

Supplementary Materials: Gravure Printing for PVDF Thin-Film Pyroelectric Device Manufacture

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Table S1. Raman bands assignment identified for the PVDF.

Raman Bands	Specific Vibration Assignment
485	α -CF ₂ rocking [68], γ -vibration [70]
514	β -CF ₂ bending [68,69]
605	α -CF ₂ scissoring/CCC scissoring [68–71]
799	α -CH ₂ rocking [67–71]
812	γ -CH ₂ wagging [67,70]
840	β -CH ₂ rocking/CF ₂ antisymmetric stretching [67,69,70]
881	α e β -antisymmetric stretching CC, α symmetric stretching CF ₂ ns [67,69,71]

Table S2. Results of surface tension measurements carried out on PVDF diluted in DMSO/Acetone solutions.

DMSO/Acetone (%w/w)	PVDF (wt%)	Surface Tension (mN/m)
100/0	0	44
50/50	0	29
50/50	8	29
50/50	10	29
50/50	12	28
0/100	0	25

Table S3. Preliminary printing tests results changing PVDF ink concentration, printing speed and force (ranking: ++ = Best quality/high resolution; + = Medium quality/acceptable resolution; - = Low quality/low resolution; X = Poor quality/layer defects). The printing results were the same for both Aluminum foil and PET-ITO substrates.

Ink Concentration (wt% of PVDF)	Ink Viscosity (mPa s)	Ink Surface Tension (mN/m)	Printing Speed (m/min)	Printing Force (N)	Ca	Printing Quality
15	68	27	12	300	0.5	-
				500	0.5	-
				700	0.5	-
			36	300	1.5	X
				500	1.5	X
				700	1.5	X
			60	300	2.5	X
				500	2.5	X
				700	2.5	X
12	45	28	12	300	0.3	-
				500	0.3	-
				700	0.3	-
			36	300	1.0	+
				500	1.0	+
				700	1.0	+
			60	300	1.6	-
				500	1.6	-
				700	1.6	-
10	36	29	12	300	0.2	-
				500	0.2	-
				700	0.2	-
			36	300	0.7	+
				500	0.7	++
				700	0.7	+
			60	300	1.2	-
				500	1.2	+
				700	1.2	+
8	30	29	12	300	0.2	-
				500	0.2	-
				700	0.2	-
			36	300	0.6	-
				500	0.6	+
				700	0.6	+
			60	300	1.0	-
				500	1.0	+
				700	1.0	+

Table S4. Layer characteristics of the gravure printed PVDF on Aluminum foil and PET-ITO substrates.

Printing Substrate	Number of Overlapped Printed Layers	Ink Concentration Profile	Printing Conditions (force; speed)	Printed Layer Thickness (μm)	Surface Roughness (Sq) (μm)
Aluminum foil	-	-	-	-	0.20 ± 0.02
PET-ITO	-	-	-	-	0.010 ± 0.004
Aluminum foil	1	10 wt% of PVDF	500 N; 36 m/min	0.51 ± 0.11	0.18 ± 0.05
PET-ITO	1	10 wt% of PVDF	500 N; 36 m/min	0.41 ± 0.04	0.05 ± 0.01
PET-ITO	5	Fixed (10 wt% of PVDF)	500 N; 36 m/min	1.88 ± 0.25	0.19 ± 0.07
PET-ITO	5	Decreasing (12, 11, 10, 9 and 8 wt% of PVDF)	500 N; 36 m/min	1.68 ± 0.12	0.10 ± 0.03

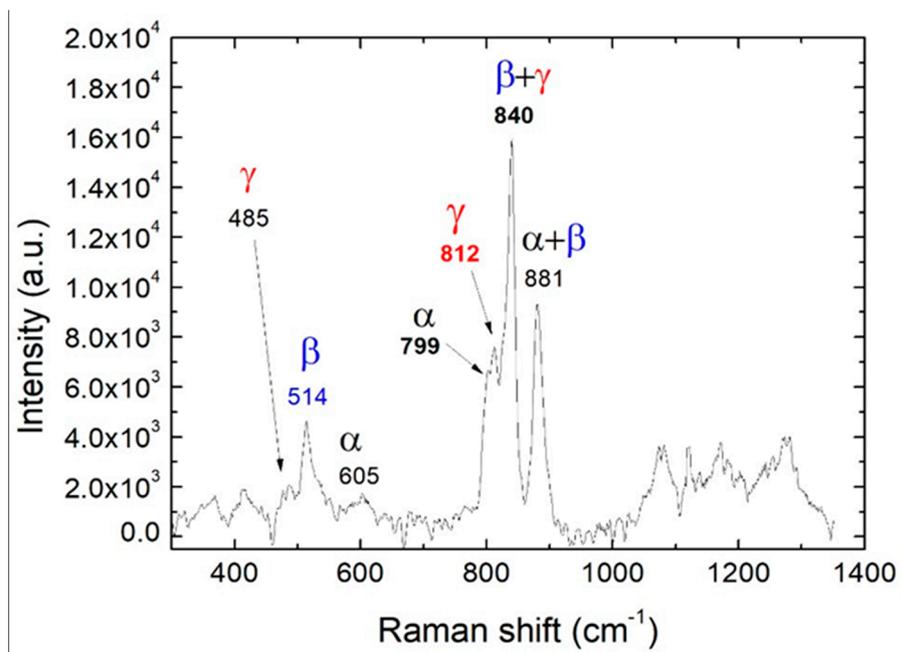


Figure S1. Typical Raman spectrum of a PVDF film deposited on Aluminum foil by wire-bar coating.

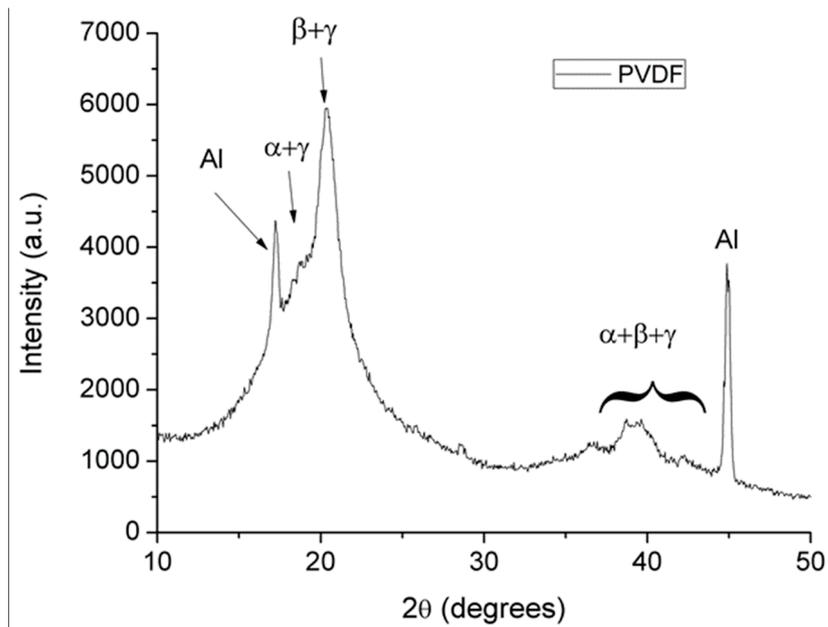


Figure S2. X-rays data of PVDF film obtained by depositing PVDF (15 wt%) dissolved in a mixture of 50/50 (%w/w) DMSO/acetone on Aluminum foil.

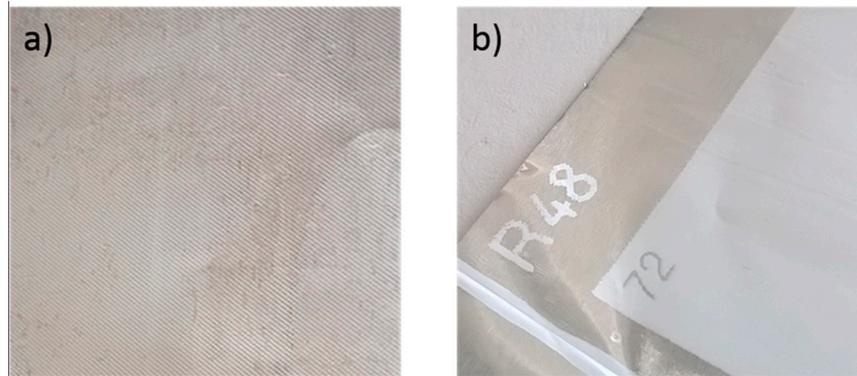


Figure S3. Examples of preliminary printing tests on Aluminum foil: defects obtained using 15 wt% PVDF ink (a); high printing quality using 10 wt% PVDF ink (b).



Figure S4. Example of gravure printed PVDF on PET-ITO substrate pre-treated by Corona at a power of 50 W.

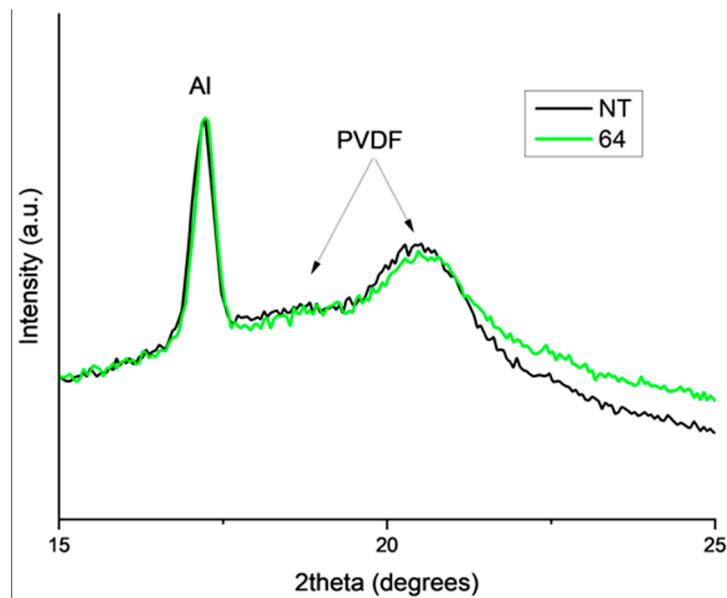


Figure S5. X-ray diffraction patterns (Cu $K\alpha$) of a gravure printed multilayer PVDF film (5 layers) on Aluminum foil: pristine (NT) and treated by corona at the nominal power of 120 W for 64 s (64).

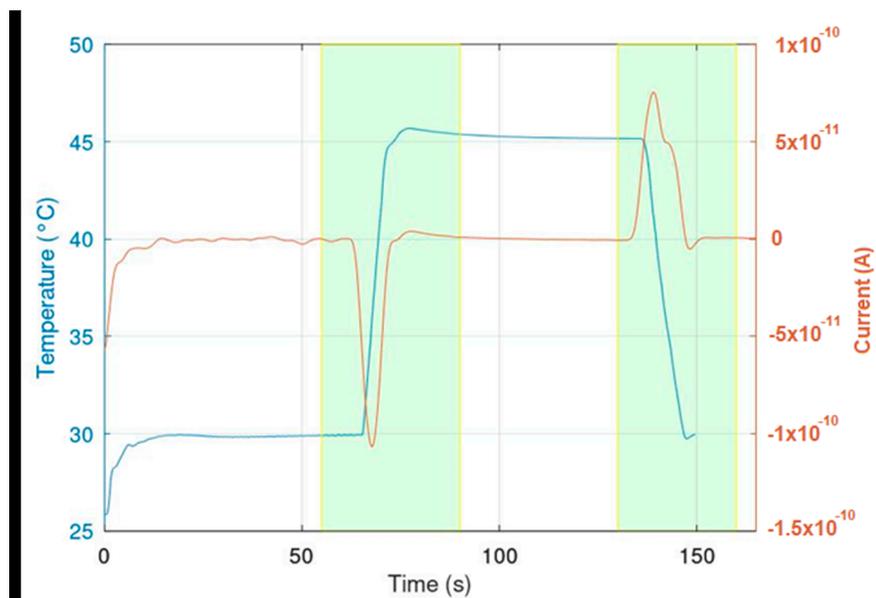


Figure S6. Temperature and electric current vs time for a multilayer PVDF device printed on a PET-ITO substrate treated by Corona at a nominal power of 120 W for 64 s.