

Grafting Ink for Direct Writing: Solvation Activates Covalent Functionalization of Graphene

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Covalent functionalization of graphene (CFG) is of interest to tune the electronic, mechanical, optical and thermal properties of graphene. However, facile, efficient, and large-scale CFG remains challenging. Herein, we present a diazonium-based grafting ink with high grafting efficiency. The grafting ink consists of only two components, i.e. the diazonium salt and the solvent dimethyl sulfoxide (DMSO). We discuss the mechanism and efficiency of the grafting in terms of the DMSO induced n-doping of graphene, in combination with solvation of the diazonium cations, promoting the electron transfer from graphene to reduce the diazonium cation, while stabilizing the diazonium salt in solution. The grafting density of CFG is controlled by the functionalization time and reaches very high levels of functionalization, up to the failing of the Tuinstra-Koenig (TK) relation,^[1] while the functionalization layer remains at monolayer height. Additionally, the organic-addend group can be readily adjusted by using different diazonium cations in the grafting ink. The grafting ink can be used at ambient conditions and renders the covalent modification of graphene as easy as writing on paper. A combination of this approach with inkjet-printing would allow the direct and spatially selective functionalization of graphene or other 2D materials.^[2]

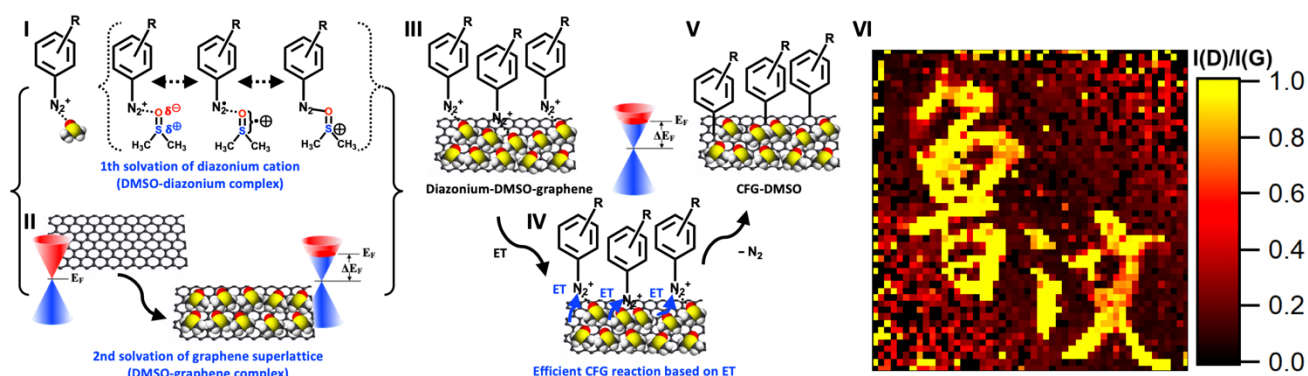


Figure 1. Solvation promotes ET for efficient CFG. I) Solvation of diazonium cation by DMSO based on dipole interaction; II) Solvation of graphene lattice by DMSO based on dipole-induced dipole interaction; III-V) The aryl diazonium-DMSO-graphene interface promotes the EF for CFG; VI) Raman map of the spatially functionalized graphene/SiO₂/Si by direct hand-writing using soft Chinese brush dipped with the grafting ink at ambient condition. Scanning size 1 by 1 cm².

References

- [1] L. G. Cancado *et al.*, *Nano Lett.*, 11(2011), 3190-3196.
- [2] Daryl McManus *et al.*, *Nat. Nanotech.*, 12(2017), 343-350.