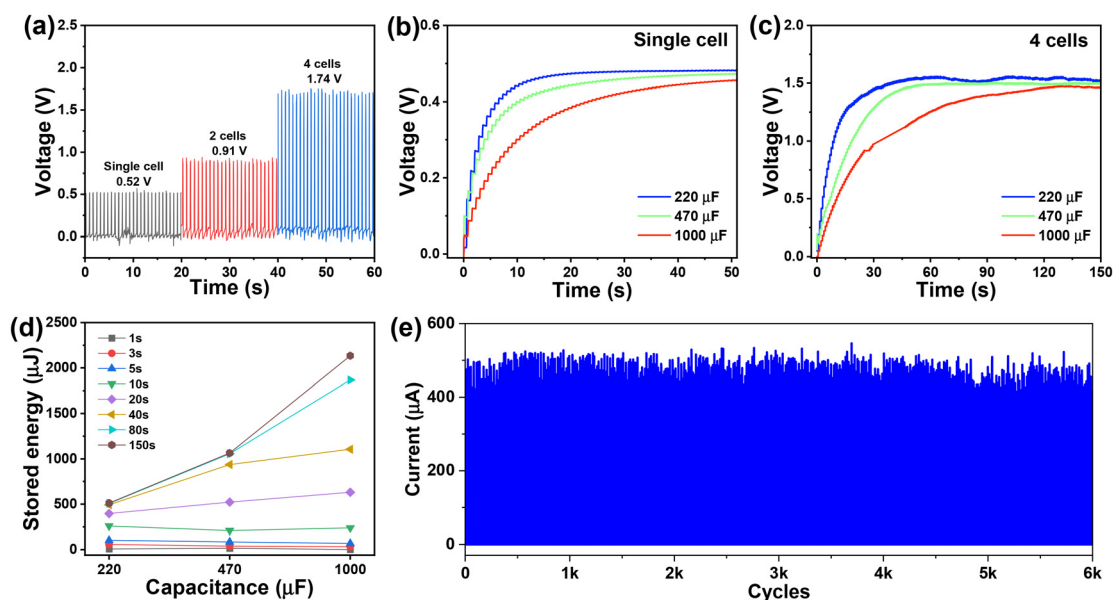


Fig. 6 (a) Output voltage of S10-TiO₂/PVDF-TENG when connected individually and in series; charged power curves of (b) a single TENG cell and (c) four TENG cells connected in series for various capacitors; (d) energy stored in different capacitors as function of the capacitance for various charging durations; (e) stability of S10-TiO₂/PVDF-TENG over 6000 cycles.

These results demonstrate the direct capacitor-charging capability of the S10-TiO₂/PVDF-TENG.

Moreover, Fig. 6d quantitatively presents the stored energy (E) as a function of capacitance and charging duration, calculated using:

$$E = \frac{1}{2}CV^2 \quad (6)$$

The stored energy increases with both charging time and capacitance, reaching approximately 2100 μ J for a 1000 μ F capacitor after 150 s. This energy level is sufficient to power small electronic components such as sensors or low-power wireless modules, demonstrating practical applicability. Furthermore, the long-term stability and mechanical robustness in high humidity of the S10-TiO₂/PVDF-TENG were assessed, as shown in Fig. 6e. The device exhibited excellent durability, maintaining stable performance over 6000 operational cycles. Only minor fluctuations under 3% were detected, likely due to gradual mechanical wear and slight variations in hydration within the ionic network. The absence of performance decay under high humidity indicates robust interfacial bonding and stable Schottky junction characteristics, even in moisture-rich environments. This resilience is particularly important for real-world mechanical energy harvesting applications where environmental stability is critical.

Fig. 7 demonstrates the humidity-dependent electrical response of the optimized S10-TiO₂/PVDF-TENG, highlighting its strong potential as a self-powered humidity sensor. As

shown in Fig. 7a, the output current exhibits a pronounced dependence on relative humidity (RH). At low humidity (33% RH), the device generates only a weak current (14 μ A), whereas the current increases progressively with increasing RH, reaching 522 μ A at 100% RH. The distinct and stable current levels under each humidity condition indicate high sensitivity and good signal resolution across a wide RH range (33–100%). This behavior can be attributed to the intrinsically hydrophilic nature of the TiO₂ layer, which promotes efficient adsorption of water molecules through surface hydroxyl groups. Moreover, the porous electrospun fibrous architecture of the TiO₂/PVDF membrane significantly enlarges the effective surface area and facilitates moisture diffusion throughout the network, thereby further enhancing water uptake capability. The synergistic effect of strong hydrophilicity and high porosity intensifies surface charge trapping and proton conduction under elevated humidity conditions.

The quantitative relationship between current and RH is summarized in Fig. 7b. A linear fitting yields:

$$I = 7.8 \times RH - 297.9 \text{ (}\mu\text{A)} \quad (7)$$

with a correlation coefficient $R^2 = 0.907$, confirming a strong linear dependence between output current and humidity level. The sensitivity of 7.8 μ A per % RH indicates that small variations in ambient humidity produce measurable and proportional current changes, which is essential for practical humidity monitoring applications.

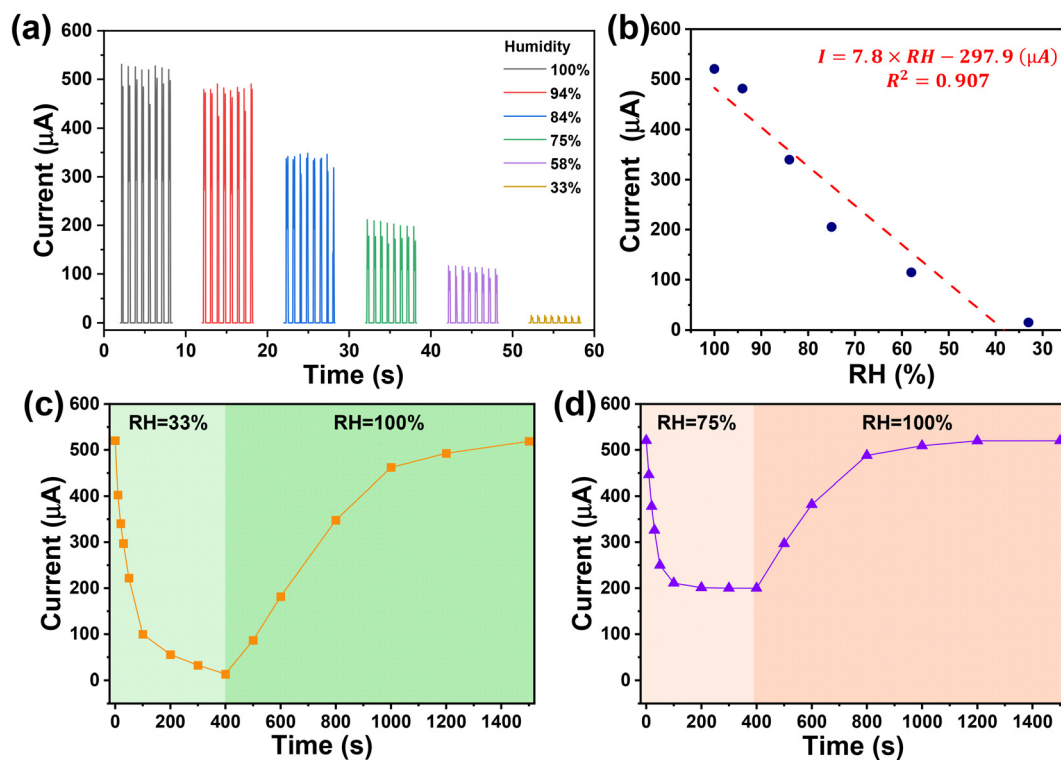


Fig. 7 (a) Relative humidity-dependent current output and (b) linear fitting characteristics of S10-TiO₂/PVDF-TENG measured under different RH levels ranging from 33% to 100%, dynamic response and recovery behavior during switching between (c) 33–100% RH and (d) 75–100% RH.

The dynamic response and recovery characteristics are presented in Fig. 7c and d. When the humidity is abruptly switched from 33% RH to 100% RH, the current initially decreases due to transient adsorption kinetics and surface equilibration, followed by a rapid increase as moisture adsorption stabilizes and interfacial polarization is enhanced. The current recovers to around 520 μA within several hundred seconds, demonstrating effective response behavior and reversible humidity sensing capability. This reversible switching confirms that the sensing mechanism is governed primarily by physical adsorption and interfacial charge modulation rather than irreversible chemical reactions. Fig. 7d further illustrates the repeatability and stability of the device under alternating humidity conditions (75% RH $\leftrightarrow$ 100% RH). The output current shows reproducible transitions between distinct levels (200 μA at 75% RH and 520 μA at 100% RH). Importantly, the S10-TiO₂/PVDF-TENG operates without any external power supply or rectifying circuit, directly converting mechanical stimuli into a humidity-dependent DC signal. This self-powered sensing capability, combined with high sensitivity, linear response, wide detection range, and good stability, demonstrates that the Schottky-engineered TiO₂/PVDF architecture is not only effective for energy harvesting but also highly promising for humidity self-powered sensing systems.

4. Conclusions

In summary, we have developed a conformal TiO₂/PVDF-TENG through spatial atomic layer deposition-enabled interfacial engineering. By optimizing the TiO₂ thickness to 10 nm, the device achieves a peak current of 521 μA and a maximum power density of 40.7 $\mu\text{W cm}^{-2}$, reflecting enhanced interfacial polarization and efficient carrier transport across the metal-semiconductor junction. The intrinsic DC output enables direct capacitor charging without the need for external rectification circuits, storing up to 2100 μJ of energy. The optimized S10-TiO₂/PVDF-TENG maintains stable performance over 6000 contact-separation cycles at 100% relative humidity, demonstrating robust interfacial integrity and environmental resilience. Furthermore, the device exhibits a linear humidity-dependent current response, enabling reliable self-powered humidity sensing. Overall, this work establishes nanoscale Schottky interface engineering as an effective route to simultaneously regulate charge generation, carrier dynamics, and multifunctional performance. This work demonstrates a scalable Schottky-interface engineering strategy for humidity-resilient DC energy harvesting and self-powered sensing.

Author contributions

Thi Thuong Nguyen: writing – original draft, methodology, investigation, formal analysis, data curation. Quang Tan Nguyen: writing – review & editing, methodology, formal analysis, conceptualization. Ting-Han Lin: writing – review &

editing, methodology visualization. Nguyen Xuan Duong: writing – review & editing, visualization, validation. Dinh Nam Nguyen: validation, investigation, formal analysis. Hung-Anh Tran Vu: investigation, data curation. Ming-Chung Wu: writing – review & editing, supervision. Viet Huong Nguyen: writing – review & editing, supervision, visualization. Duy Linh Vu: writing – review & editing, writing – original draft, supervision, project administration, conceptualization, methodology.

Conflicts of interest

The authors declare that they have no conflicts of interest.

Data availability

The data supporting the results of this study are included in the article. Additional raw datasets generated during this research are available from the corresponding author upon reasonable request. The data supporting this article has been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d6nr01028h>.

Acknowledgements

This research is funded by Phenikaa Innovation Foundation (Phenikaa Group) under grant no. ĐMST-2022.04.

References

- 1 B. Huang, P. Wang, L. Wang, S. Yang and D. Wu, *Nanotechnol. Rev.*, 2020, **9**, 716–735.
- 2 Q. T. Nguyen, D. L. Vu, C. D. Le and K. K. Ahn, *Sensors*, 2023, **23**, 5888.
- 3 M. Rajasekar and M. Sivakumar, *RSC Adv.*, 2025, **15**, 49600–49642.
- 4 W. G. Kim, D. W. Kim, I. W. Tcho, J. K. Kim, M. S. Kim and Y. K. Choi, *ACS Nano*, 2021, **15**, 258–287.
- 5 T. Cheng, J. Shao and Z. L. Wang, *Nat. Rev. Methods Primers*, 2023, **3**, 39.
- 6 O. Gulahmadov, L. Gahramanli, M. Muradov, N. Musayeva, S. Bellucci and C. Trapalis, *J. Polym. Res.*, 2025, **32**, 437.
- 7 H. He, J. Zhang, J. Pan, Z. Wang, M. Deng, X. Liu and F. Fu, *ACS Appl. Energy Mater.*, 2024, **7**, 2980–2988.
- 8 X. Han, J. Niu, Y. Wang, X. Jin, L. Peng, J. Chen, X. Wei, X. Liu, W. Wang, H. Wang and T. Lin, *Nano Energy*, 2022, **104**, 107956.
- 9 Y. Guo, Y. Cao, Z. Chen, R. Li, W. Gong, W. Yang, Q. Zhang and H. Wang, *Nano Energy*, 2020, **70**, 104517.
- 10 X. S. Meng, H. Y. Li, G. Zhu and Z. L. Wang, *Nano Energy*, 2015, **12**, 606–611.
- 11 T. Bhatta, P. Maharjan, H. Cho, C. Park, S. H. Yoon, S. Sharma, M. Salauddin, M. T. Rahman, S. S. Rana and J. Y. Park, *Nano Energy*, 2021, **81**, 105670.

- 12 O. Gulahmadov, L. Gahramanli, M. Muradov, N. Musayeva, S. Bellucci, N. Todorova and C. Trapalis, *RSC Adv.*, 2025, **15**, 31917–31930.
- 13 M. M. Hasan, N. S. Ety, F. Islam, S. Bhowmik, Kamaruzzaman and S. M. Sohel Rana, *RSC Adv.*, 2026, **16**, 3281–3295.
- 14 Y. Wu, X. Zhao, R. Mu, Y. Jin, G. Wei and Z. Su, *Nanoscale*, 2025, **17**, 26477–26513.
- 15 T. Kim, D. Y. Kim, J. Yun, B. Kim, S. H. Lee, D. Kim and S. Lee, *Nano Energy*, 2018, **52**, 95–104.
- 16 Y. Du, S. Fu, C. Shan, H. Wu, W. He, J. Wang, H. Guo, G. Li, Z. Wang and C. Hu, *Adv. Funct. Mater.*, 2022, **32**, 1–9.
- 17 Z. Zhang, D. Jiang, J. Zhao, G. Liu, T. Bu, C. Zhang and Z. L. Wang, *Adv. Energy Mater.*, 2020, **10**, 1903713.
- 18 X. Xu, J. Li, X. Tao, Q. Yan, H. Wu, Z. Guan, L. Liu, X. Chen and W. Ou-Yang, *Nano Energy*, 2022, **94**, 106957.
- 19 K. Wang, Z. Qiu, J. Wang, Y. Liu, R. Chen, H. An, J. H. Park, C. H. Suk, C. Wu, J. Lin and T. W. Kim, *Nano Energy*, 2022, **93**, 106880.
- 20 K. S. Moreira, D. Lermen, L. P. dos Santos, F. Galembeck and T. A. L. Burgo, *Energy Environ. Sci.*, 2021, **14**, 353–358.
- 21 Q. T. Nguyen, V. T. Tran, D. L. Vu, C. D. Le, W. M. Choi and K. K. Ahn, *Nano Energy*, 2024, **132**, 110353.
- 22 D. Linh, Q. Tan, P. Seung and K. Kwan, *J. Alloys Compd.*, 2024, **1004**, 175778.
- 23 S. Lao, Z. Duan, Q. Zhao, Z. Yuan, Y. Jiang and H. Tai, *Nanoscale*, 2025, **17**, 23763–23787.
- 24 Y. Huang, H. Cheng, C. Yang, H. Yao, C. Li and L. Qu, *Energy Environ. Sci.*, 2019, **12**, 1848–1856.
- 25 Z. Yan, N. Li, Q. Chang, C. Xue, J. Yang and S. Hu, *Chem. Eng. J.*, 2023, **467**, 143443.
- 26 K. Liu, P. Yang, S. Li, J. Li, T. Ding, G. Xue, Q. Chen, G. Feng and J. Zhou, *Angew. Chem., Int. Ed.*, 2016, **55**, 8003–8007.
- 27 X. Liu, H. Gao, L. Sun and J. Yao, *Adv. Mater.*, 2024, **36**, 2300748.
- 28 N. Li, Y. Tian, J. Zhang, Z. Sun, J. Zhao, J. Zhang and W. Zuo, *J. Membr. Sci.*, 2017, **528**, 359–368.
- 29 C. Boo, J. Lee and M. Elimelech, *Environ. Sci. Technol.*, 2016, **50**, 12275–12282.
- 30 I. Vázquez-Fernández, A. Bouzina, M. Raghibi, L. Timperman, J. Bigarré and M. Anouti, *J. Mater. Sci.*, 2020, **55**, 16697–16717.
- 31 A. Mondal, M. Faraz and N. Khare, *Appl. Phys. Lett.*, 2024, **124**, 103901.
- 32 D. T. K. Ong, J. S. C. Koay, M. T. Sim, K. C. Aw, T. Nakajima, B. Chen, S. T. Tan and W. C. Gan, *Nano Energy*, 2023, **113**, 108555.
- 33 M. D. F. Rabbi, J. H. Ahn, D. L. Vu and K. K. Ahn, *Adv. Mater.*, 2026, **n/a**, e22834.
- 34 M. F. Rabbi, D. L. Vu and K. K. Ahn, *J. Alloys Compd.*, 2025, **1038**, 182531.
- 35 X. Liu, Y. Shang, J. Zhang and C. Zhang, *ACS Appl. Mater. Interfaces*, 2021, **13**, 14334–14341.
- 36 A. Sabu, P. U, M. B. Nair, D. K. Shukla, R. Patel, P. K. Annamalai, A. Malakar, S. Bose and R. Brahmadesam Thoopul Srinivasa Raghava, *Nanoscale*, 2025, **17**, 23296–23314.
- 37 V. Singh, S. Rana, R. Bokolia, A. K. Panwar, R. Meena and B. Singh, *J. Alloys Compd.*, 2024, **978**, 173416.
- 38 D. L. Vu, C. D. Le, Q. T. Nguyen and K. K. Ahn, *Int. J. Energy Res.*, 2023, **2023**, 1–11.
- 39 D. N. Nguyen, T.-H. Lin, H. T. V. Nguyen, M.-C. Wu, N. X. Duong and D. L. Vu, *J. Taiwan Inst. Chem. Eng.*, 2026, **189**, 106869.
- 40 P. C. Lee, Y. L. Hsiao, J. Dutta, R. C. Wang, S. W. Tseng and C. P. Liu, *Nano Energy*, 2021, **82**, 105702.
- 41 S. B. K. Aydin, D. E. Yildiz, H. K. Çavuş and R. Şahingöz, *Bull. Mater. Sci.*, 2014, **37**, 1563–1568.
- 42 D. L. Vu, P. T. Lan, T. T. Nguyen, H. A. T. Vu, Q. T. Nguyen, V. H. Nguyen, S. G. Yoon and N. Van Hieu, *Small*, 2026, 1–13.
- 43 O. Gulahmadov, M. B. Muradov, H. Mamedov and J. Kim, *MRS Commun.*, 2024, **14**, 114–120.
- 44 S. Sardana, P. Mahajan, A. Mishra and A. Mahajan, *J. Phys. D: Appl. Phys.*, 2024, **57**, 125502.
- 45 C. Du, Z. Wang, G. Liu, W. Wang and D. Yu, *Colloids Surf., A*, 2021, **624**, 126790.
- 46 W. C. Tsen, *Polym. Eng. Sci.*, 2020, **60**, 1832–1841.
- 47 W.-H. Kim, H. Kim and H.-B.-R. Lee, *J. Coat. Technol. Res.*, 2017, **14**, 177–183.
- 48 O. Gulahmadov, L. Gahramanli, M. Muradov, H. Mamedov, A. Musayev, C. V. Gomez and S. Bellucci, *J. Ovonic Res.*, 2024, **20**, 831–839.
- 49 E. Dikicioğlu, M. B. Balı, S. Sağlam, H. Berberoğlu, I. Pavlov, A. Goodarzi and E. Orhan, *ACS Omega*, 2024, **9**, 21346–21352.
- 50 B. Padha, Z. Ahmed, S. Dutta, A. Pandey, N. Padha, M. Tomar, A. Sharma, I. Yadav and S. Arya.
- 51 C. Sun, J. Zhang, Y. Zhang, F. Zhao, J. Xie, Z. Liu, J. Zhuang, N. Zhang, W. Ren and Z.-G. Ye, *Appl. Surf. Sci.*, 2021, **562**, 150126.
- 52 P. Poodt, A. Lankhorst, F. Roozeboom, K. Spee, D. Maas and A. Vermeer, *Adv. Mater.*, 2010, **22**, 3564–3567.
- 53 J. Lee, J.-H. Noh, J.-T. Kim, D. Lee, J. H. Choi, J.-M. Lee, J.-H. Ahn, T. J. Park and W.-H. Kim, *ACS Appl. Mater. Interfaces*, 2025, **17**, 38608–38618.
- 54 M. Aghaee, P. S. Maydannik, P. Johansson, J. Kuusipalo, M. Creatore, T. Homola and D. C. Cameron, *J. Vac. Sci. Technol., A*, 2015, **33**, 41512.
- 55 G. Ma, Z. Wang, Y. Gao, Z. Li, X. Jiang, Y. Wen, B. Shan, F. Yang and R. Chen, *Chem. Eng. J.*, 2025, **517**, 164236.
- 56 P. Poodt, D. C. Cameron, E. Dickey, S. M. George, V. Kuznetsov, G. N. Parsons, F. Roozeboom, G. Sundaram and A. Vermeer, *J. Vac. Sci. Technol., A*, 2011, **30**, 10802.
- 57 Z. Q. Dong, X. H. Ma, Z. L. Xu and Z. Y. Gu, *RSC Adv.*, 2015, **5**, 67962–67970.
- 58 Z. Li, J. Wang, S. Liu and J. Li, *Appl. Water Sci.*, 2024, **14**, 1–12.
- 59 J. Li, S. Guo, Z. Xu, J. Li, Z. Pan, Z. Du and F. Cheng, *J. Membr. Sci.*, 2019, **574**, 349–357.

- 60 D. Linh, Q. Tan, T. Van Tam, W. Mook and K. Kwan, *Nano Energy*, 2025, **143**, 111322.
- 61 J. T. Dickinson, E. E. Donaldson and M. K. Park, *J. Mater. Sci.*, 1981, **16**, 2897–2908.
- 62 Y. Zhang, Y. Liu and Z. L. Wang, *Adv. Mater.*, 2011, **23**, 3004–3013.
- 63 G. Hu, W. Guo, R. Yu, X. Yang, R. Zhou, C. Pan and Z. L. Wang, *Nano Energy*, 2016, **23**, 27–33.
- 64 C. Wu, *J. Appl. Phys.*, 1982, **53**, 5947–5950.
- 65 B. M. Omer and A. Merazga, *AIP Adv.*, 2021, **11**, 25140.
- 66 H. Shao, J. Fang, H. Wang, L. Dai and T. Lin, *Adv. Mater.*, 2016, **28**, 1461–1466.
- 67 X. Ding, H. Shao, H. Wang, W. Yang, J. Fang, D. Zhang and T. Lin, *Nano Energy*, 2021, **89**, 106367.
- 68 Y. Lu, Z. Hao, S. Feng, R. Shen, Y. Yan and S. Lin, *iScience*, 2019, **22**, 58–69.