Supplementary Information

Flexographic printed microwave-assisted grown zinc oxide nanostructures for sensing applications

Maria Morais,^a Emanuel Carlos,^{a,*} Ana Rovisco,^a Tomás Calmeiro,^a Hugo Gamboa,^b Elvira Fortunato,^a Rodrigo Martins^a and Pedro Barquinha^{a,*}

^a CENIMAT|i3N, Department of Materials Science, School of Science and Technology, NOVA University Lisbon and CEMOP/UNINOVA, Caparica, Portugal

^b LIBPhys (Laboratory for Instrumentation, Biomedical Engineering and Radiation Physics), NOVA School of Science and Technology, Campus de Caparica, 2829-516, Portugal

*e.carlos@fct.unl.pt; **pmcb@fct.unl.pt

The supplementary information contains relevant data concerning the equipments used to produce the pressure sensors and characterizations of the seed layers and zinc oxide (ZnO) nanorod samples resulting from different synthesis conditions. Table S1 compares the production process and performance of the developed sensors with that of previously reported ZnO-based pressure sensors. The lab-scale flexographic printing equipment and stamps used to pattern the seed layers on PET-ITO substrates are presented in Figure S1. Figure S2 shows the 2D atomic force microscopy (AFM) images of the seed layers with different zinc acetate dihydrate concentrations (0.25, 0.50 and 1 M). Figure S3 exhibits non-patterned seed layers produced by depositing solutions with varying zinc acetate concentrations on PET-ITO substrates. Table S2 lists the length, diameter and density of nanorod arrays synthesized with different conditions. Crosssectional SEM images of a 1 M zinc-based seed layer deposited on a PET-ITO substrate and the ZnO nanorods grown from this layer are presented in Figure S4. The diffractograms of the seed layers with different zinc acetate dihydrate concentrations, namely 0.25, 0.50 and 1 M, are presented in Figure S5. The SEM images of the nanostructures produced from 1 M seed layers, annealed at 140 °C, using growth solutions with different molar ratios of zinc nitrate hexahydrate and hexamethylenetetramine (HMTA) are shown in Figure S6. The response of sensors based on ZnO nanorods grown from 1 M seed layers using 25 mM zinc nitrate hexahydrate and HMTA growth solutions is presented in Figure S7. The sensitivity values of the sensors based on ZnO nanorods grown from seed layers composed of 1 square and 16 squares are presented in Table **S3.** Figure S8 presents the output voltage of a patterned sensor over 5000 impact cycles.

S1. Production process and performance of ZnO-based pressure sensors reported in the literature

Table S1. Production process and performance of pressure sensors based on ZnO nanostructures reported in the literature.

ZnO morphology	Seed layer	Growth method	Substrate	Working range	Ref
• 8/	Dip-coating (90 °C, 20 min)	Hydrothermal synthesis (24 h, 85 °C)	PET-ITO (60 Ω/sq)	GF ~ 160	
2D ZnO sheets	Solution: 0.5 mM potassium permanganate	Growth solution: 7.5 mM ZN, 3.75 mM HMTA, 0.10 M NH ₃ , 2 mM PEI, 0.5 mM KCl and 7.5 mM MEA	Top electrode: PET-ITO $A = (50 \times 15)$ mm^2	(curvatures between 30 and 90°)	1
2D ZnO nanosheets	Dip-coating (100 °C, 10 min) Solution: 0.9 mM ZAc, 30 mM NaOH (methanol)	Hydrothermal synthesis (8 h, 80 °C) Growth solution: 0.02 M ZN and	Anodic aluminum oxide <i>Top electrode:</i> Gold	S = 0.0318 V/kPa 29.4 N $\rightarrow 5.9 V$	2
ZnO nanowires	-	HMTA Chemical vapor deposition (900 °C, 1h) Precursors: Graphite	$A = 1 \text{ cm}^{2}$ PET-ITO (60 Ω/sq) Top electrode: Gold	S = 0.18 V/kPa 45 kPa to 61 kPa \rightarrow 1.5V to 7.5V	3
ZnO film	-	and ZnO powder RF sputtering	$PET-ITO$ electrode $A = 1 \text{ cm}^2$	$P = 10 \text{ kPa} \rightarrow 37.50 \text{ V}$	4
ZnO-PTFE composites	-	Co-sputtering	$PET-ITO$ electrode $A = 1 \text{ cm}^2$	$S_1 = 75.2 \text{ V/kPa}$ (0.01–1 kPa) $S_2=12.53 \text{ V/kPa}$ (1- 10 kPa) $P = 10 \text{ kPa} \rightarrow$ 121.3 V	4
ZnO nanowires	-	Electrodeposition (80 °C, 400 rpm, -1.0 V, 2 h) Growth solution: 1 M sodium nitrate + 1 mM ZN (water) Counter electrode: Platinum-coated titanium plate	Au (50 nm)/Ti (5 nm) on nanoimprinted PMMA substrate <i>Top electrode:</i> Au (50 nm)/Ti (5 nm) A = 0.75 cm ²	Strain = $0.015 \rightarrow 1.03 \text{ V}$	5

Reference electrode: Silver/silver chloride saturated with KCl

ZnO nanowires	-	Hydrothermal synthesis (4 h, 85 °C) Growth solution: 40 mM zinc nitride and HMTA	Ni/Au (10 nm/25 nm) in p-GaN film <i>Top electrode:</i> ITO	Tensile strain = 0.79% → 9 V (bending)	6
ZnO nanorod arrays	Magnetron sputtering	Hydrothermal growth (2 h, 90 °C) Growth solution: 50 mM ZN and HMTA	ITO Top electrode: Au $A = 2.25 \text{ cm}^2$	$S= 52.9 \text{ kPa}^{-1}$ (0-100 kPa) ~ 22 kPa \rightarrow 1.031 V	7
Dispersed ZnO nanorods	Solvothermal synthesis (8 h at 150 °C) Growth solution: 0.175 M ZAc (ethylene glycol/deionized water)	Spray coating (80 °C) Solution: 10 mg/mL ZnO NPs (IPA)	PET-ITO <i>Top electrode:</i> Ag	37 Hz, acceleration of 14.715 m/s2 → 9.12 V	8
PVDF-ZnO vertically aligned structures	Spin-coating (100 °C, 1h) Solution: 0.03 M ZAc (ethanol)	Hydrothermal synthesis (3 h, 100 °C) Growth solution: 0.025 M ZN and HMTA	PET-ITO <i>Top electrode:</i> PET-ITO	12 to 14 kPa → 46.64 V	9
ZnO nanorods	Flexographic printing (140 °C, 10 min) Solution: 1M ZAc (MEP)	Hydrothermal synthesis (30 min, 100 °C) Growth solution: 0.050 M ZN and HMTA	PET-ITO Top electrode: PET-ITO $A = 4 \text{ cm}^2$	S = (0.09 ± 0.04) V/kPa	This work
ZnO nanorods	Flexographic printing (140 °C, 10 min) Solution: 1M ZAc (MEP)	Hydrothermal synthesis (30 min, 100 °C) Growth solution: 0.050 M ZN and HMTA	PET-ITO Top electrode: PET-ITO $A = (16 \times 0.25)$ cm^2	S = (0.06 ± 0.01) V/kPa	This work

ZN: zinc nitrate hexahydrate; HMTA: hexamethylenetetramine; NH₃: Ammonia; PEI: Polyethylenimine; KCI: potassium chloride; MEA:monoethanolamine; ZAc: Zinc acetate dihydrate; MEP: 1-methoxy-2-propanol

S2. Lab-scale flexographic printing equipment and stamps used to deposit the seed layers

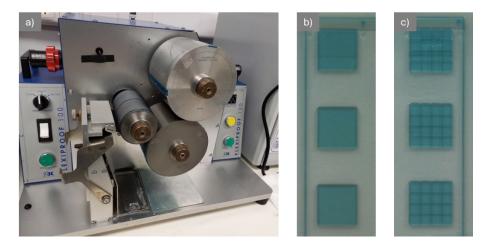


Figure S1. a) Flexographic printing equipment and (b and c) stamps used to deposit the seed layers on PET-ITO substrates. The square in b) has 4 cm² and the pattern in c) is composed of 16 squares of 0.25 cm² spaced by 0.5 μ m.

S3. AFM images of the ZnO films with different zinc precursor concentrations

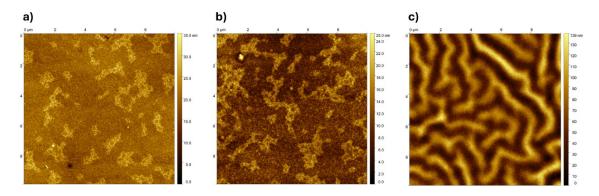


Figure S2. AFM images of the seed layers printed on PET-ITO substrates using solutions with a zinc acetate dihydrate concentration of a) 0.25, b) 0.50 and c) 1.0 M.

S4. Morphological analysis of seed layers deposited on PET-ITO substrates using solutions with different zinc precursor concentration

Concentration of zinc precursor in the seed layer solution

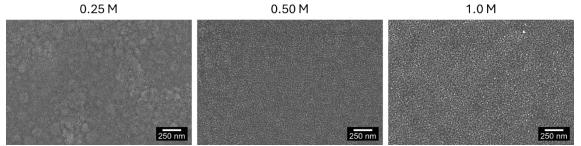


Figure S3. SEM images of the seed layers printed on PET-ITO substrates with 0.25, 0.50 and 1.0 M zinc acetate precursor solutions (non-patterned).

S5. Length, diameter and density of ZnO nanorods hydrothermally grown using different synthesis conditions

		Length (µm)	Diameter (µm)	Density (nanorods/µm²)
Seed layer	0.25 M	0.6 ± 0.1	0.18 ± 0.04	7 ± 1
	0.50 M	0.20 ± 0.04	0.0469 ± 0.005	297 ± 7
concentration	1.0 M	0.27 ± 0.04	0.05 ± 0.01	296 ± 6
	Zinc acetate 0.4 ± 0.1	0.05 ± 0.01	229 ± 2	
Zinc precursor	Zinc chloride	0.28 ± 0.04	0.046 ± 0.005	137 ± 33
	Zinc nitrate	0.27 ± 0.04	0.05 ± 0.01	296 ± 6
Precursors ratio	2:1	0.7 ± 0.2	0.27 ± 0.07	6 ± 1
(Zn:HMTA)	$1:1 0.27 \pm 0.$	0.27 ± 0.04	0.05 ± 0.01	296 ± 6
(ZII.IIWITA)	1:2	0.32 ± 0.05	0.055 ± 0.005	300 ± 25

Table S2. Average values of the ZnO nanorods' length, diameter and density according to their growth conditions.

S6. SEM-EDS analysis of 1 M zinc acetate films

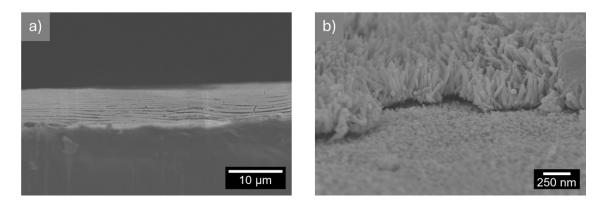


Figure S4. Cross-sectional SEM images of a) a 1 M seed layer deposited on a PET-ITO substrate and the b) ZnO nanorods grown from this layer.

S7. X-ray diffraction patterns of ZnO seed layers

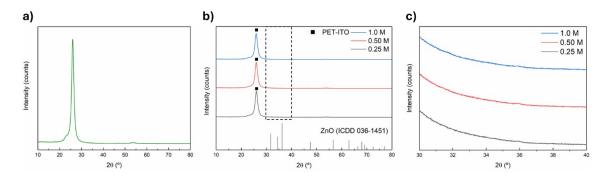


Figure S5. XRD patterns of the a) PET-ITO substrate, b) seed layers deposited on it with different zinc precursor concentrations and c) Zoom-in in the region between 30 and 40°.

S8. Morphological analysis of ZnO nanorods grown using different growth solutions

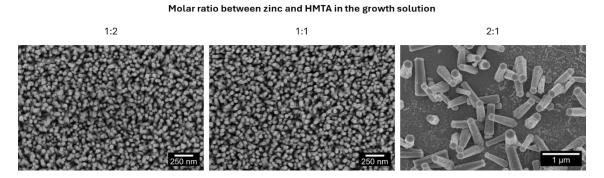


Figure S6. SEM images of ZnO nanorods grown from 1 M seed layers using growth solutions with different zinc and HMTA molar ratios.

S10

S9. Response of pressure sensors based on ZnO nanorods grown from 25 mM zinc nitrate and HMTA solution

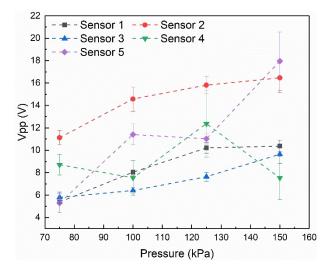


Figure S7. Peak-to-peak voltage of sensors based on nanorods grown from 1 M seed layers (single square) using 25 mM equimolar zinc nitrate hexahydrate and HMTA growth solutions.

S10. Sensitivity of the pressure sensors based ZnO nanorods with nonpatterned and patterned seed layers

Pattern		Sensitivity (V/kPa)	R ²
	Sensor 1	0.0891 ± 0.0009	0.99
1	Sensor 2	0.06 ± 0.02	0.89
1 square $(A = 4 \text{ am}^2)$	Sensor 3	0.042 ± 0.003	0.99
$(A = 4 \text{ cm}^2)$	Sensor 4	0.11 ± 0.02	0.96
	Sensor 5	0.153 ± 0.001	0.99
	Sensor 1	0.08 ± 0.01	0.96
16 squares	Sensor 2	0.038 ± 0.001	0.99
$A = 0.25 \text{ cm}^2$	Sensor 3	0.045 ± 0.004	0.99
$x = 0.25 \text{ cm}^{-}$	Sensor 4	0.06 ± 0.01	0.96
	Sensor 5	0.06 ± 0.01	0.96

Table S3. Sensitivity values of the pressure sensors with 1 and 16 squares of ZnO.

S11. Output voltage of a patterned ZnO-based sensor over time

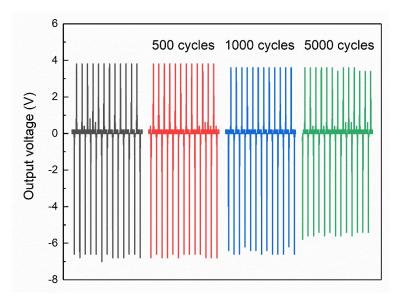


Figure S8. Output voltage of a patterned ZnO-based pressure sensor (sensor 4) for 5000 cycles.

References

- 1 G. Arrabito, A. Delisi, G. Giuliano, G. Prestopino, P. G. Medaglia, V. Ferrara, F. Arcidiacono, M. Scopelliti, D. F. Chillura Martino and B. Pignataro, Self-Cleaning Bending Sensors Based on Semitransparent ZnO Nanostructured Films, *ACS Appl. Eng. Mater.*, 2023, **1**, 1384–1396.
- 2 S. Rafique, A. K. Kasi, Aminullah, J. K. Kasi, M. Bokhari and Zafar Shakoor, Fabrication of Br doped ZnO nanosheets piezoelectric nanogenerator for pressure and position sensing applications, *Curr. Appl. Phys.*, 2021, **21**, 72–79.
- 3 M. Kumari, R. K. Prasad, M. K. Singh, P. K. Iyer and D. K. Singh, Piezo-resistive pressure sensor based on CVD-grown ZnO nanowires on Polyethylene Tetrathalate substrate, *arXiv* (Cornell Univ.
- 4 S. Ippili, V. Jella, J. M. Lee, J.-S. Jung, D.-H. Lee, T.-Y. Yang and S.-G. Yoon, ZnO– PTFE-based antimicrobial, anti-reflective display coatings and high-sensitivity touch sensors, *J. Mater. Chem. A*, 2022, **10**, 22067–22079.
- 5 H. Eom, J. Hur, S.-K. Sung, J.-H. Jeong and I. Park, Density-controlled electrochemical synthesis of ZnO nanowire arrays using nanotextured cathode, *Nanotechnology*, 2024, **35**, 185301.
- Y. Peng, M. Que, H. E. Lee, R. Bao, X. Wang, J. Lu, Z. Yuan, X. Li, J. Tao, J. Sun, J. Zhai,
 K. J. Lee and C. Pan, Achieving high-resolution pressure mapping via flexible GaN/ ZnO nanowire LEDs array by piezo-phototronic effect, *Nano Energy*, 2019, 58, 633–640.
- F. Wang, J. Jiang, Q. Liu, Y. Zhang, J. Wang, S. Wang, L. Han, H. Liu and Y. Sang, Piezopotential gated two-dimensional InSe field-effect transistor for designing a pressure sensor based on piezotronic effect, *Nano Energy*, 2020, **70**, 104457.
- 8 E. A. Elvira-Hernández, J. Romero-García, A. Ledezma-Pérez, A. L. Herrera-May, E. Hernández-Hernández, L. A. Uscanga-González, V. A. Jarvio-Cordova, G. Hurtado, C. Gallardo-Vega and A. de León, Synthesis of ZnO Nanorod Film Deposited by Spraying with Application for Flexible Piezoelectric Energy Harvesting Microdevices, *Sensors*, 2020, **20**, 6759.
- A. Anand and M. C. Bhatnagar, Role of vertically aligned and randomly placed zinc oxide (ZnO) nanorods in PVDF matrix: Used for energy harvesting, *Mater. Today Energy*, 2019, 13, 293–301.