Covalent functionalization of self-assembled aryl diazonium salts onto high quality graphene by electrochemistry

Z. Xia[1], F. Leonardi[1], Y. Liu[2], M. Gobbi[3], E. Treossi[1], X. Feng[2], E. Orgiu[3],
P. Samorì[3], V. Palermo[1*]

[1] Istituto per la Sintesi Organica e la Fotoreattività - Consiglio Nazionale delle Ricerche, via Gobetti 101, 40129 Bologna, Italy

[2] Max Planck Institute for Polymer Research, Ackermannweg 10, Mainz 55128, Germany

[3] Nanochemistry Laboratory, ISIS & icFRC Université de Strasbourg & CNRS, 8 Allée Monge, 67000, Strasbourg, France

[1*] Istituto per la Sintesi Organica e la Fotoreattività - Consiglio Nazionale delle Ricerche, via Gobetti 101, 40129 Bologna, Italy; E-mail: palermo@isof.cnr.it

Single layer graphene (SLG), a two-dimensional honeycomb structure of carbon atoms, has been widely studied in academia and industry with its fantastic electronic, mechanical, and thermal properties. However, this semi-metal material has some drawback: zero band-gap limited its application in electronic devices. Although thermal or photo-induced [2+1] cycloadditions of graphene with nitrene and carbene intermediates are common approaches for covalent functionalization, the long reaction time and low yield hinders an efficient tailoring of graphene [1,2].

Compared to the above methods, electrochemical grafting of diazonium salt is a well-established functionalization route, which ensures a stable grafting of aryl molecules with short reaction time and high surface coverage [3]. Anyhow, this method has poor spatial control and random deposition of the diazo radicals from the bulk solution. Meanwhile, the active radicals in solution could further react with the grafted aryl molecules on graphene, forming an unavailable multiple poly-aryl layer.

Hereby, we describe a fast, efficient and versatile method combining supramolecular and covalent approaches to functionalize high quality graphene with organic molecules. The rationally designed molecule is an alkylbenzene derivative bearing a long alkyl chain fostering supramolecular array on graphene, and a diazonium salt moiety for successive covalent grafting. First, a thin molecular layer is physically adsorbed on graphene from solution. Then, the sample is transferred in a non-solvent, to fix the molecules on the surface and avoid desorption. Quantitative covalent grafting is finally achieved in a three-electrode setup by applying a negative voltage to the graphene surface (Figure 1). The successful grafting is monitored *in situ* using cyclic voltammetry, and *ex situ* with Raman spectroscopy, atomic force microscopy (AFM) and Kelvin Probe Force Microscopy (KPFM).

References

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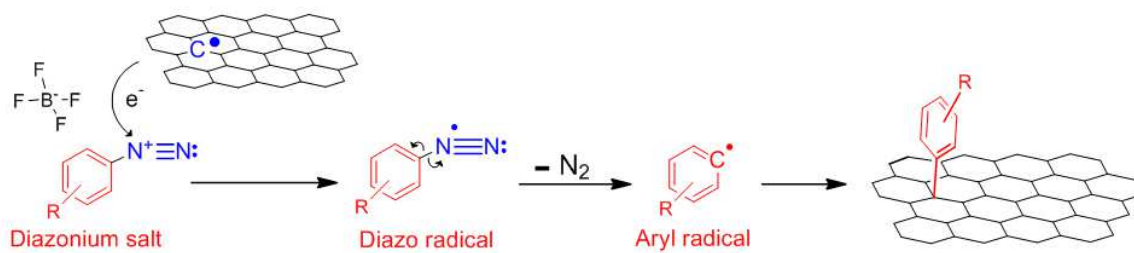
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Figure 1: Synthetic mechanism of the electrochemical reduction of diazonium salt.