Electronic Supporting Information for:

## "3D-Printed Poly(vinylidene fluoride) / Carbon Nanotube Composites as a Tuneable, Low-Cost Chemical Vapour Sensing Platform"

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PVDF filament thickness with MWCNT loading:



**Figure S1**: Average (n > 3) diameter of filament after extrusion at 200 °C through a 1.56 mm diameter die. PVDF-HFP exhibited a similar reduction in filament diameter as PVDF homopolymer when blended with MWCNTs; however, the swelling was suppressed to a lesser extent at each ratio.



**Figure S2:** A two-layer (10:90)-MWCNT/PVDF dogbone sensor held between two sets of tweezers demonstrating the high flexibility of the printed composite materials.



**Figure S3**: Structural characterization of (15:85)-MWCNT/PVDF 3D-printed composites using XRD as printed (room temp.), heated at 90 °C for 4 h, and 150 °C for 4 h. Reference patterns for CNTs,  $\alpha$ -PVDF, and  $\gamma$ -PVDF are provided.

<u>Further discussion of XRD results</u>: Thin-film samples are extruded and printed with exposure to high temperature for only seconds at each step. To assess this short-term exposure, denoted as the 'RT' condition, relative to a longer-term heating treatment, the printed coupon was annealed at increased temperatures for extended time periods. Heating of the sample at 90 °C for 4 h (Figure S3) did not result in noticeable PVDF phase changes. However, upon heating the sample at 150 °C for 4 h, the overall diffraction intensity of PVDF decreased relative to the CNT peak at  $2\theta = 26^{\circ}$  significantly, suggesting reduced crystallinity in the polymer.



Figure S4: Top-down HeIM image of a 3D-printed (15:85)-MWCNT/PVDF dogbone.



**Figure S5:** Results from acetone sensing over 25 exposure-vacuum cycles (2 min each) with a printed, single-layer (15:85)-MWCNT/PVDF dogbone sensor. The first and last 8 cycles are shown for clarity.

MWCNT loading (%)	R <sub>avg</sub> increase w/ acetone (%), 4 cycles	R <sub>avg</sub> decrease w/ vacuum (%), 4 cycles
5	$161.3 \pm 24.7$	139.6 ± 21.5
10	$78.5\pm9.6$	$60.3 \pm 10.3$
15	$26.0 \pm 2.8$	$19.5 \pm 1.2$

**Table S1**: Results from acetone sensing over 4 exposure-vacuum cycles as a function of MWCNT content in MWCNT/PVDF printed dogbone sensors composed of a single printed layer. (*Plotted in Figure 7 of the main text*).