Electrochemical Functionalization of Graphene at the Nanoscale with Self-Assembling Diazonium Salts

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We describe a fast and versatile method to functionalize high-quality graphene with organic molecules by exploiting the synergistic effect of supramolecular and covalent chemistry. With this goal, we designed and synthesized molecules (DBT) comprising a long aliphatic chain and an aryl diazonium salt.

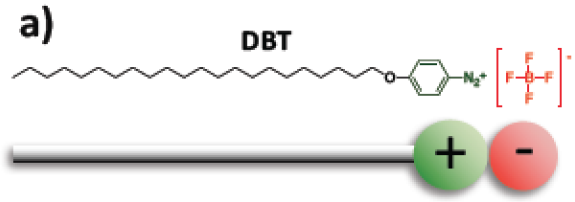
Thanks to the long chain these molecules physisorb from solution onto CVD graphene or bulk graphite, self-assembling in an ordered monolayer. The sample is successively transferred into an aqueous electrolyte, to block any reorganization or desorption of the monolayer. An electrochemical impulse is used to transform the diazonium group into a radical capable of grafting covalently to the substrate and transforming the physisorption into a covalent chemisorption. During covalent grafting in water the molecules retain the ordered packing formed upon self-assembly.

Our two-step approach is characterized by the independent control over the processes of immobilization of molecules on the substrate and their covalent tethering, enabling fast covalent functionalization of graphene. This strategy is highly versatile and works with many carbon-based materials including graphene deposited on silicon, plastic and quartz, as well as highly oriented pyrolytic graphite.[1]

References

1. Z. Xia, F. Leonardi, M. Gobbi, Y. Liu, V. Bellani, A. Liscio, A. Kovtun, R. Li, X. Feng, E. Orgiu, P. Samorì, E. Treossi, V. Palermo. ACS Nano, 10 (2016) 7125.

Figures



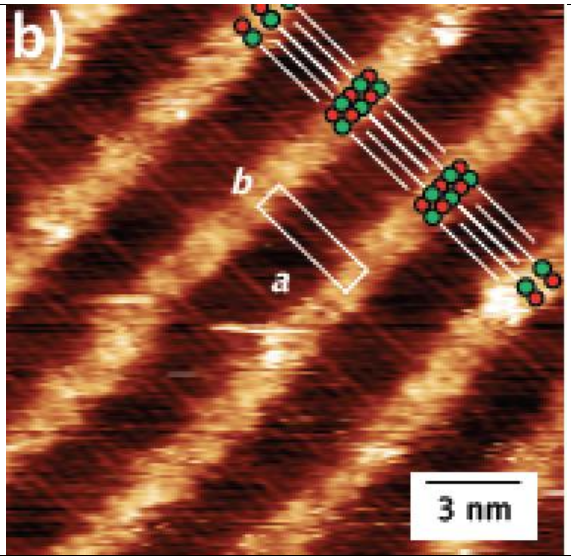


Figure 1: a) Molecular structure of DBT. b) STM image of DBT assembly on graphite.