A hybrid nanosensor for TNT vapor detection

– Supporting Information

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1. TNT vapor generation

TNT vapor was generated by placing a solid grain (varying from 1-100 μg) of TNT or by drying up solutions in TNT containing acetonitrile on a resistive heating element. The heating element, together with the sensor chip, was enclosed in a Teflon cell. The temperature of the heating element was ramped up and then maintained at 60 C° with a homemade electronic circuit. The PEDOT nanojunction sensor was activated by sweeping WE2 vs. the Ag reference electrode between -0.3V to 0.3V while keeping a fixed bias between WE1 and WE2 at 50mV. In the meantime, the electrochemical detection of TNT was controlled by sweeping the potential of WE3 from -1.8V and -1.2 V within which the reduction of TNT took place. The conductance of the PEDOT nanojunction (between WE1 and WE2) and the electrochemical current of WE3 were recorded.

2. Diffusion of reaction products

Figure S1 shows a current vs. gate voltage curve (red curve) recorded 3 min after releasing TNT vapor, showing a ~100 mV negative shift of the curve (black curve). By stirring the ionic liquid using a pipette, an additional ~550mV was observed. The large additional shift indicates that the diffusion is the limit for the current sensor. Electrode geometry as well as the distance from WE3 to polymer nanojunction and the ionic liquid layer thickness can be optimized to improve diffusion efficiency.
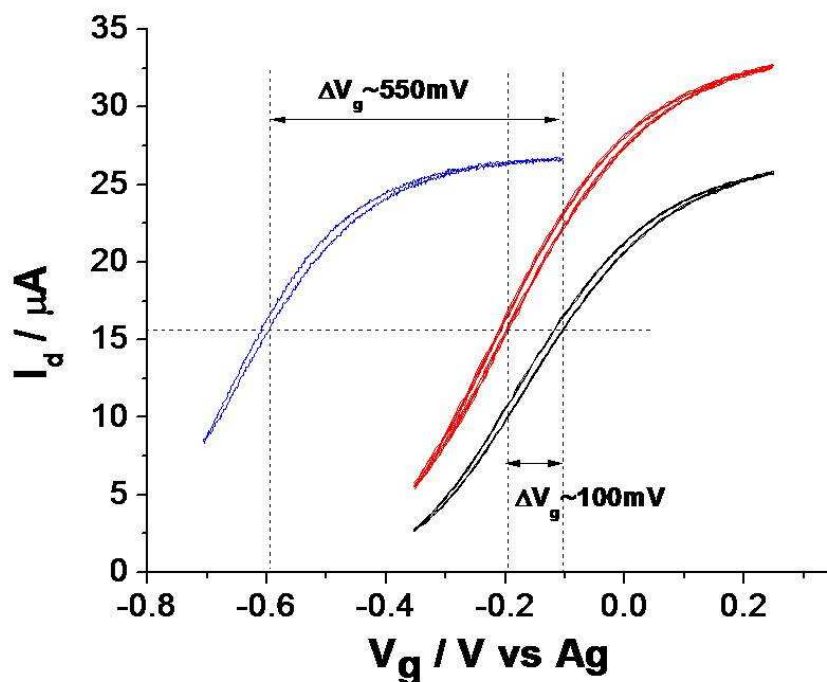

Fig. S1. I_d vs V_g plot of a PEDOT nanojunction exposed to vapors generated by heating a ~1 μg TNT sample. The black curve is taken before TNT reduction on WE3. After the reduction process a shift of ~100mV is observed (red curve). When mechanicaly disturbed, more reaction product of TNT can reach the polymer junction, thus resulting in a much greater shift in the I_d vs. V_g plot.

3. Thermal stability of the polymer nanojunctions

In order to determine the effect of temperature changes on the sensor, a polymer nanojunction was exposed to 60 C° heat pulses. The polymer nanojunction was fist stabilized for 20 mins in the ionic liquid, and heating pulses with time intervals of 30, 60, 120 and 180 seconds were applied using the same heating element for TNT vapor generation. The heating did not produce any visible changes in the charge transport characteristics of the polymer nanojunctions.
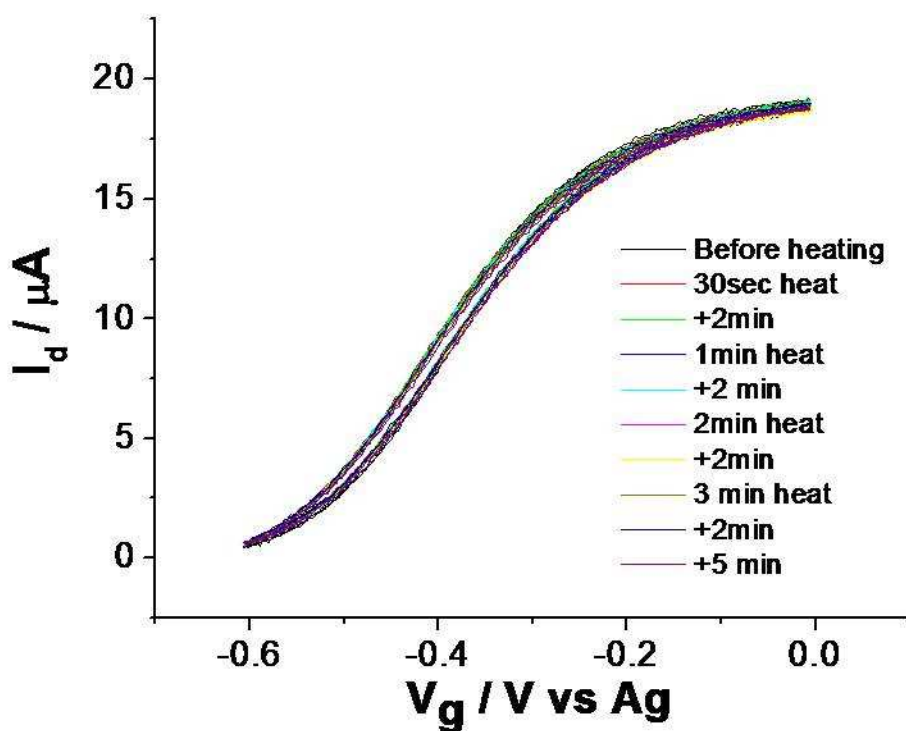

Fig. S-2. I_d vs. V_g plot of a PEDOT nanojunction exposed to heating periods to characterize the effect of temperature on the polymer. The same heating element employed for TNT evaporation is used without a TNT sample. A heating pulse of 30 sec, 1, 2 and 3 min is applied at 60C followed by a 2 min period in between. No effect is observed on the PEDOT nanojunction.

4. TNT concentrations from vapor generation

In order to estimate the TNT concentrations obtained in the ionic liquid from TNT vapor generation with our home-made heating element, we determined the evaporated TNT mass using a quartz tuning fork mass loading sensor (18 ng/Hz sensitivity). The tuning fork sensor placed at the same location as the hybrid sensor chip detects TNT vapor during the heating process (Fig. S-3). Due to the high affinity of TNT on quartz, the TNT vapor condenses on and stick well to the quartz surface, which was observed as an irreversible increase in mass. The ionic liquid is also expected to capture the TNT vapor with high efficiency, as we found in recent study described in Ref. [1]. So the tuning fork mass sensor provides a good estimate of the amount of TNT vapor captured by the ionic liquid.
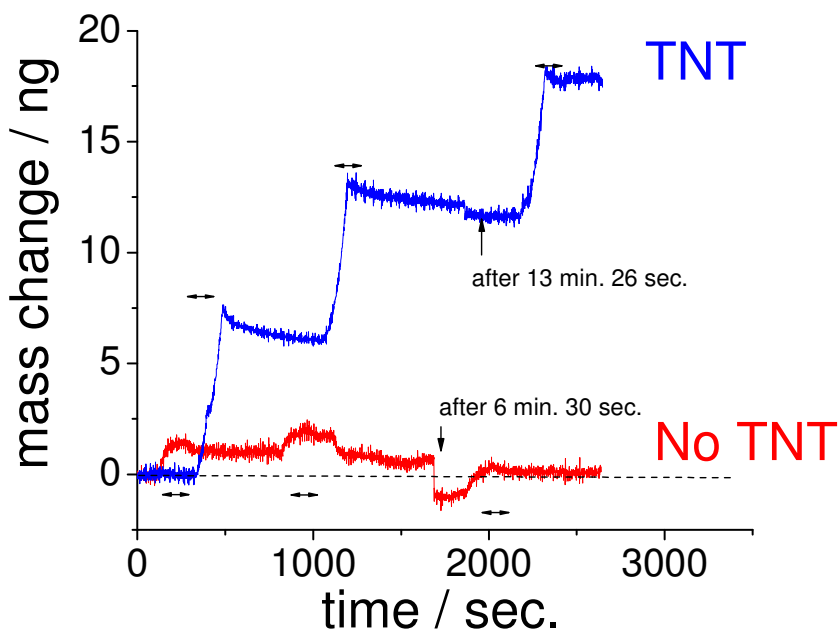
Fig. S-3. TNT mass evaporation from the heating element used in the hybrid sensor experiments. TNT mass changes resulting from heating steps of 2-3 min. in absence and presence of a TNT

sample of ~ 100 μg. A tuning fork of 0.15-cm^2 area and mass sensitivity of 18 ng/Hz was used as mass loading sensor in a position equivalent to the hybrid sensor position. Horizontal arrows show the time corresponding to heating periods of 60 ^{0}C.

5. Interference studies

Samples of some common interferents, including perfume (Antonio by Antonio Banderas), mouthwash (Listerine), body spray (Calgon, Coty US LLC), cigarette smoke and water vapor, were prepared in Tedlar bags. Appropriate concentrations of the interferents were prepared by diluting the corresponding saturated vapors with ambient air using a gas diluter (Model 1010, Custom Sensor Solutions, Inc., Oro Valley, AZ). For perfume, mouthwash and body spray the concentrations were kept at 2% of the saturated vapors. This concentration range safely covers the range of interferents' concentration under realistic conditions. The humidity test used controlled humidity varying from 50 to 100% and also ambient humidity at ~40%. Finally dilutions of, 2, 20, 50 and 100% of cigarette smoke were tested. In each case, the sensor was exposed to the interferents for 3 min under constant flow (0.3L/ min) and then flushed with ambient air. No interference effects were observed in the polymer nanojunction except in the case of relative humidity (see discussion below).
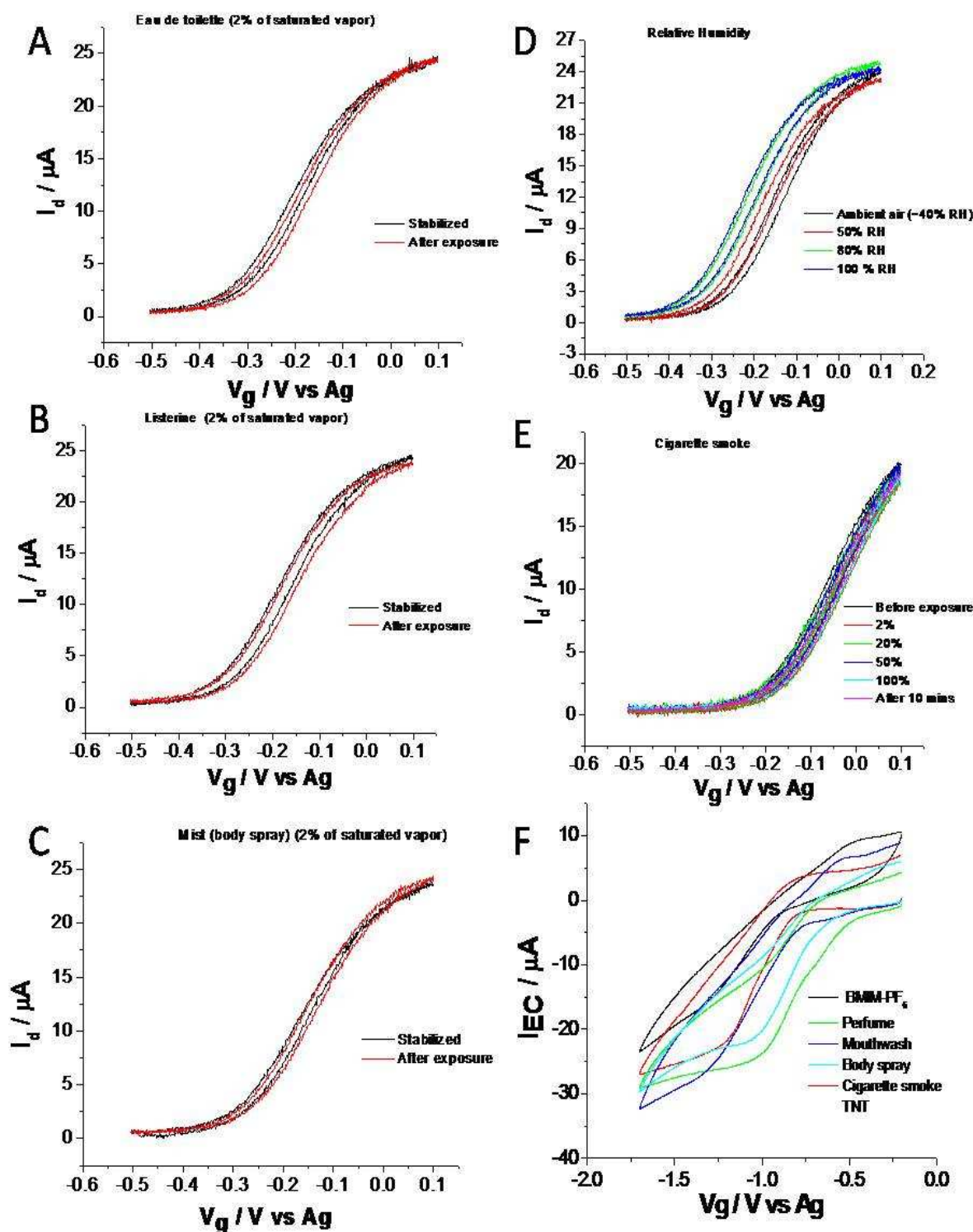
Fig. S-4. I_d - V_g plots of possible interferents collected on the sensor from vapors of (a) 2% of the saturated vapors of a perfume, (b) 2% of the saturated vapors of a mouthwash, (c) 2% of the

saturated vapors of a body spray, (d) 50%, 80% and 100% relative humidity and (e) 2%, 20%, 50% and 100% of cigarette smoke. (f) Cyclic voltammograms showing electrochemical reductions on WE3 after exposure to perfume, mouthwash, body spray, cigarette smoke and TNT.

6. Humidity effects

From the interferent study described above we observe that exposure to RH changes introduces a shift on the $I_d - V_g$ characteristics of the sensor. Figure S-5 gives a better insight of the magnitude of the interference shift. The maximum shift observed for 100% humidity is 71mV. This confirms that sudden humidity changes can interfere with the detection of trace TNT levels below 100ppt. Thus humidity control is desirable in order to detect a few ppt of TNT.
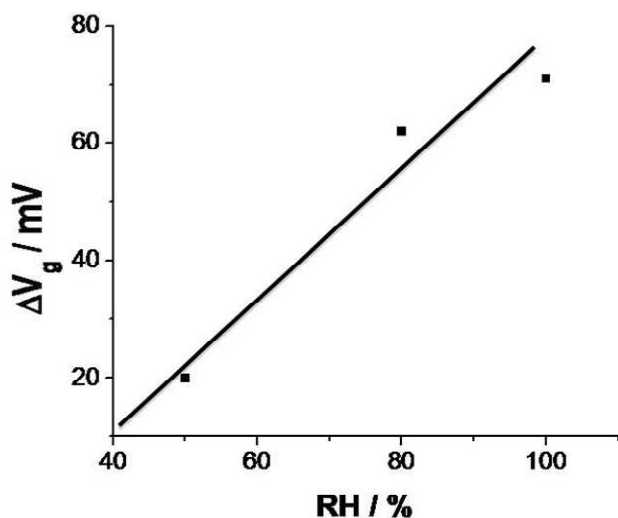

Fig. S-5. Potential Shift (ΔV) in mV vs. Relative Humidity in percentage plot of a PEDOT nanojunction exposed to 50, 80 and 100% RH (shown in Fig. S-4d). The initial humidity in the ambient air was approximately 40%. The total shift from 100% humidity was 71mV.

Reference

1- Forzani, E. S.; Lu, D.; Leright, M. J.; Aguilar, A. D.; Tsow, F.; Iglesias, R. A.; Zhang, Q.; Lu, J.; Li, J.; Tao, N. *Journal of the American Chemical Society* **2009,** 131, (4), 1390-1391.