

## SUPPORTING INFORMATION

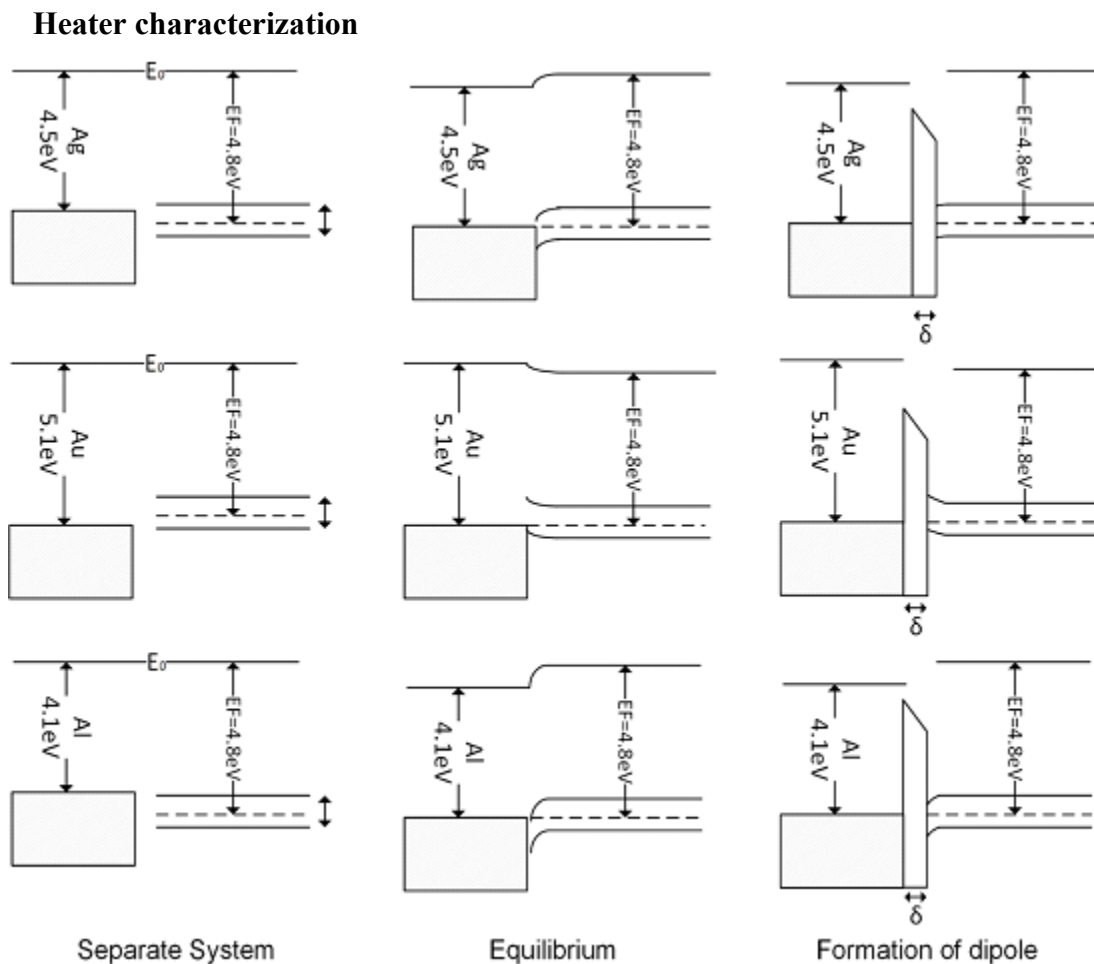


Figure S1. Band diagram of the considered metals (Ag, Au and Al) in vacuum (first column) and at the thermal equilibrium (second column). The third column presents the actual band structure resulting from the formation of an interface dipole during processing.

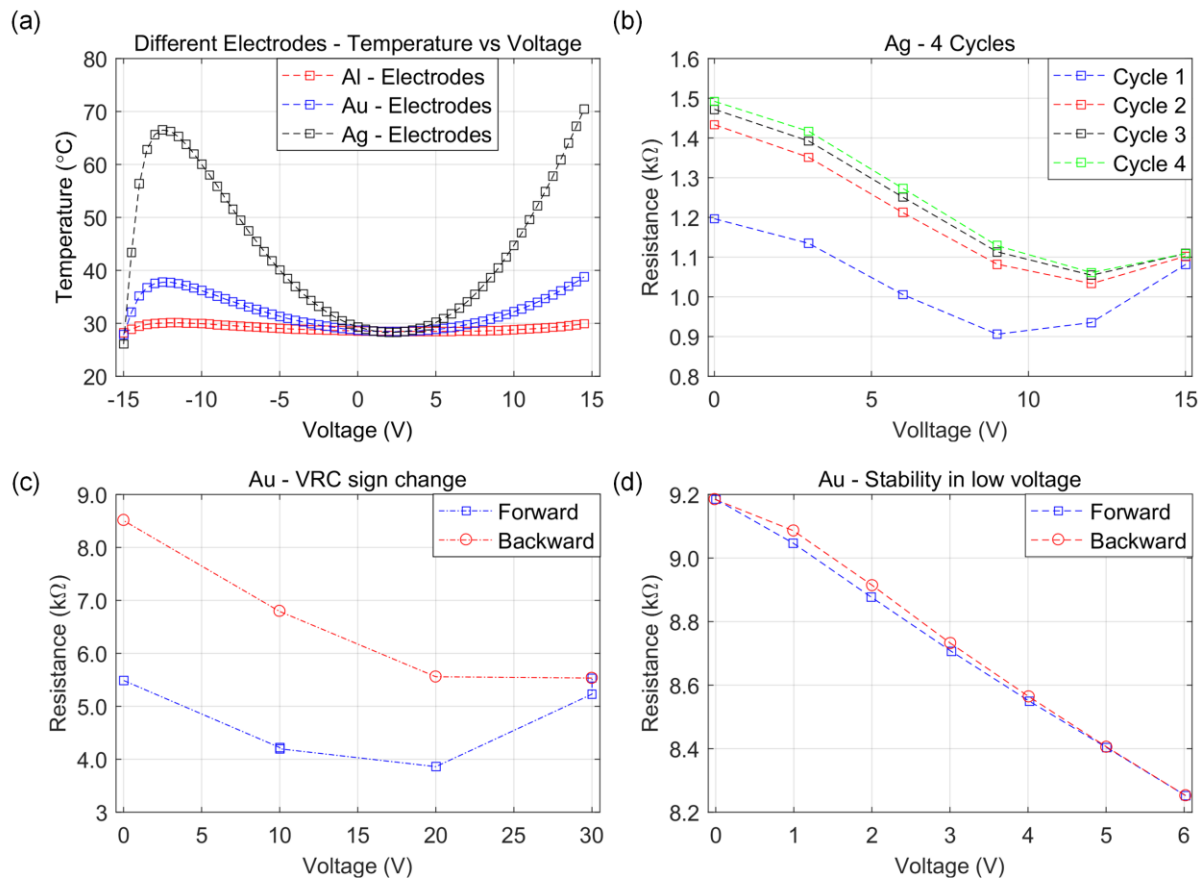


Figure S2. (a) Temperature vs. voltage curve for the different metal electrodes; (b) Resistance vs. voltage for Ag electrodes, consecutive cycles; (c) Resistance vs. voltage for Au electrodes, up to the VRC change, forward and backward; (d) Resistance vs. voltage for Au electrodes, within the VRC stability range.

Figure S2 gives more insights on the basic behavior of CNT films with metallic electrodes, when a voltage is applied. Panel (a) presents the temperature reached from the back side of the sensor upon the application of a DC voltage. The voltage level is increased of 0.5 V every 3 seconds, hence, at the starting point (-15 V) the temperature does not immediately spike up. Panel (b) presents multiple voltage cycles for devices with Ag electrodes. The resistance of the film is decreasing for two connected reasons: the non-linearity of the barriers and the increased

temperature. Aim of this plot is to show how past a certain voltage (circa 10 V), an increase in voltage does not correspond to a reduction of the resistance, any more. We can also define the ratio of resistance change to a voltage step as a “Voltage Resistance Coefficient” (VRC) and observe how this value turns from negative to positive, once the system is brought to a turning point. Such behavior is consistent with previous works, where the relationship between temperature and CNT-film resistance was investigated. Especially In low-density CNT films, it can be observed a “U-shape” attributable to the irreversible desorption of oxygen (and consequent de-doping) of the film, with loss of conductivity<sup>1</sup>. The turning point is shifted further to high voltages (high temperatures), when the procedure is iterated. Panel (c) shows a similar experiment, performed for Au-based devices. In this case, since the resistance is higher, it is necessary to apply higher voltages to reach the turning point temperature (circa 20 V). Finally, Panel (d) presents a voltage sweep on an Au-based device, in which the voltage is been kept below the turning point voltage (0 V – 6 V). By doing so, the hysteresis is very limited and the device is able to fully recover to its initial resistance.

<sup>1</sup> S. Colasanti, V. Robbiano, F. C. Loghin, A. Abdelhalim, V. D. Bhatt, A. Abdellah, F. Cacialli and P. Lugli, IEEE Transactions on Nanotechnology, 2016, 15, 171-178.

## Gas Sensor characterization

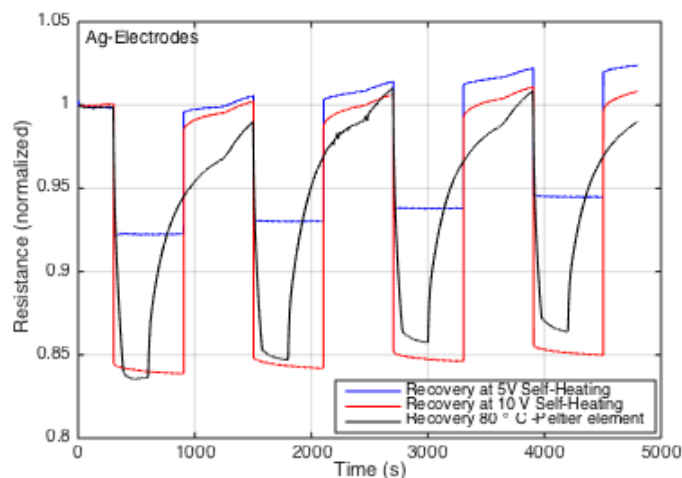


Figure S3. Time Vs Resistance for Ag-CNT-based gas sensors exposed to 2500 ppm of CO<sub>2</sub> under different operating conditions, different recovery conditions for Ag electrodes: self-heating at 5 V, self-recovery at 10 V and external heating at 80 °C.

The response of gas sensors produced with Ag electrodes does not significantly differ from their Au-electrode based counterpart. It is, however, worth observing the behavior of the resistance after the self-recovery at 10 V (Figure S3, red curve). Since the devices with Ag electrodes presented a lower starting resistance with respect to devices with Au electrodes, the application of an identical voltage to the two class of devices results in a stronger heating of the Ag based ones. Resultantly, for Ag based devices, a recovery process at 10 V introduces a non-negligible temperature change, reflected in the non-flat resistance curve after the recovery cycle.