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Covalent Functionalization of Surface-Supported Graphene and MoS2: Chemical versus Electrochemical Routes

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Two-dimensional (2D) materials which consist of atomically thin sheets of materials arrived on the scene in early 2000s with the successful isolation of graphene. Graphene is a single atom thick sheet of sp^2-hybridized carbon bonded in a honeycomb lattice. It has exceptional electronic, optical, mechanical and thermal properties that outperform those of most of the existing materials. The research on graphene further prompted emergence of related layered materials such as black phosphorous, silicene, germanene and transition metal dichalcogenides (TMDs) such as MoS_2. Due to their exotic properties, these materials offer virtually endless opportunities for fundamental research as well as cutting edge applications.[1]

Most of these layered materials however exist as single layers only when supported by another solid surface or when stabilized by physisorbed or chemisorbed organic molecules. Given their layered nature, most layered materials are extremely difficult to disperse in typical solvents. Covalent attachment of organic molecules onto their basal plane allows dispersion of these materials in (organic) solvents thereby improving their processability. Such dispersions can be used in composite materials and as functional inks. Moreover, covalent functionalization allows modification of the intrinsic electrical, electronic and optical properties of these 2D materials.[2]

In this contribution, I will discuss covalent modification graphene, graphite and MoS_2 using diazonium chemistry. Two different routes for reductive decomposition of diazonium salts namely, chemical and electrochemical, will be discussed in detail. Special focus is on sub-nanometer characterization of modified materials using scanning tunneling and atomic force microscopy (STM and AFM). The use of covalently modified graphene surfaces as seed layers for atomic layer deposition (ALD) will also be discussed briefly.

References

[1] R. Mas-Balleste, C. Gomez-Navarro, J. Gomez-Herrero and F. Zamora, *Nanoscale* **2011**, *3*, 20-30.
[2] M. Gobbi, E. Orgiu and P. Samorì, *Adv. Mater. 0*, 1706103.