

## Nanostructured covalent functionalization of 2D materials

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The research on graphene and related 2D materials has matured into an independent field of scientific inquiry. An important aspect is the chemistry of graphene. The interest in the covalent chemistry of graphene started pretty much with its first successful isolation. The lack of band gap and poor solution processability of graphene meant that there was pressing need to explore its covalent chemistry. However, given the poor reactivity of the basal plane, highly reactive chemistries are often needed for achieving meaningful functionalization.<sup>1</sup>

When carried out with bulk exfoliated material, covalent attachment of organic units onto the basal plane of graphene allows dispersion of these materials in (organic) solvents thereby improving their processability. Such dispersions can be used in composite materials and as functional inks. When studied on pristine graphene supported by solid substrates, covalent functionalization of graphene serves as a testbed for evaluating the efficiency of the chemistry used for functionalization, and moreover, it also allows modification of the intrinsic electrical, electronic and optical properties. The covalent chemical patterning of graphene, where one targets the precise positioning of organic functional groups on its basal plane, is relevant to several applications such as those in electronics, catalysis, sensing and photonics.<sup>2</sup>

In this contribution, I will discuss covalent modification of graphene, graphite and MoS<sub>2</sub> using diazonium chemistry. Our approach is to invest into simple, straightforward protocols that allow nanostructured functionalization of 2D materials with a special focus on chemical patterning ranging from micrometer to the nanometer scale. I will also highlight a judiciously chosen toolbox of surface analytical techniques employed for the characterization of such functionalized materials which involves scanning probe microscopy (STM, AFM, AFM-IR), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).<sup>3</sup>

### References

- [1] G. Bottari, M. Á. Herranz, L. Wibmer, M. Volland, L. Rodríguez-Pérez, D. M. Guldi, A. Hirsch, N. Martín, F. D'Souza, T. Torres, *Chem. Soc. Rev.* **2017**, *46*, 4464.
- [2] M. Gobbi, E. Orgiu, P. Samorì, *Adv. Mater.* **2018**, *30*, 1706103.
- [3] K. Tahara, T. Ishikawa, B. E. Hirsch, Y. Kubo, A. Brown, S. Eyley, L. Daukiya, W. Thielemans, Z. Li, P. Walke, S. Hirose, S. Hashimoto, S. De Feyter, Y. Tobe, *ACS Nano* **2018**, *12*, 11520.
- [4] K. Tahara, Y. Kubo, S. Hashimoto, T. Ishikawa, H. Kaneko, A. Brown, B. E. Hirsch, S. De Feyter, Y. Tobe, *J. Am. Chem. Soc.* **2020**, *142*, 7699.
- [5] Y. Xia, C. Martin, J. Seibel, S. Eyley, W. Thielemans, M. van der Auweraer, K. S. Mali, S. De Feyter *Nanoscale*, **2020**, *12*, 11916.
- [6] M. C. Rodríguez González, A. Brown, S. Eyley, W. Thielemans, K. S. Mali, S. De Feyter *Nanoscale*, **2020**, *12*, 18782.
- [7] M. C. Rodríguez González, A. Leonhardt, H. Stadler, S. Eyley, W. Thielemans, S. De Gendt, K. S. Mali, S. De Feyter, *ACS Nano* **2021**, just accepted (doi: 10.1021/acsnano.1c03373)