

New tools for the chemical modification of 2D materials

Emilio M. Pérez

C/Faraday 9, Ciudad Universitaria de Canto Blanco, E28049 Madrid, Spain

emilio.perez@imdea.org

The extraordinary properties of graphene and transition metal dichalcogenides (TMDCs) can be further improved/tuned by decoration with adequate molecular entities.^[1] However, the chemistry of 2D materials remains quite a challenge, in particular due to the typically low reactivity -that makes them stable- and the large number of identical atoms -which hinders selective functionalization.

In this presentation, we will describe a method to functionalize graphene covalently with exquisite (>97%) atomic selectivity and yield (92%). The periodic landscape is provided by a single monolayer of graphene grown on Ru(0001) that presents a moiré pattern due to the mismatch between the carbon and ruthenium hexagonal lattices. The moiré contains periodically arranged areas where the graphene–ruthenium interaction is enhanced and shows higher chemical reactivity.^[2] Furthermore, we will show how this type of functionalized graphene acts as a catalyst for an unusual and reversible C-C bond forming reaction.^[3]

With regards to TMDCs, we will describe improved methods for their production through liquid-phase exfoliation (LPE),^[4] and describe strategies for their noncovalent^[5] and covalent^[6] functionalisation. The covalent functionalisation is very mild (room temperature) and exploits the inherent soft-nucleophilicity of sulfur to functionalize MoS₂ and WS₂ with the prototypical electrophilic counterpart of S: maleimides. Finally, we will report simple strategies to construct functioning electronic devices from colloidal suspensions of 2D materials obtained by LPE.^[7]

References

- [1] S. Bertolazzi, M. Gobbi, Y. Zhao, P. Samori, C. Backes, *Chem. Soc. Rev.* **2018**, *47*, 6845-6888.
- [2] a) J. J. Navarro, S. Leret, F. Calleja, D. Stradi, A. Black, R. Bernardo-Gavito, M. Garnica, D. Granados, A. L. Vazquez de Parga, E. M. Pérez, R. Miranda, *Nano Lett.* **2016**, *16*, 355-361; b) J. J. Navarro, F. Calleja, R. Miranda, E. M. Pérez, A. L. V. d. Parga, *Chem. Commun.* **2017**, *53*, 10418-10421.
- [3] J. J. Navarro, M. Pizarra, B. Nieto-Ortega, J. Villalva, C. G. Ayani, C. Díaz, F. Calleja, R. Miranda, F. Martín, E. M. Pérez, A. L. Vázquez de Parga, *Science Adv.* **2018**, *4*, eaau9366.
- [4] M. M. Bernal, L. Alvarez, E. Giovanelli, A. Arnaiz, L. Ruiz-Gonzalez, S. Casado, D. Granados, A. M. Pizarro, A. Castellanos-Gomez, E. M. Pérez, *2D Mater.* **2016**, *3*, 035014/035011
- [5] A. J. Molina-Mendoza, L. Vaquero-Garzon, S. Leret, L. d. Juan-Fernández, E. M. Pérez, A. Castellanos-Gomez, *Chem. Commun.* **2016**, *52*, 14365-14368.
- [6] M. Vera-Hidalgo, E. Giovanelli, C. Navio, E. M. Pérez, *J. Am. Chem. Soc.* **2019**, *141*, 3767-3771.
- [7] E. Burzuri, M. Vera-Hidalgo, E. Giovanelli, J. Villalva, A. Castellanos-Gomez, E. M. Pérez, *Nanoscale* **2018**, *10*, 7966-7970.