Tailoring active sites in graphene nanoribbons for chemical sensing

Martina Corso[1, 2]
Paula Angulo-Portugal[1], Andrea Aguirre[1], Frederik Schiller[1], Manuel Vilas-Varela[3], Mamun Sarker[4], Jeong Ha Hwang[5], Amogh Kinikar[5], Martin Irizar[2], Daniel Sánchez-Portal[1], Aran Garcia-Lekue[2], Ignacio Piquero-Zulaica[1], Luca Schio[6], Luca Floreano[6], Alexander Sinitskii[5], Roman Fasel[6], Gabriela Borin Barin[6], Diego Peña[3], Dimas Garcia de Oteyza[7]
[1] *Centro de Física de Materiales CSIC/UPV-EHU, Manuel Lardizabal 5, 20018 San Sebastian, Spain.*
[2] *Donostia International Physics Center (DIPC), Manuel de Lardizabal 4, E-20018 San Sebastian, Spain.*
[3] *CiQUS, Universidade de Santiago de Compostela, Santiago de Compostela, 15782, Spain*
[4] *Department of Chemistry and Nebraska Center for Materials and Nanoscience, University of Nebraska − Lincoln, Lincoln, Nebraska 68588, United States*
[5] *Empa Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, 8600, Switzerland*
[6] *CNR-IOM, Laboratorio TASC, Sincrotrone Trieste, Trieste, 34149, Italy*
[7] *Nanomaterials and Nanotechnology Research Center (CINN), CSIC-UNIOVI-PA, El Entrego, Spain*
Contact: martina.corso@ehu.eus

Graphene and 2D materials have revealed high potential as groundbreaking materials for chemical sensing [1, 2]. Their large surface-to-volume ratio maximizes the sensing area for material-analyte interactions even at very low concentrations. Despite the enhanced sensitivity, they still lack selectivity. The addition to the surface of covalent or non-covalent modifiers, capable to interact selectively with guest analytes without compromising the physico-chemical properties of the 2D material, remains a challenge [3].

In this work, we use on-surface synthesis to add with atomic precision active sites in 1D graphene nanoribbons (GNRs) suitable for gas sensing technologies. By surface sensitive techniques in ultra-high vacuum combined with DFT calculations, we demonstrate the capability to tune the electronic structure of semiconducting GNRs by periodic addition at the edges or backbone of functional sites as chemical groups, metal atoms or pores.

The addition of cyano (CN) chemical groups dopants at the zig-zag edges of (3,1) chiral GNRs (CN-chGNRs) induces bandgap opening which we associate to a modified conjugation pattern. Efficient coordination of CN groups with metal atoms allows to further tune the electronic structure. In fact, coordination to Fe atoms shrinks the semiconducting ribbons' bandgap to less than half of its value without the metal and shifts the frontiers bands to lower energies. CN groups, similarly to ketone ones [4], protect the ribbons edges and make them stable to controlled O_2 and NO_2 exposure and even in air. Thanks to this enhanced stability, CN-chGNRs survive polymer-free transfer processes to non-conductive substrates [5] proofing the feasibility of their possible implementation in nanodevices.

We finally demonstrate that selective trapping of gas molecules occurs at metallic centers in Fe coordinated CN-chGNRs and in the pores of porous GNRs thus demonstrating an efficient chemical sensitivity of the metal-organic and porous ribbons.

Our work demonstrates that endowing GNRs with functional sites is a robust strategy for the implementation of even reactive GNRs in nanoelectronics and sensing technologies.

References

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