Design of Highly Responsive Room Temperature Chemiresistor-Based Sensors via Non-Covalent Functionalization of Graphene

Daniele Perilli [a], Sonia Freddi [b,c], Luca Vaghi [a], Antonio Papagni [a], Luigi Sangaletti [b], Cristiana Di Valentin [a]

[a] *Department of Materials Science, University of Milano-Bicocca, via R. Cozzi 55, 20125 Milano, Italy*

[b] *Surface Science and Spectroscopy Lab@I-Lamp, Department of Mathematics and Physics, Università Cattolica del Sacro Cuore, 25123, Brescia, Italy*

[c] *Istituto di Fotonica e Nanotecnologie-Consiglio Nazionale Delle Ricerche (IFN-CNR), LNESS Laboratory, Como, Italy*

Corresponding author email: daniele.perilli@unimib.it

The development of gas-sensing materials is arousing great interest driven by pressing issues like environmental and human health monitoring [1]. Ideal materials must exhibit high sensitivity, rapid response, low operating temperature, and cost-effectiveness. In this context, graphene-based materials functionalized by the deposition of thermally evaporated or drop-casted molecules are emerging as promising systems for gas sensing [2]. In this combined experimental and theoretical work [3], we explored the gas sensing capabilities of a functionalized single-layer graphene towards NH_3, an electron donor gas molecule. We developed a cost-effective method for molecular functionalization exploiting tetrazole chemistry, discovering that tetrazole molecules dimerize into tetrazine (T) molecules upon thermal treatment. Testing the T/Gr interface as a chemiresistor revealed high sensitivity to NH_3 at room temperature, expanding detection to sub-ppm ranges. With the help of DFT calculations, we elucidated the sensing mechanism and unveiled a dual functionality exhibited by the tetrazine molecules. Specifically, they serve as (i) concentrators for ammonia and (ii) facilitate electron transfer between ammonia and graphene.

[1] I. Banga, A. Paul, D.C. Poudyal, S. Muthukumar, S. Prasad, *ACS Sensors* 2023, 8, 3307-3319.

[2] D. Tyagi, H. Wang, W. Huang, L. Hu, Y. Tang, Z. Guo, Z. Ouyang, H. Zhang, *Nanoscale* 2020, 12, 3535-3559.

[3] S. Freddi, D. Perilli, L. Vaghi, M. Monti, A. Papagni, C. Di Valentin, L. Sangaletti, *ACS Nano* 2022, 16, 10456-10469.