Electronic Supplementary Material (ESI) for Nanoscale.

Nanostructuring mechanical cracks in a flexible conducting polymer thin film for ultra-sensitive vapor sensing

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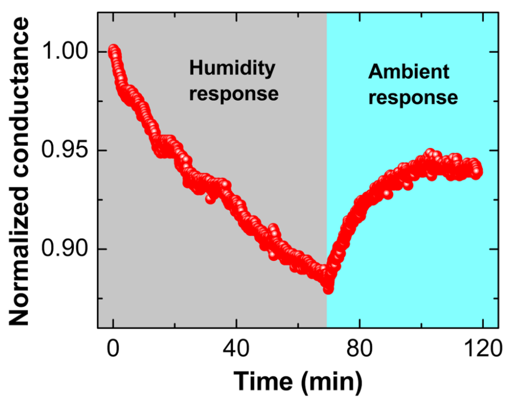

Fig. S1: Conductance change (G/G_{dry}) of pristine PEDOT:PSS thin film, first exposed to saturated humidity (100% RH) and subsequently to ambient, respectively. This figure shows the partially reversible swelling of the pristine film.

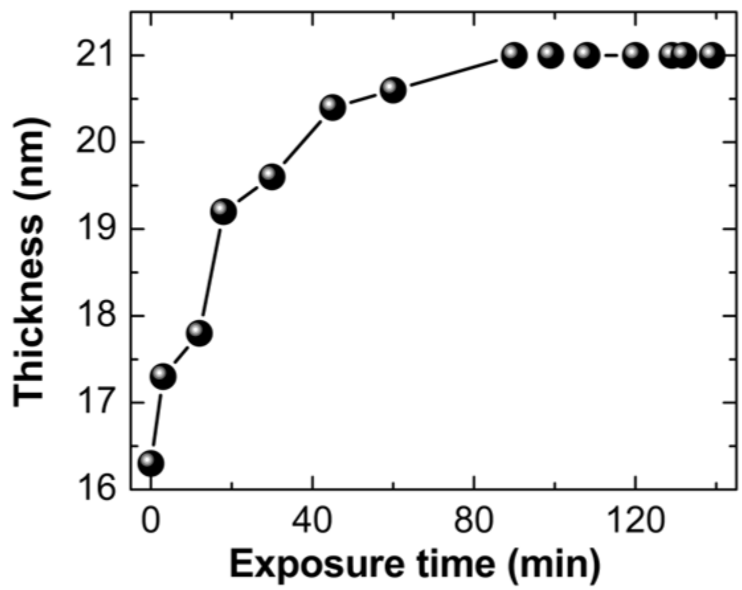

Fig. S2: Evolution of film thickness as a function of prolonged exposure time to 100% RH, obtained using X-ray reflectivity (XRR) technique.

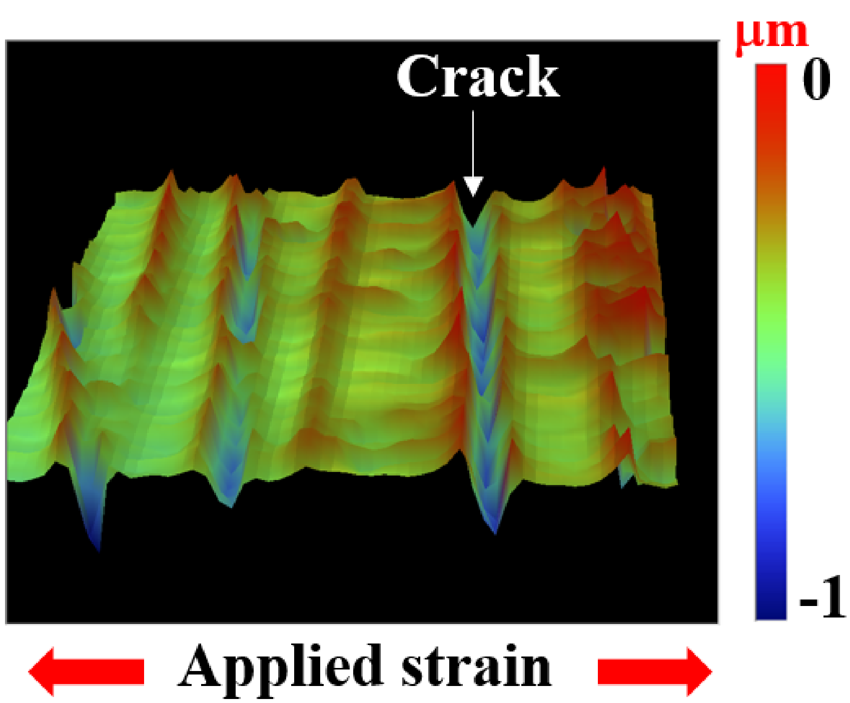

Fig. S3: A representative surface morphology of 20% strained PEDOT:PSS thin film casts on a flexible substrate PDMS obtained using three-dimensional optical profilometry.

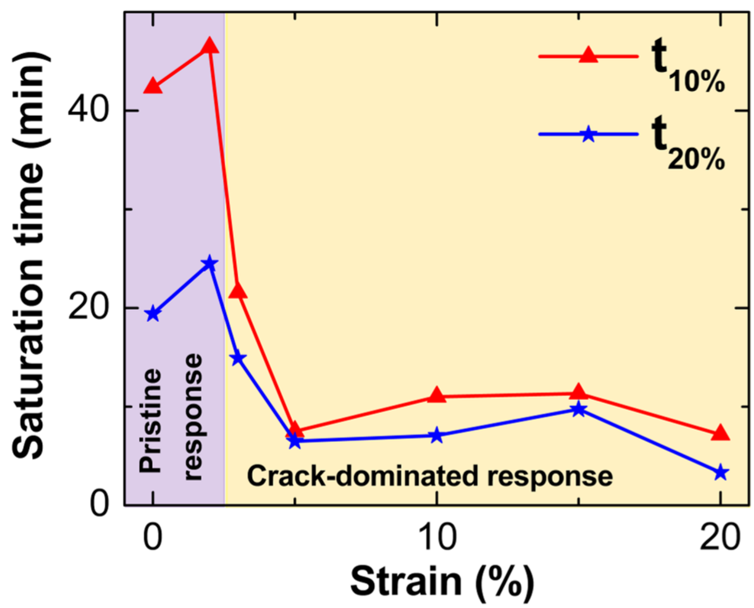

Fig. S4: Saturation time of pristine PEDOT:PSS thin film exposed to 100% RH as a function of uniaxial applied strain.

The uniaxially applied strain can be used to tune the behavior of vapor-induced electrical response, as illustrated in Fig. 1d in the main text. The saturation time denoted as $t_{10\%}$, $t_{20\%}$ are defined as 10% and 20% decrease of the final saturation value ($\sim$ 90 minutes) and a representative plot is shown in Fig. S4. This figure shows two distinct regimes such as (a) a pristine response and (b) a crack-dominated response. Therefore, we emphasize that the saturation time to humidity strongly correlates the uniaxially applied strain. The saturation time can significantly be reduced by inducing a uniaxial strain to the films. For instance, the exposure time (t_{10}%) is about 42 minutes for pristine sample whereas it is only about 7 minutes for 20% strained sample.

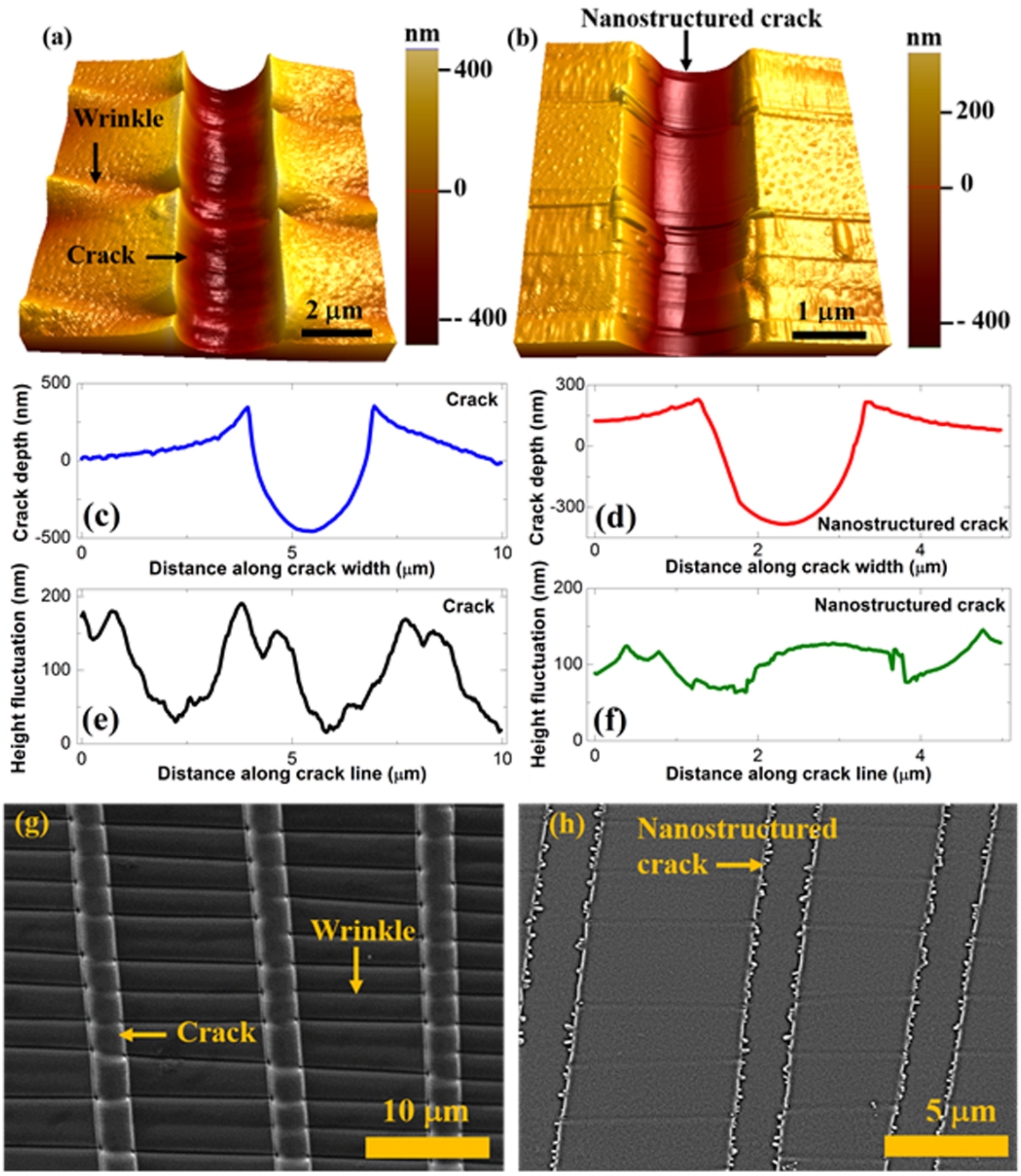

Fig. S5: (a) Three-dimensional AFM image showing morphology of the film with crack (b) Three-dimensional AFM image of the film with nanostructured crack, with the residual polymer removed (c) Plot of crack depth versus position across crack width for cracked film (d) Plot of crack depth versus position across crack width for nanostructured crack [Note that the same crack location cannot be easily identified after nanostructuring, hence a representative location is taken for this plot] (e) Plot of height fluctuations versus distance along crack line for cracked film (f) Plot of height fluctuations versus distance along crack line for nanostructured film (g) SEM image of the film morphology with cracks (h) SEM image of the film morphology with nanostructured cracks, after the removal of residual polymer.

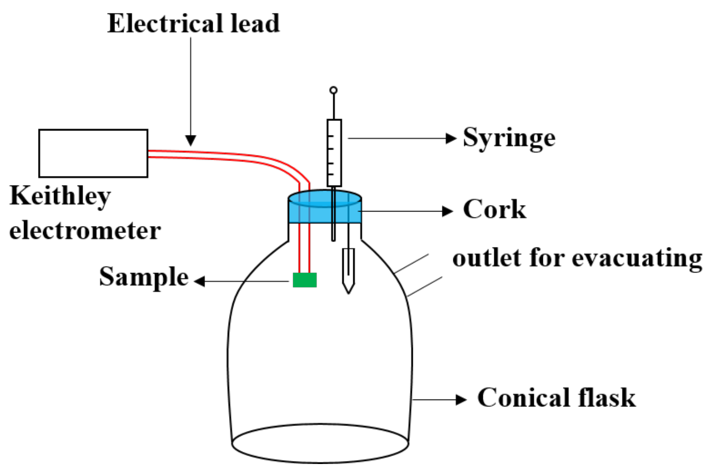

Fig. S6: Experimental set up for alcohol sensing measurement.

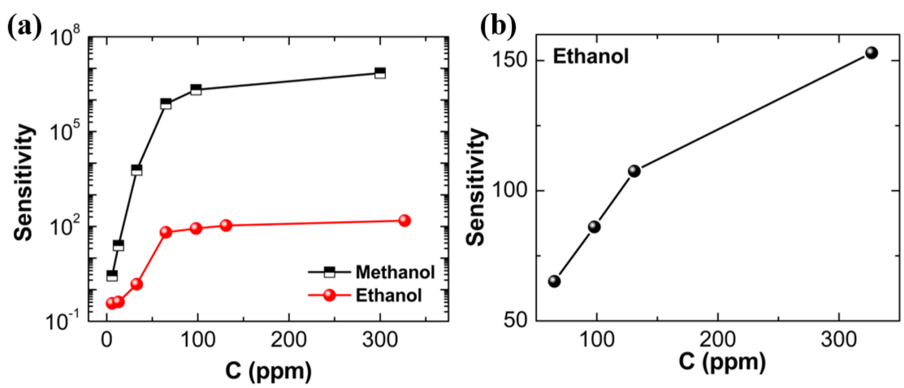

Fig. S7: (a) Sensitivity plot of nanostructured PEDOT:PSS thin film as a function of concentration of methanol and ethanol vapor in ppm unit (b) Sensitivity plot of nanostructured PEDOT:PSS thin film as a function of concentration for 65 ppm, 98 ppm, 131 ppm and 327 ppm of ethanol vapor.

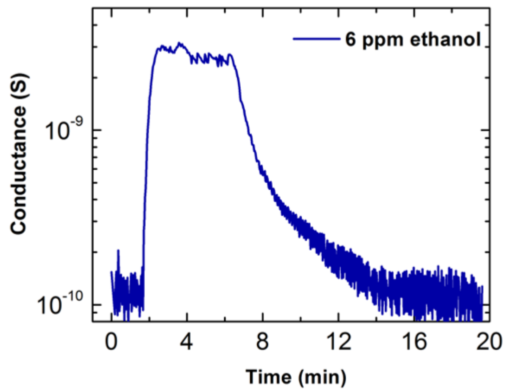

Fig. S8: Steady state response of nanostructured PEDOT:PSS thin film to ethanol vapor exposure for low concentration (6 ppm).

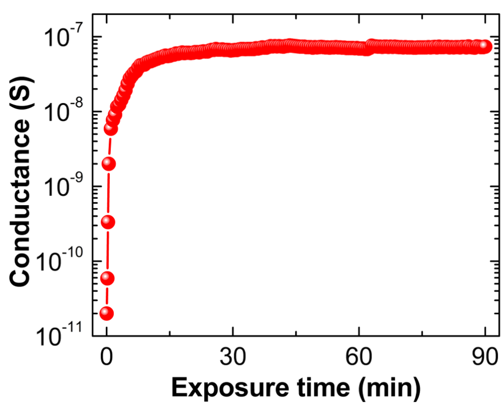

Fig. S9: Conductance of nanostructured PEDOT:PSS thin film as a function of exposure time to humidity at a fixed RH (100%).

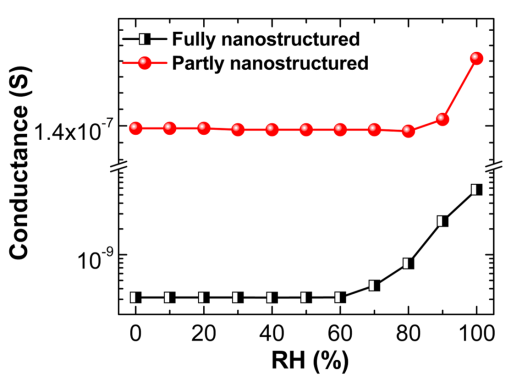

Fig. S10: Conductance as a function of RH (0% - 100%) for partly and fully nanostructured PEDOT:PSS thin film.

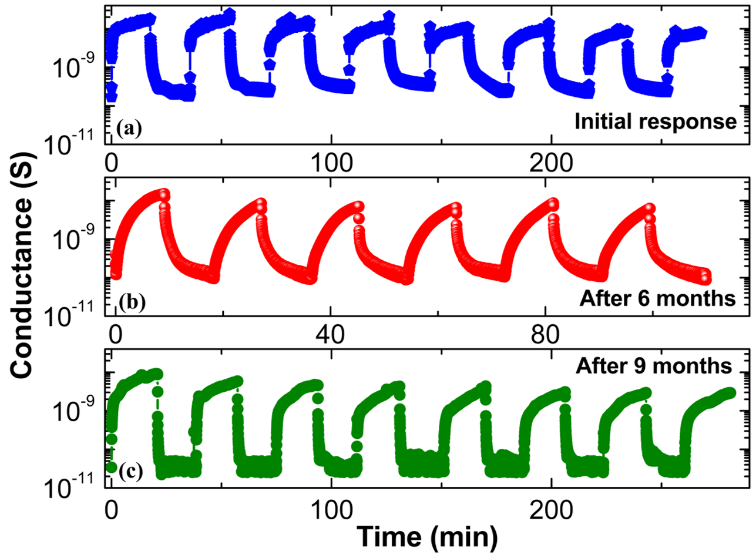

Fig. S11: Long-term stability test of the sensor (a) initial response (b) after 6 months (c) after 9 months.

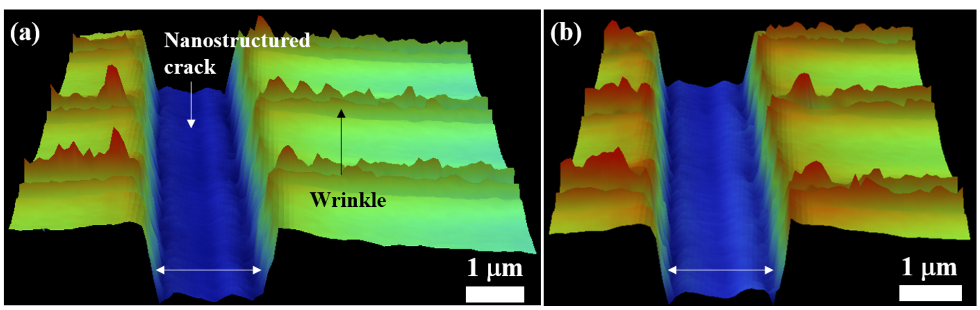

Fig. S12: Three-dimensional optical profilometry images of nanostructured crack (a) before exposed to 100% RH and (b) after exposed to 100% RH. [scale bar: 1 μm]

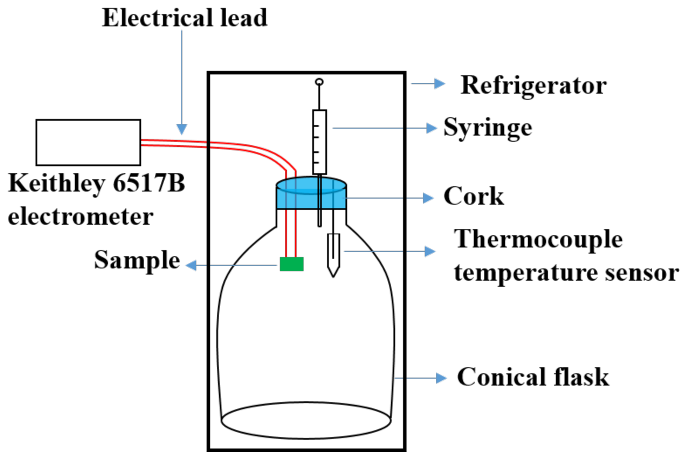

Fig. S13: Schematic representation of temperature dependent conductance measurement of nanostructured PEDOT:PSS samples using a refrigerator.

Fig. S13 represents the experimental set up for the measurement of conductance with varying temperature for nanostructured PEDOT:PSS samples using a refrigerator. The experimental set up comprises of a conical flask, with sample, electrical leads, thermocouple sensor, cork and syringe which is used to introduce the solvents such as methanol inside the flask. The whole set up is enclosed using a refrigerator. The conductance of the PEDOT:PSS samples as a function of temperature is measured using a Keithley 6517B electrometer which is placed outside the refrigerator.

To identify the dominant conduction mechanism, we performed temperature dependent studies on a pre-swollen film. A conventional cryostat could not be used, since it was desirable not to pump or evacuate the swollen films to retain their state of hydration. Hence, we preferred using a refrigerator. A sealed conical flask with the electrical leads and connected sample is placed in the refrigerator. The sample is pre-swollen using a syringe inserted on the flask cork. A cyclic measurement of humidity-induced conductance versus temperature is performed over the temperature ranges from -10° C to 30° C, and results are shown in Fig. 5b. The nanostructured PEDOT:PSS thin film is allowed to swell in 100% RH until the electrical conductance reaches the saturation value at ambient temperature (30° C), and subsequently the temperature of the completely swollen film is lowered down to -10° C using a refrigerator. Simultaneously, the conductance is recorded as a function of temperature. As the temperature decreases to -10° C, water vapor condenses on the surface of the swollen nanostructured PEDOT:PSS thin film. The dry film has G $\sim 4.2 \times 10^{-11}$ S, and this increases up to 9.9×10^{-7} S for the swollen film (at 100% RH). In the forward cycle, the electrical conductance of the swollen PEDOT:PSS thin film decreases from 9.9×10^{-7} S to 1.14×10^{-7} S, while the temperature goes down from 30° C to -10° C. In the reverse cycle, the electrical conductance of the swollen film remains almost constant for the temperature interval -10° C to 12° C. Finally, the conductance further decreases to 2.59×10^{-10} S at 30° C when the film is removed from 100% RH (humid environment) to 60% RH (ambient), as expected from the expulsion of water.

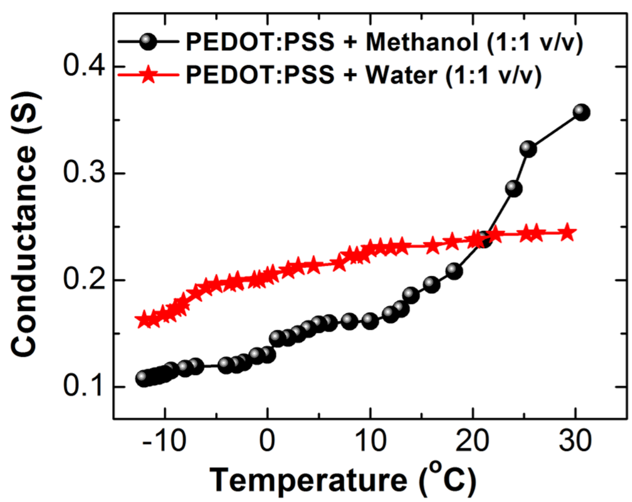

Fig. S14: Conductance change (G/G_{dry}) of PEDOT:PSS in water diluted with water (1:1 v/v ratio) and diluted with methanol (1:1 v/v ratio) as a function of temperature in the range 33° C to -10° C.

Table S1: Table compares the sensitivity of O_2 plasma etched film and nanostructured film exposed to alcohol vapors and to humidity.

Vapors	Sensitivity of etched film	Sensitivity of nanostructured film
Methanol (300 ppm)	~ 118	$\sim 10^6$
Ethanol (327 ppm)	~ 64	$\sim 2\times10^2$
Humidity (60 - 100% RH)	~ 24	$\sim 1.5\times10^2$