

Covalent grafting of self-assembled aryl diazonium salt on graphene via electrochemical reduction

Zhenyuan Xia¹, Francesca Leonardi¹, Marco Gobbi², Yi Liu³, Vittorio Bellani⁴, Andrea Liscio¹, Alessandro Kovtun¹, Rongjin Li³, Xinliang Feng³, Emanuele Orgiu², Paolo Samori², Emanuele Treossi¹, Vincenzo Palermo¹

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

² ISIS & icFRC Université de Strasbourg & CNRS, 8 Allée Monge, 67000, Strasbourg, France

³ Max Planck Institute for Polymer Research, Ackermannweg 10, Mainz 55128, Germany

⁴ Dipartimento di Fisica, Università degli Studi di Pavia via Bassi 6, 27100 Pavia, Italy

zhenyua.xia@isof.cnr.it

Abstract

Hereby, we describe a fast and versatile method to functionalize high-quality graphene with organic molecules by exploiting the synergetic effect of supramolecular and covalent chemistry [1-3]. Towards this goal, we designed and synthesized a molecule comprising a long aliphatic chain and an aryl diazonium salt. These molecules are self-assembled from solution onto graphene, forming an ordered monolayer. Then, the sample is transferred into water, to hinder both the structural reorganization within the monolayer and the molecular desorption (Fig. 1). An electrochemical stimulus is used to transform the diazonium head-group into a radical capable of grafting covalently to graphene. During covalent grafting in water the molecules retain the ordered packing formed upon self-assembly before the covalent linkage.

Our 2-steps approach is characterized by the independent control over the processes of immobilization of molecules on graphene and their covalent tethering, enabling massive and fast ($t < 10$ sec) covalent functionalization of graphene. This strategy is highly versatile: it can be operated using different solvents and on many carbon-based materials including graphene deposited on silicon, plastic, quartz, as well as glassy carbon and highly oriented pyrolytic graphite.

References

- [1] G. L. C. Paulus, Q. H. Wang, M. S. Strano, *Accounts of Chemical Research*, **46** (2013) 160
- [2] J. Greenwood, T. H. Phan, S. D. Feyter et. al, *ACS Nano*, **9** (2015) 5520
- [3] C. Saby, B. Ortiz, G. Y. Champagne, D. Eelanger, *Langmuir* **13** (1997) 6805

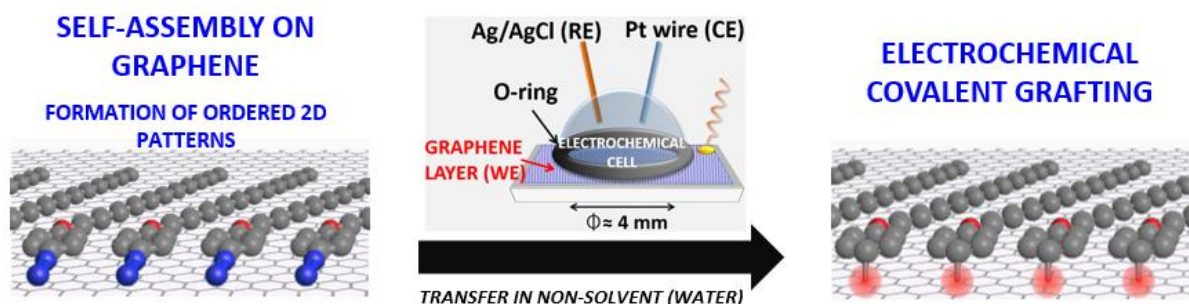


Figure 1. Schematic demonstration of the separate self-assembly and electrochemical bonding steps.