Electronic Supplementary Information (ESI)

ZnO Nanoparticle Confined Stress Amplified All-Fiber Piezoelectric Nanogenerator for Self-powered Healthcare Monitoring

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Text S1:

In the finite element method, we solved the following linear mechanical equation S11 that links the stress T to the applied force F on the BPNG and the Poisson equation S12 that links the electric displacement D to the fixed charge density ρ_V,

$$-\nabla . T = F \,, \tag{S11}$$

$$\nabla . D = \rho_V \,, \tag{S12}$$

The coupling between the structural and electrical domains can be expressed in the form of a connection between the material stress and its permittivity at constant stress or as a coupling between the material strain and its permittivity at constant strain. The equations (S11, S12) are coupled to the piezoelectric equations of strain-charge form (S13, S14) and stress-charge form (S15, S16) that correlate the stress T tensor, strain S, electric displacement D and the electric field E using the permittivity ε , elasticity tensor c and piezoelectric coupling tensor e and d.

Strain-Charge form:

The strain-charge form of a piezoelectric material is written as,

$$S = s_E . T + d^T . E \,, \tag{S13}$$

$$D = d . T + \varepsilon_0 . \varepsilon_{rT} E \,, \tag{S14}$$

The material parameters s_E, d, and ε_{rT} correspond to the material compliance, coupling properties, and relative permittivity at constant stress. ε_0 is the permittivity of free space.

Stress-Charge form:

The stress-charge form of the piezoelectric material is written as,

$$T = c_E . S + e^T . E, \quad \text{(S15)}$$

$$D = e . S + \varepsilon_0 . \varepsilon_{rS} . E, \quad \text{(S16)}$$

The material parameters c_E, e, and ε_{rS} correspond to the material stiffness, coupling properties, and relative permittivity at constant strain.

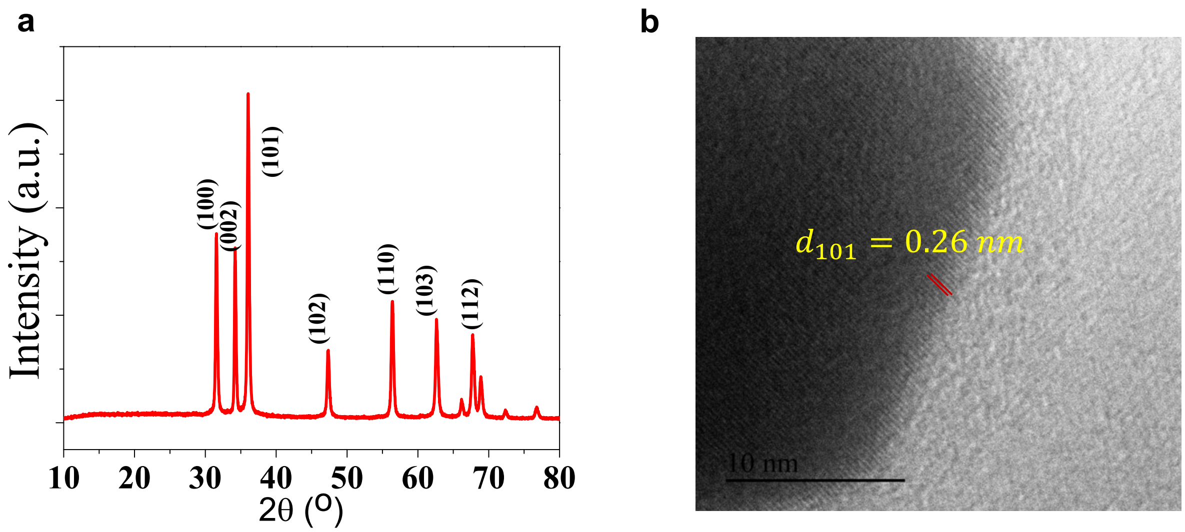

Fig. S1 (a) XRD pattern of the ZnO nanorod powder. (b) HR-TEM image (scale bar~ 10 nm) of a single ZnO nanorod with marked d-spacing of 0.26 nm.

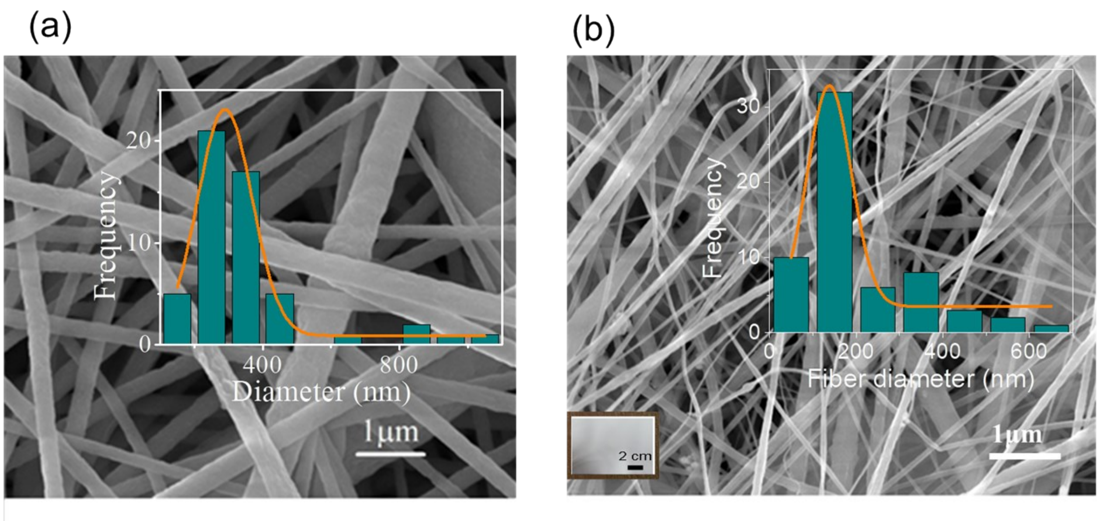

Fig. S2 FE-SEM images of elctrospun nanofibers mat of (a) neat PVDF and (b) PVDF-ZnO composite nanofibers with histogram plot (Gaussian fit) of nanofiber diameter distribution in the inset.

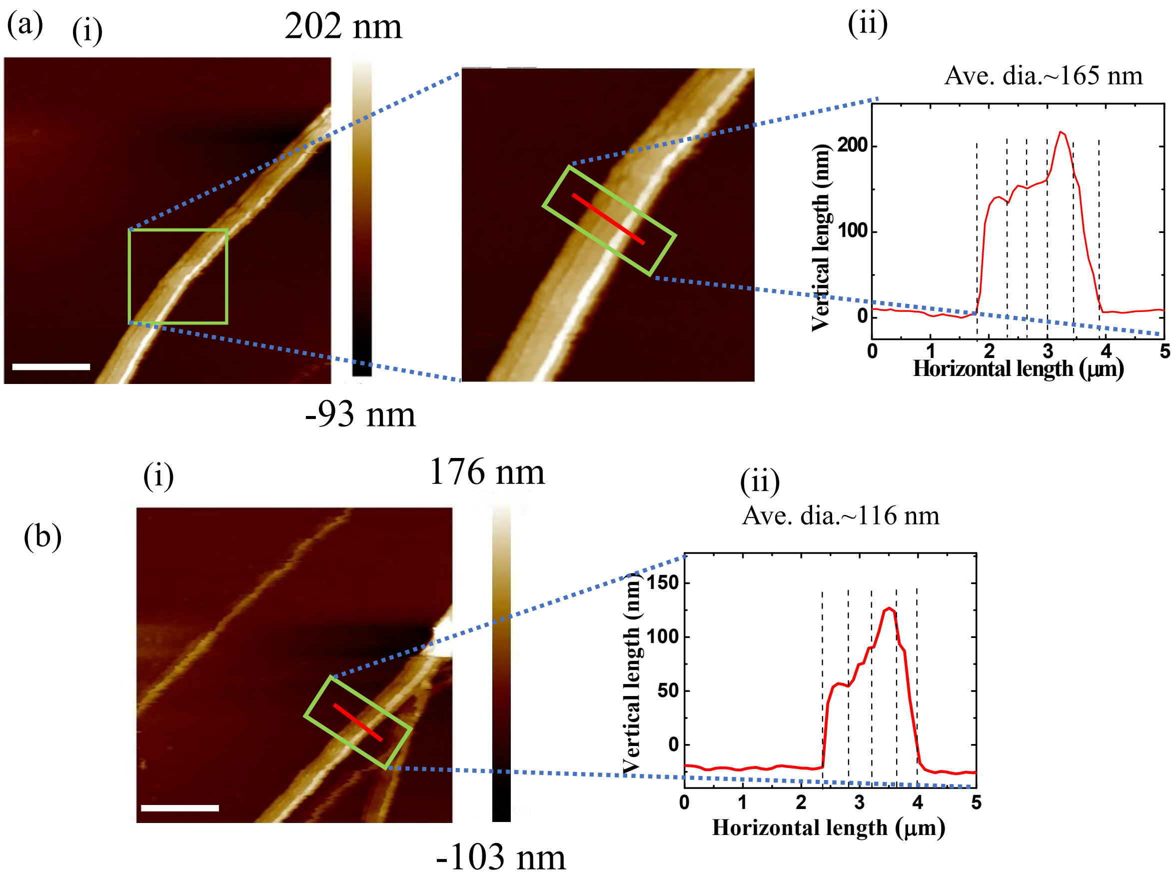

Fig. S3 (a) (i) Topography image (scan area: 20 μm × 20 μm) and the corresponding enlarged view of the nanofiber used in the PFM study and (ii) line profile of the nanofiber (marked in blue colour line) showing the height difference between the substrate and the fiber at several places are less than 200 nm. The dotted lines are indicating the fibers are placed side-wise and thus also indicating the average fiber diameter is ~ 165 nm (b) (i) Topography image (scan area: 20 μm × 20 μm) of another nanofiber on the substrate and (ii) height profile of the line scan on the blue colour region again showing fiber diameter less than 200 nm and average diameter is ~ 116 nm. (All the scale bars: 5 μm).

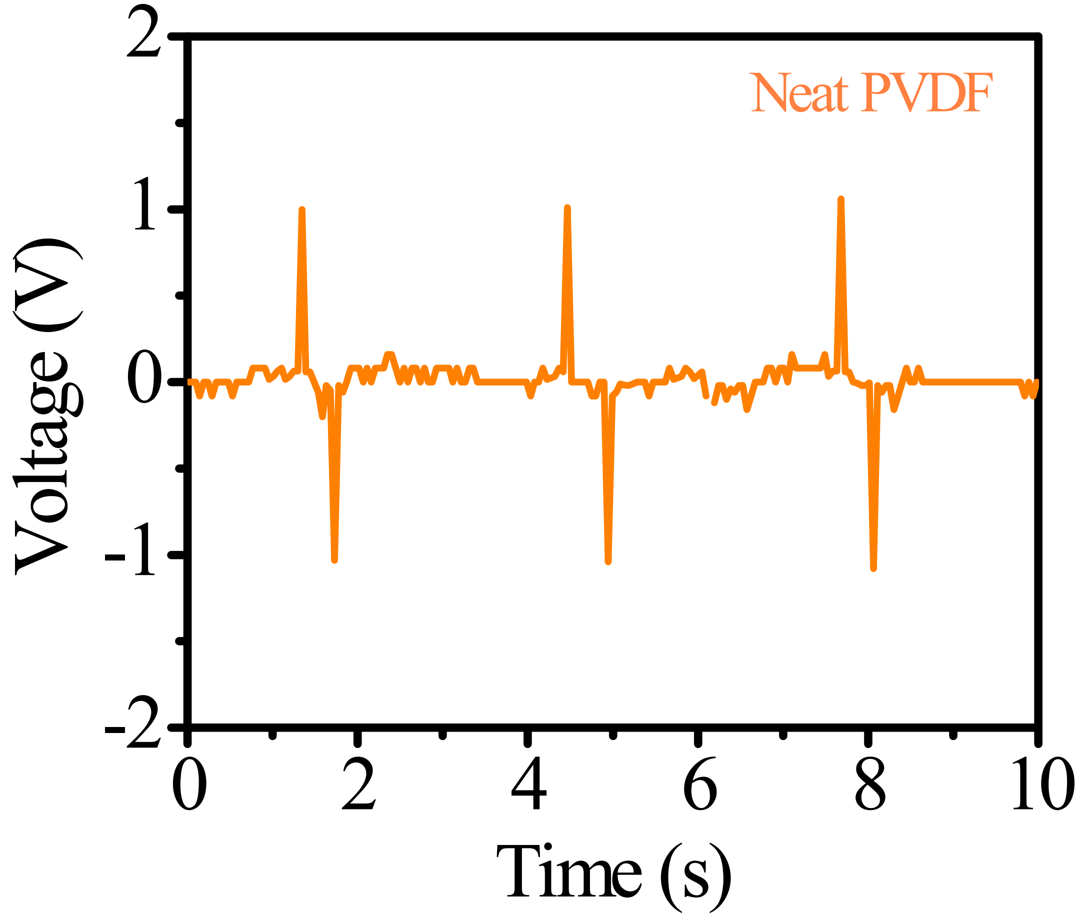

Fig. S4 Output open circuit voltage (V_{oc}) of neat PVDF nanofiber based all-fiber nanogenerator under 18 kPa of pressure amplitude.

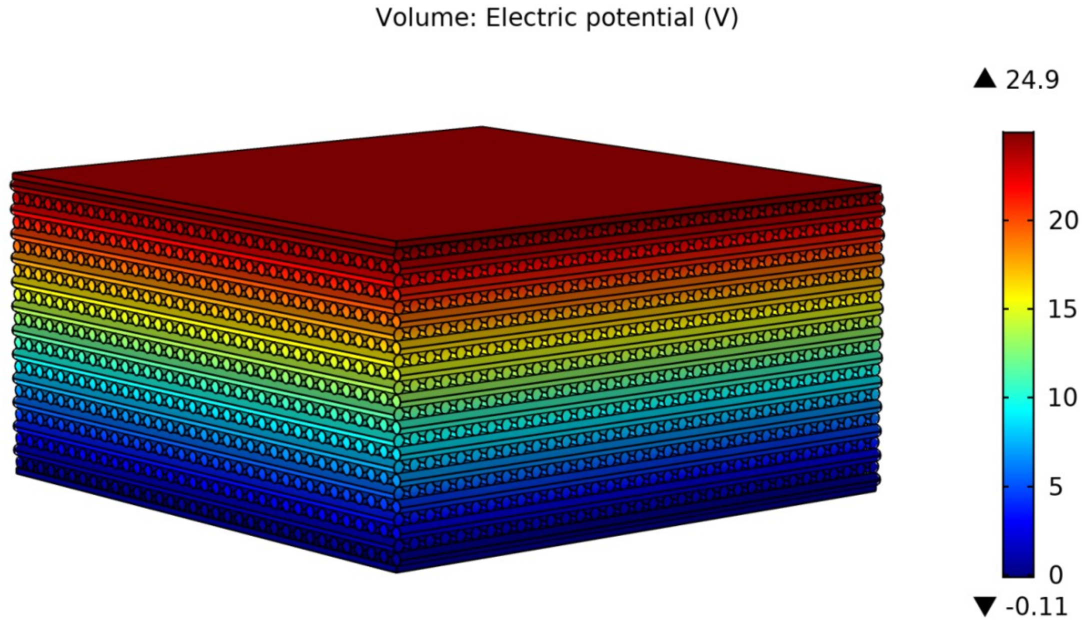

Fig. S5. Theoretically simulated output voltage under the pressure of 18 kPa using COMSOL multiphysics software. Details of the simulation is provided in ref. 29.

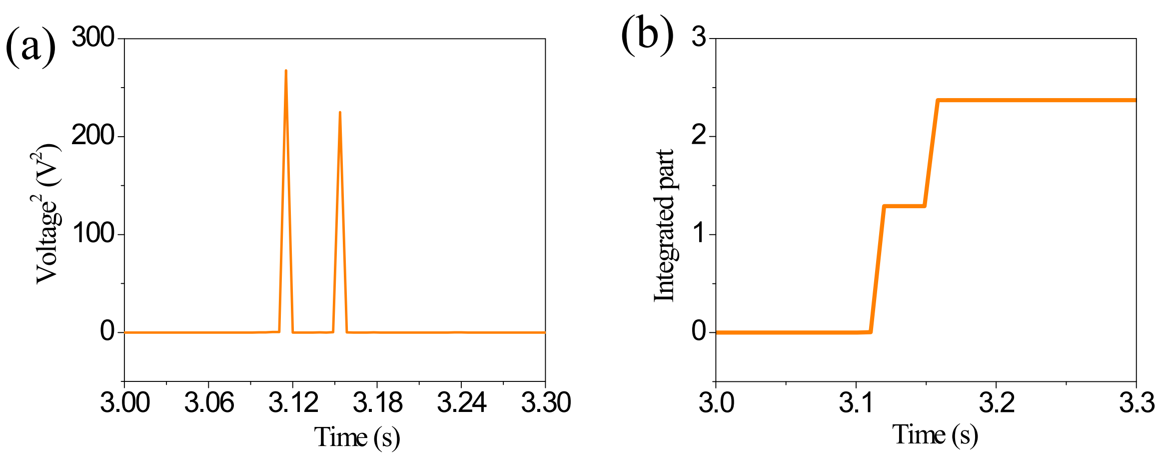

Fig. S6 (a) The square of the measured rectified output voltage at an external load of 10 MΩ for the integration to obtain the instantaneous electric power output. (b) The integration part of the time dependent V_{oc}.

Table S1 Mechano-sensitivity of reported piezoelectric based pressure sensors.

Material	Sensitivity (V/kPa)	Reference
Piezoelectric fiber array vertically integrated P(VDF-TrFE)	0.027	1
P(VDF-TrFE)/CMOS transistor	0.011	2
P(VDF-TrFE) film	2.2×10^{-5}	3
Carbonized electrospun polyacrylonitrile/barium titanate (PAN-C/BTO) nanofiber film	0.324	4
Aligned P(VDF-TrFE)/MWCNT composites	0.121	5
Cellular fluorocarbon	1.54	6
P(VDF-TrFE) thin film	7.5×10^{-4}	7
Eletrospun PVDF fabric	8.2×10^{-4}	8
P(VDF-TrFE) nanotube	0.05	9
Electrospun	0.017	10

PVDF/$BaTiO_3$ nanowire (NW) nanocomposite fibers		
Laterally aligned PZT angle-crystal nanowires	0.14	11
PVDF-MWCNT-OMMT	0.0176	12
PVDF-ZnO nanofibers	0.00312	13
PVDF-ZnO NPs nanofibers	*1.0*	*This work*

Table S2 A piezoelectric nanogenerator related data for comparison of device active materials, electrode materials, output performance. (¥NM: Not Mentioned).

Electrospun fiber	Electrode	Voltage/Current	Power	Ref.
PVDF	Cu foil	76 mV and 39 nA	577.6 pW/cm^2	14
PVDF/$NaNbO_3$	Ag coated fabric	3.4 V, 4.4 µA	¥NM	15
ZnO/PVDF	Ag conductive fabric	8.36 V, 0.17 µA	77.69 nWcm^{-2}	16
PVDF/$CH_3NH_3PbI_3$	Ni- Cu coated fabrics	2 V/50 nA	0.8 mW/m^2	17
PVDF	PEDOT	1 V, 0.15 mA	52 µWcm^{-3}	18
$BaTiO_3$/PZT/CNT/PVDF	carbon filled polyethylene	6V/ 4 nA	NM	19
PVDF-TrFE	conductive thread	16.2 mV	NM	20
PVDF	conductive nanofiber membrane (PVP, PEDOT:PSS, ethyl alcohol, ethylene glycol and	8 V/3.76 µA	NM	21

	ionic liquid)			
PVDF-MoS_2		12 V, 12nA	0.01 μW/cm^2	22
Random PVDF	Al foil	2.21 V/ 4 μA	0.16 mW/cm^3	23
PVDF/graphene oxide	Cu−Ni plated fine knit polyester fabric	7 V	0.62 μW/cm^2	24
PVDF-ZnO nonorods	Copper foil	85 V/2.2 μA	NM	25
PVDF-ZnO NPs nanofibers	*Ni- Cu coated fabrics*	*18 V*	*26.7 μW/cm^2*	*This work*

Table S3 A piezoelectric nanogenerator related data for comparison of previously reported PVDF/ZnO composites. (¥NM: Not Mentioned).

Material	d_{33}	Voltage/Current	Power	References
PVDF-ZnO nanorod	¥NM	8.36V/139.36nA	77.69 nW/cm^2	Polymers 2018, 10, 745
PVDF-ZnO nanorod	NM	~356mV/456 nA	NM	RSC Adv., 2019, 9, 10117–10123
Cowpea-structured PVDF/ZnO nanofibers	NM	~10 V/500 nA	NM	Nano Energy, 55, 2019, 516-525
PVDF-ZnO nanorods	NM	1.12 V/ 1.6 l μA	0.2 l μW cm^{-2}	J Mater Sci 54, 2754–2762 (2019)
PVDF-ZnO nanowires	NM	2.5 V/0,1 μA	NM	Phys. Chem. Chem. Phys., 2014, 16, 5475—5479
PVDF-ZnO nanowires	NM	480 mV	NM	Mater. Res. Express 5 (2018) 035057
PVDF-ZnO nanorods	14.91±4.39 pm/V	NM	NM	2018 IEEE 18th International Conference on Nanotechnology (IEEE-NANO), Materials Science, DOI:10.1109/NANO.2018.8626362
PVDF-ZnO	-1.17	1.81 V/0.57μA	0.21 μW/cm^2	Polym Adv Technol. 2017;1–8.

nanorods	pC/N			
PVDF-ZnO NWs	NM	2.4 V/152.2 µA	NM	Nanomater Nanotechnol, 2014, 4:24
PVDF-BaTiO3_ZnO	NM	12 V	NM	Polymer Testing, 79, 2019, 106001
PVDF-ZnO NPs composites nanofibers	*−32 pm/V*	*18 V*	*26.7 $\mu W.cm^{-2}$*	*This work*

Table S4 A summary or comparison of device materials, electrode materials, and capacitor charging performances of the A-PNG with the reported nanogenerators.

Active material	**Electrode**	**Charging time(s), Capacitor value (µF)**	**Saturation voltage (V), Power stored (µW)**	**References**
P(VDF-TrFE)/$BaTiO_3$	conductive fabric	250, 0.068	35, 0.17	26
aligned PVDF NFs	(PANI-PVDF) NFs mats	60, 1.0	4, 1.3	27
P(VDF-TrFE)	Al foils	1800, 47	16, 3.34	28
Pt-PVDF	Cu–Ni polyester fabric	80, 1	3, 0.06	29
PZT-NH_2 NPs	Al-coated (PI)/PET)	100, 2.2	4, 0.18	30
Hybridization sugar-encapsulated PVDF	Conducting textile	100, 1	8, 0.32	31
PVDF/ $BaTiO_3$	Al foils	76, 1	1.40, 0.01	32
(P(VDF-TrFE))/ $BaTiO_3$	ITO-coated PET	120, 4.7	1.5, 0.04	33
Poly(vinyl alcohol)	Ni–Cu	40, 1	0.72, 0.007	34

(PVA)/ ZnS nanorods	polyester fabric,			
PVDF/ ZnS nanorods	Ni–Cu polyester fabric	130, 2.2	10, 0.85	35
PVDF-niobate-based	AgNW	300, 2.2	5, 0.09	36
[P(VDF-TrFE)]	3D PMMA/Au	5, 0.1	3.2, 0.01	37
Ce^{3+}/ PVDF/Graphene	Ni-Cu plated polyester fabric	60, 4.7	0.75, 0.02	38
PVDF-ZnO *NPs nanofibers*	Ni–Cu polyester fabric	65, 2.2	4.7, 0.37	This work

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