Supplementary material to:

A Chemiresistor Sensor Array Based on Graphene Nanostructures: From the Detection of Ammonia and Possible Interfering VOCs to Chemometric Analysis

Sonia Freddi *, Michele Vergari, Stefania Pagliara and Luigi Sangaletti *

Surface Science and Spectroscopy Lab @ I-Lamp, Department of Mathematics and Physics, Università Cattolica del Sacro Cuore, Via della Garzetta 48, 25123 Brescia, Italy
* Correspondence: sonia.freddi@unicatt.it (S.F.); luigi.sangaletti@unicatt.it (L.S.)

Content:

1. Set up for gas exposures

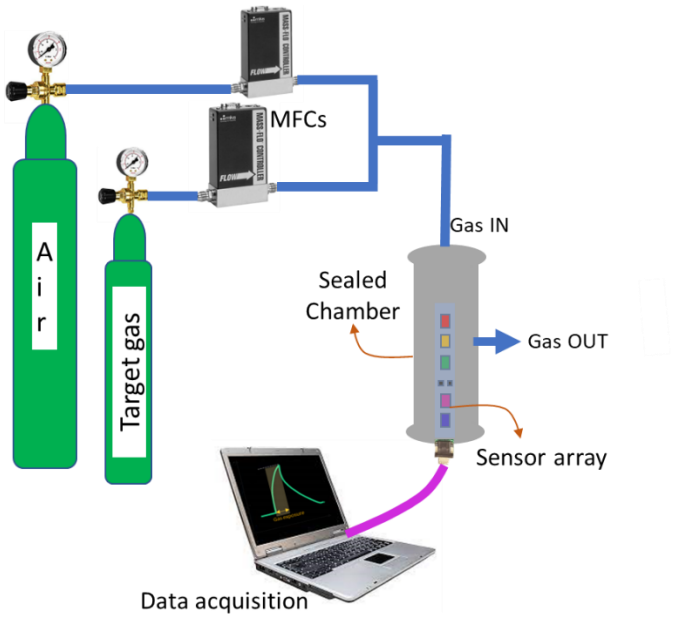

Figure S1: Schematic representation of the set up used for the gas exposures. The system comprises a sealed steal homemade chamber, connected to 2 mass flow controllers (MFCs) and a PC for data acquisition, a cylinder filled with air and a cylinder with the target gas molecules. The sensor array is hosted inside the chamber. The MCF connected to the air cylinder has a maximum flow of 500 sccm, while the max flow of the MFC connected to the analyte cylinders is 200 sccm.

2. Freundlich fitting parameters and detection limit evaluation

Table S1: fitting parameter of the calibration curve (reported in Figure 3 – right panel) of the main text), used to evaluate the limit of detection (LOD) for ammonia exposure, according to the formula reported in the main text.

Sensor	A	Pow	LOD (ppb)
Gr_CoPt	0.008 ± 0.001	0.65 ± 0.01	0.1
Gr_Fe_3O_4	0.005 ± 0.001	0.43 ± 0.01	7.2
Gr_TiO_2	0.0011 ± 0.0002	0.53 ± 0.03	101
Gr nanolapelets	0.0014 ± 0.0003	0.89 ± 0.04	720
Gr dispersion	0.0024 ± 0.0001	0.84 ± 0.01	102

3. Stability of sensor response upon time and temperature

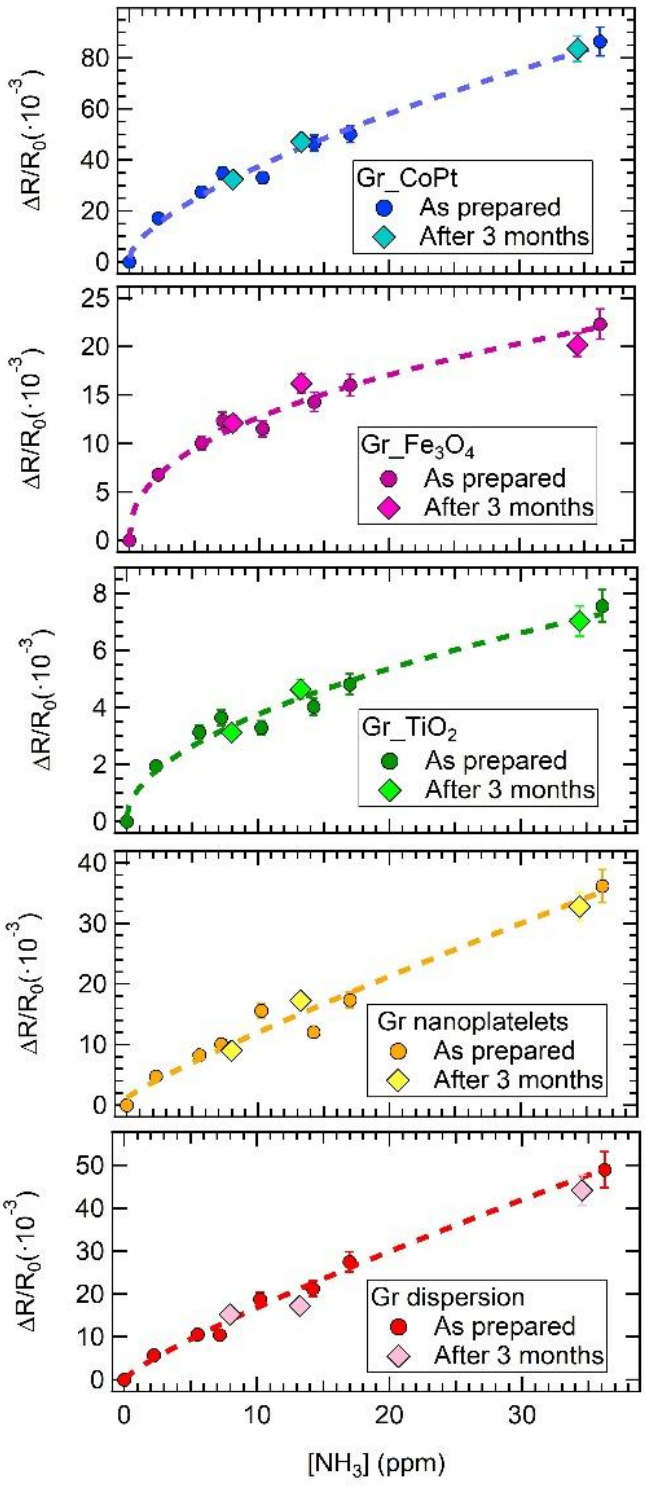

Figure S2: Proof of the stability and reproducibility of the sensors response upon ammonia exposures: calibration curves (dots) and Freundlich fit (dashed curves) evaluated after the sample preparation; rhombus data have been collected after 3 months from the sample preparation and they perfectly matched the calibration curve and Freundlich fit for all sensors.

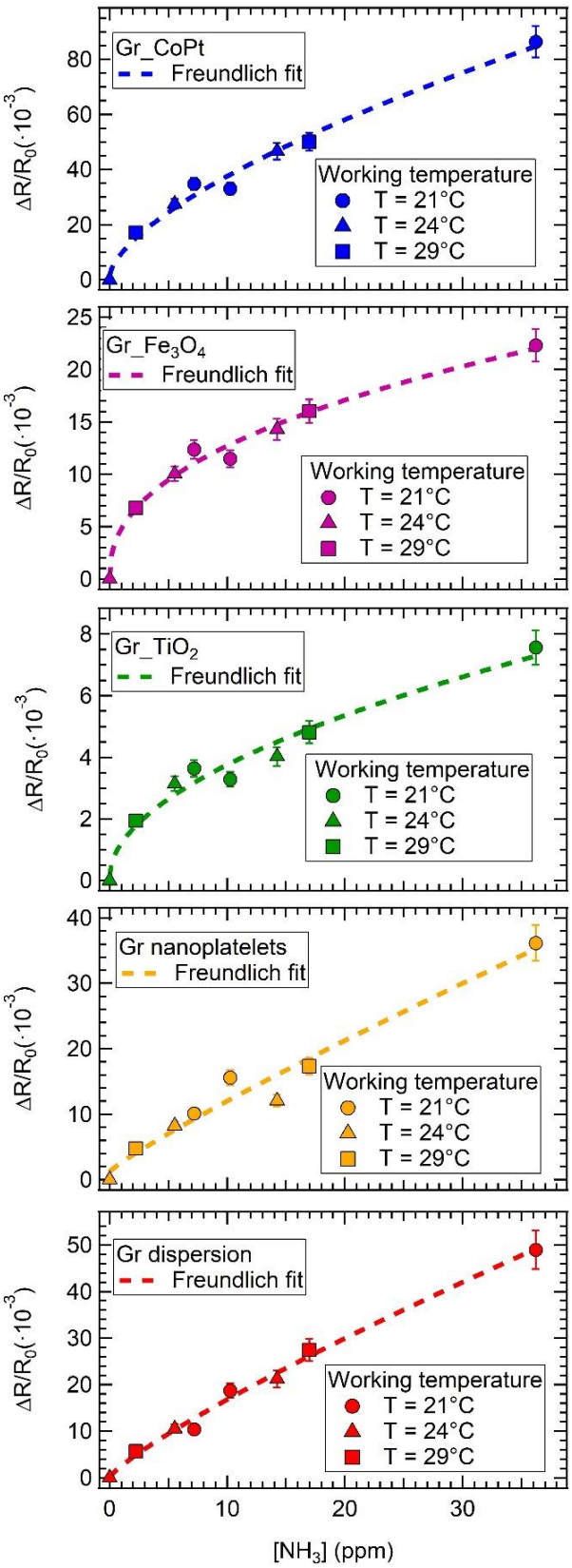

Figure S3: Proof of the stability and reproducibility of the sensors response to ammonia exposures at different working temperature: 21°C (dots), 24°C (triangles) and 29°C (squares). Dashed line is the Freundlich fit. The tested temperature range is suitable for breathomics, environmental, food quality and safety applications.

4. Sensing mechanism

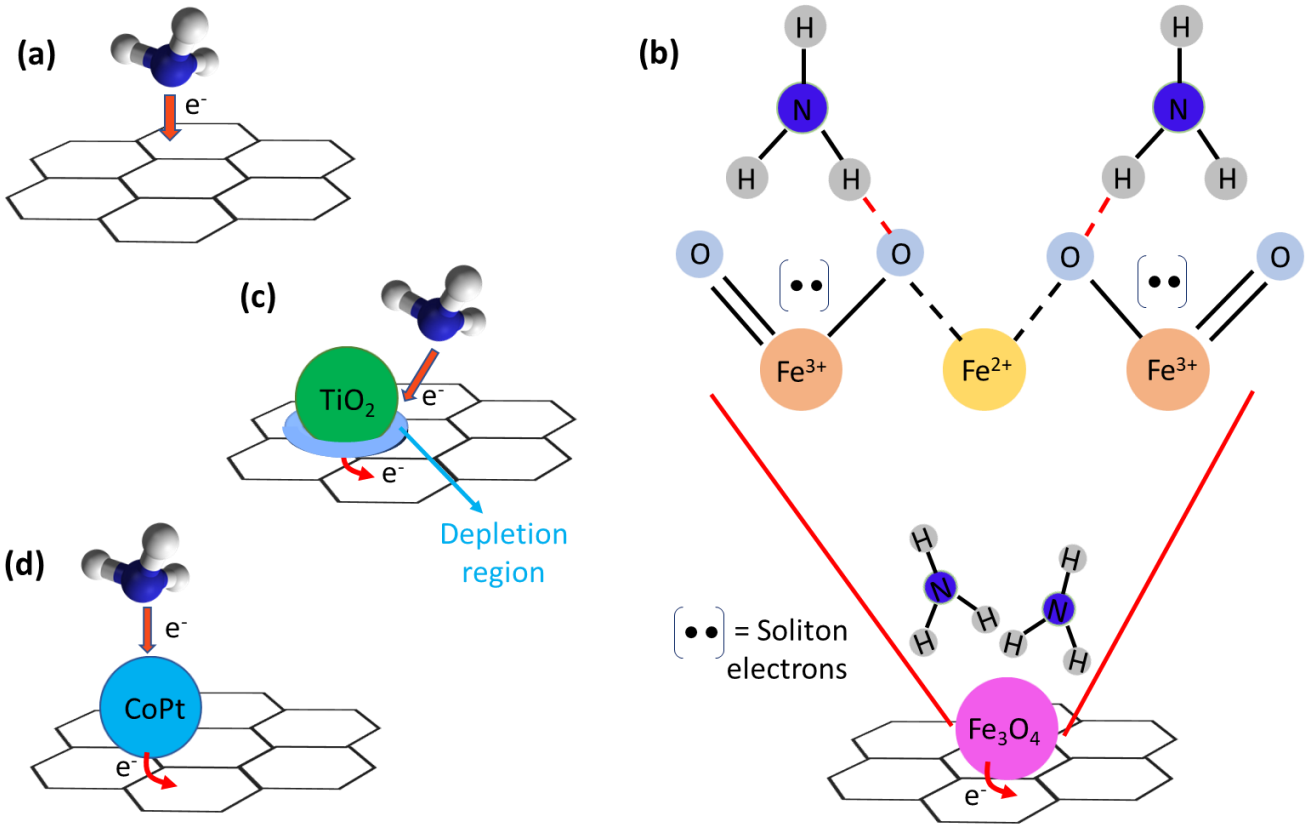

Figure S4: Scheme of the sensing mechanism to ammonia exposure for (a) Gr dispersion and Gr_nanoplatelets, (b) Gr_Fe_3O_4, (c) Gr_TiO_2 and (d) Gr_CoPt layers.

5. Sensitivity benchmarking

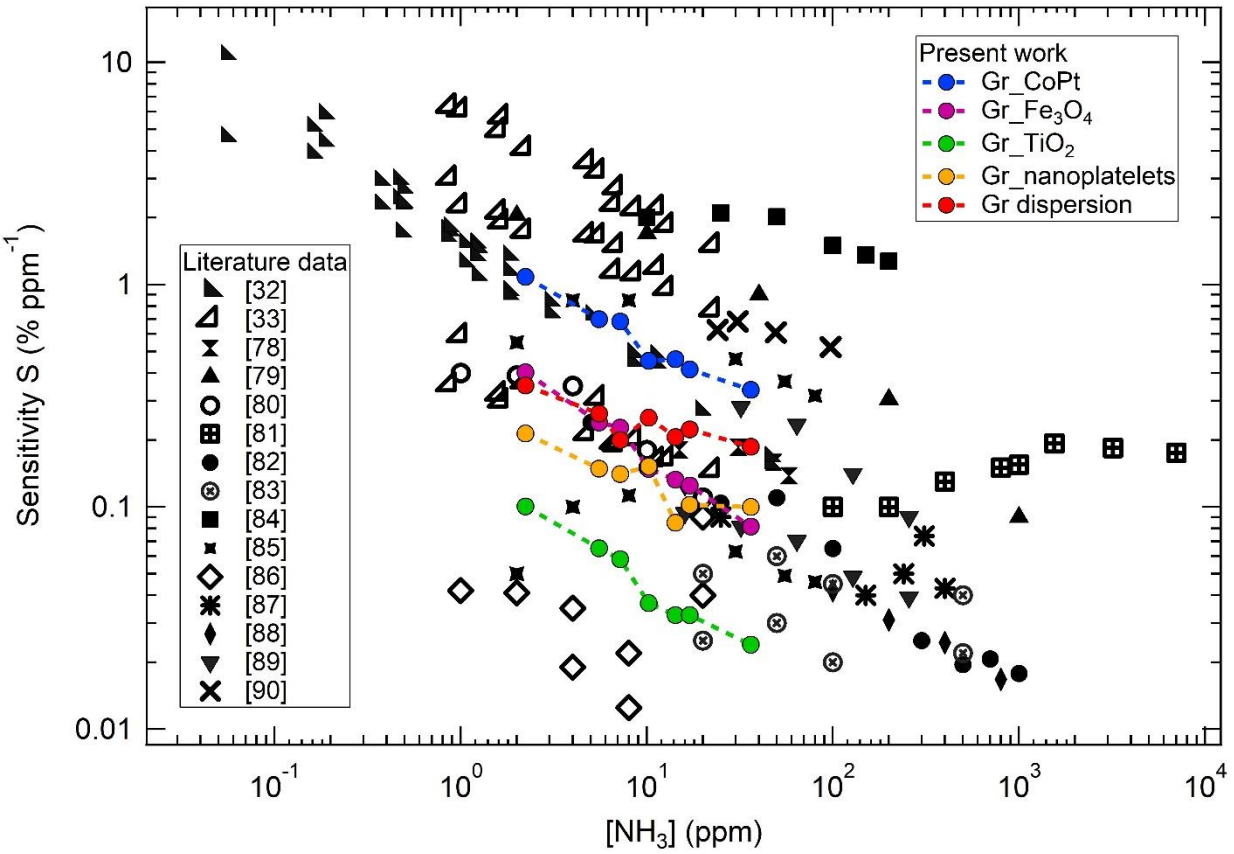

Figure S5: Benchmarking for sensitivity (defined as: $(\Delta R/R_0*100)/[NH_3]$) upon ammonia exposure, of the prepared sensors (blue, purple, green, yellow and red dots) with respect to other graphene-based chemiresistor sensitivity values reported in literature (black symbols). Literature data refer to Refs [32,33,78-90] reported in the main text. Data are presented in a log-log scale. Of note: only articles clearly reporting gas concentration and sensor response/sensitivity have been taken into account for this benchmarking.

6. Concentration range of each tested gas molecule

Table S2: Concentration range of the selected target gas molecules used for the PCA, LDA and Mahalanobis distance analysis.

Target gas	Concentration range (ppm)
Ammonia	0-36.0
Acetone	0-40.0
Ethanol	0-37.0
2-propanol	0-40.3
Sodium hypochlorite	0-0.5

7. Example of a confusion matrix for LDA cross validation with accuracy percentage evaluation

Table S3: Example of the confusion matrix upon internal cross validation of the model reported in Figure 6-b of the main text. On the raw there are the correct belonging classes, while the columns, labelled with an asterisk (*), are the predicted belonging classes. In red are enlightened the wrong assignment of data.

	Ammonia*	**Acetone***	**2-propanol***	**Ethanol***	**Sodium hypochlorite***	**Water***
Ammonia	6	0	0	0	0	0
Acetone	0	3	0	0	1	0
2-propanol	0	0	3	1	0	0
Ethanol	0	0	0	4	0	0
Sodium hypochlorite	0	0	0	1	3	0
Water	0	0	0	0	0	5

Table S4: Accuracy percentage of cross validation referred to the confusion matrix reported in table S.III. The total accuracy is 88%.

Ammonia	**Acetone**	**2-propanol**	**Ethanol**	**Sodium hypochlorite**	**Water**
100%	75%	75%	100%	75%	100%

8. Example of a confusion matrix for LDA predictive capability

Table S5. Confusion matrix obtained for classification of a random subset of training dataset containing 6 data (one for each class) projected on the LDA model reported in Figure 6-b. The accuracy of this classification is 100% since all the data are correctly identified. True class is reported on row, while the predicted class are on the columns and labelled with an asterisk (*).

	Ammonia*	**Acetone***	**2-propanol***	**Ethanol***	**Sodium hypochlorite***	**Water***
Ammonia	1	0	0	0	0	0
Acetone	0	1	0	0	0	0
2-propanol	0	0	1	0	0	0
Ethanol	0	0	0	1	0	0
Sodium hypochlorite	0	0	0	0	1	0
Water	0	0	0	0	0	1