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# (Supra)molecular Approaches to 2D Materials: from Self-Assembly to Molecule-Assisted Liquid-Phase Exfoliation

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Graphene, a one-atom thick two-dimensional (2D) material, is at the core of an ever-growing research effort due to its combination of unique mechanical, thermal, optical and electrical properties. Two strategies are being pursued for the graphene production: the *bottom-up* and the *top-down*. The former relies on the use of covalent chemistry approaches on properly designed molecular building blocks undergoing chemical reaction to form 2D covalent networks. The latter occurs *via* exfoliation of bulk graphite into individual graphene sheets. Amongst the various types of exfoliations exploited so far, ultrasound-induced liquid-phase exfoliation (UILPE) is an attractive strategy, being extremely versatile, up-scalable and applicable to a variety of environments. In this contribution, we highlight the recent developments that have led to successful non-covalent functionalization of graphene and how the latter can be exploited to promote the process of molecule-assisted UILPE of graphite. We also discuss the use of various microscopic (STM, TEM and AFM) and spectroscopic (XPS) techniques, which are key for a profound understanding of the fundamental properties of these (hybrid) materials [1-2].

Major challenge when dealing with graphene, and more generally with 2D materials, is its controlled processing. In particular, graphene has been found to be processable only in a very few solvents; however, re-aggregation into graphitic material occurs even in these special solvents. Nevertheless, combining graphene with suitably designed molecules can hinder such a re-aggregation. The interaction between these two "nano-objects" can be modulated by exploiting a supramolecular approach, the latter relying on the non-covalent functionalization of graphene with small molecular building blocks. Such interaction tailoring can offer substantial advantages in terms of processing of graphene and tunability of the properties of this wonder 2D material, thereby opening novel pathways in various research fields.

The functionalization of graphene with molecules interacting at the non-covalent level, both in dry films as well as in dispersions, has recently gathered a great interest, and the fundamental knowledge of this process has increased substantially. In this contribution, we discuss the principles of the supramolecular approach applied to graphene, which led to the successful modification of graphene properties and enhancement of its production in liquid media. In particular, we discuss the use of molecular self-assembly as a method towards the non-covalent functionalization of graphene. We then describe the UILPE of graphite and methods that are employed for the characterization of graphene produced thereof. We also highlight the importance of microscopic (STM, TEM and AFM) and spectroscopic (XPS) techniques, which allow in-depth understanding of properties of these materials [3-6].

The interaction between 2D nanosheets and molecules is accompanied by an adjustment of the properties of both initial components. Such interaction can occur *via* the physisorption of molecular building blocks through non-covalent interactions or through the chemisorption of reactive species undergoing chemical reactions with graphene to form covalent bonds onto its basal plane. Numerous approaches have been devised to tailor the electronic properties of graphene. In particular, atomic

chemical doping by nitrogen or boron atoms has been proposed as a way to open the band gap and form *p*-type or *n*-type graphene. Nevertheless, the doping is typically difficult to be controlled and frequently introduces defects and thus destroys the band structure. Another approach relies on the covalent modification, where the chemisorbed molecules form chemical bonds with graphene. However, since the covalent bond formation occurs through sp2 to sp3 hybridization, it often leads to undesirable modification or even destruction of the graphene electronic properties. Alternatively, the electronic properties of graphene can be modified by non-covalent functionalization, where the interactions between graphene and adsorbates are dispersive. Following such a strategy the properties that make unique graphene are retained [6].

In summary, in this contribution we will highlight the importance of various microscopic (STM, TEM and AFM) and spectroscopic (XPS) techniques, which are key for a profound understanding of the properties of 2D materials [7].

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