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AUGUST 31 - SEPTEMBER 03, 2021 ● ONLINE

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

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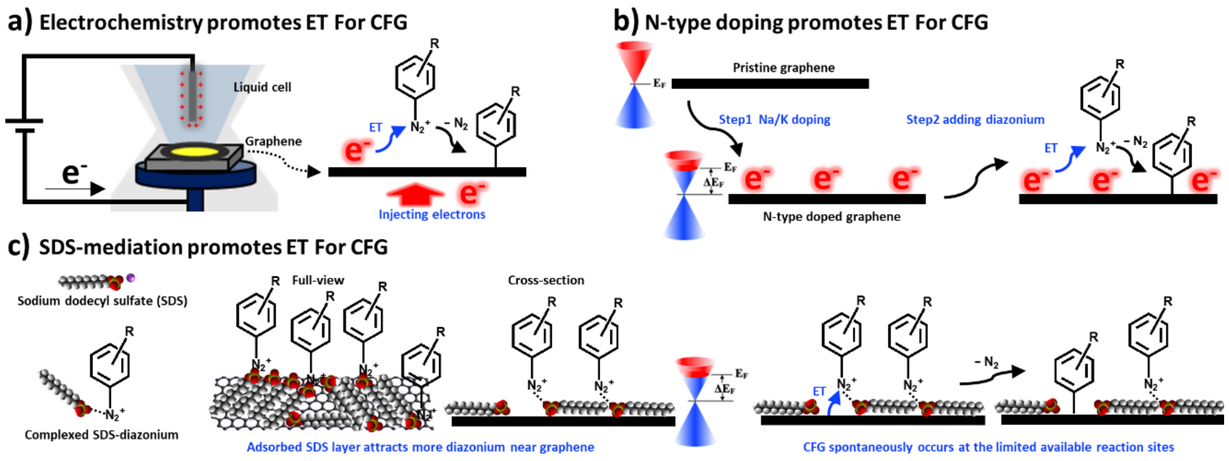
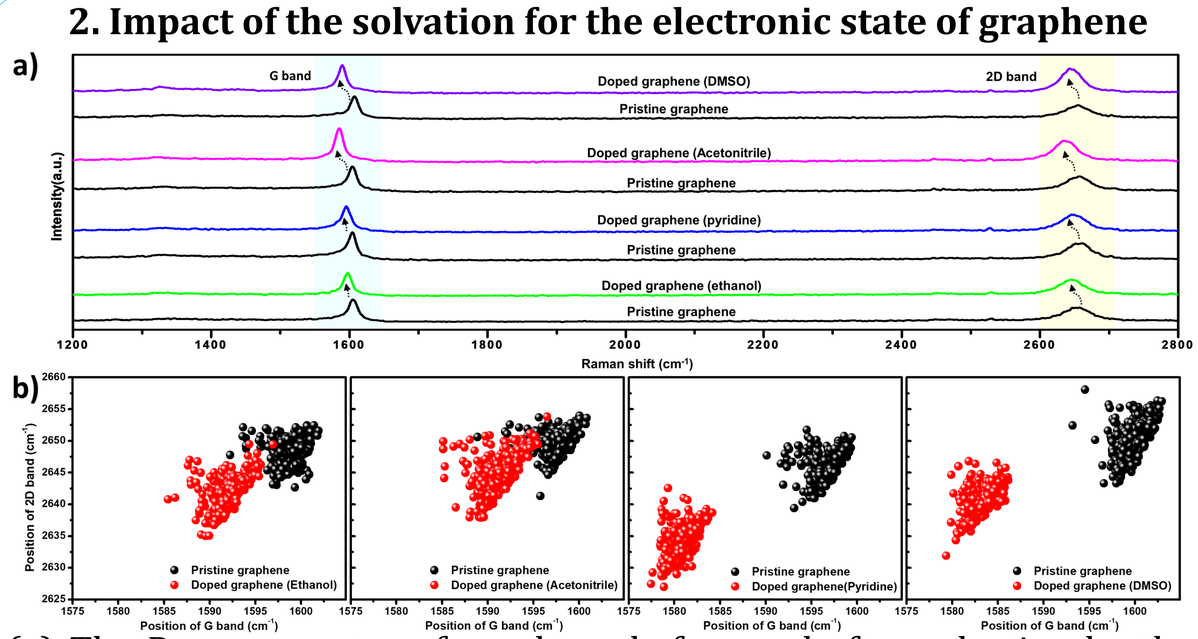
Covalent functionalization of graphene (CFG) has shown attractive advantages in tuning the electronic, mechanical, optical and thermal properties of graphene. However, the facile, large-scale, controllable and highly efficient CFG remains challenging. Therefore, we developed a diazonium-based grafting ink with high grafting efficiency. The grafting ink consists of only two components, i.e. the diazonium salt and the solvent dimethyl sulfoxide (DMSO). 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 (T-K) relation, 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.

1. Background: diazonium-based CFG based on the ET of graphene



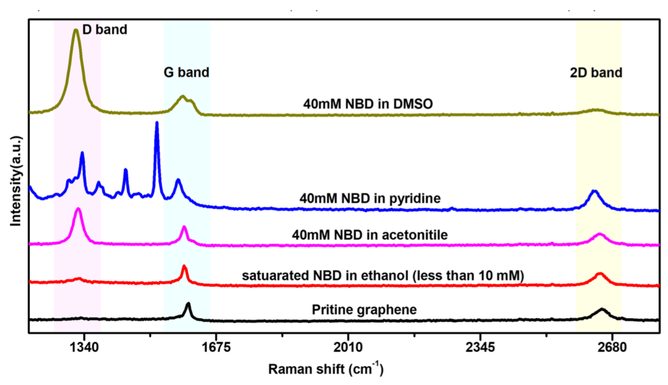
Although these reported strategies realize the CFG based on the electron transfer (ET) of graphene, they all have some intrinsic restrictions. A strategy for the facile, large-scale, controllable and efficient CFG is still urgently needed. **How to easily promote the ET of graphene for CFG?**

2. Impact of the solvation for the electronic state of graphene



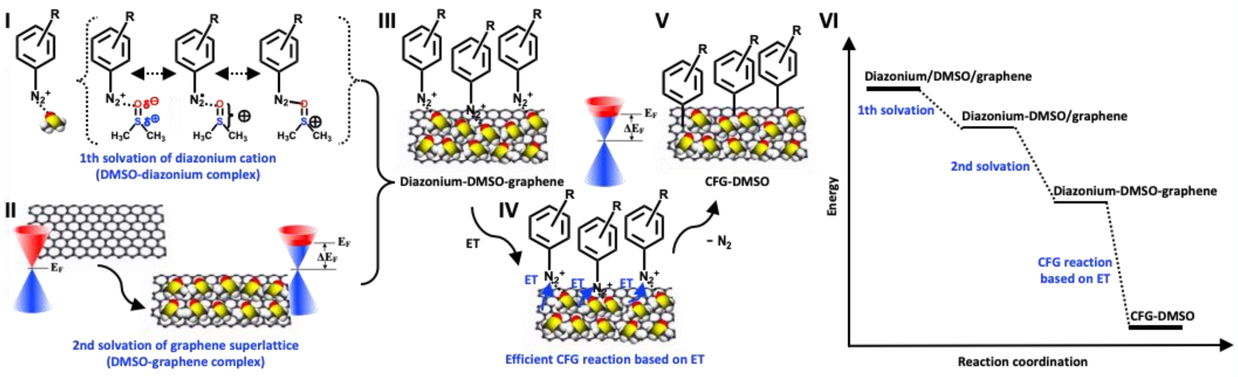
(a) The Raman spectra of graphene before and after solvation by these solvents. (b) The corresponding scattering plots of the G band positions versus the 2D band positions. The down-shifts in band positions reveal polar solvents can induce an n-doped electronic state of graphene by forming a solvation layer on graphene lattice.

3. Impact of the solvent for the diazonium-based CFG



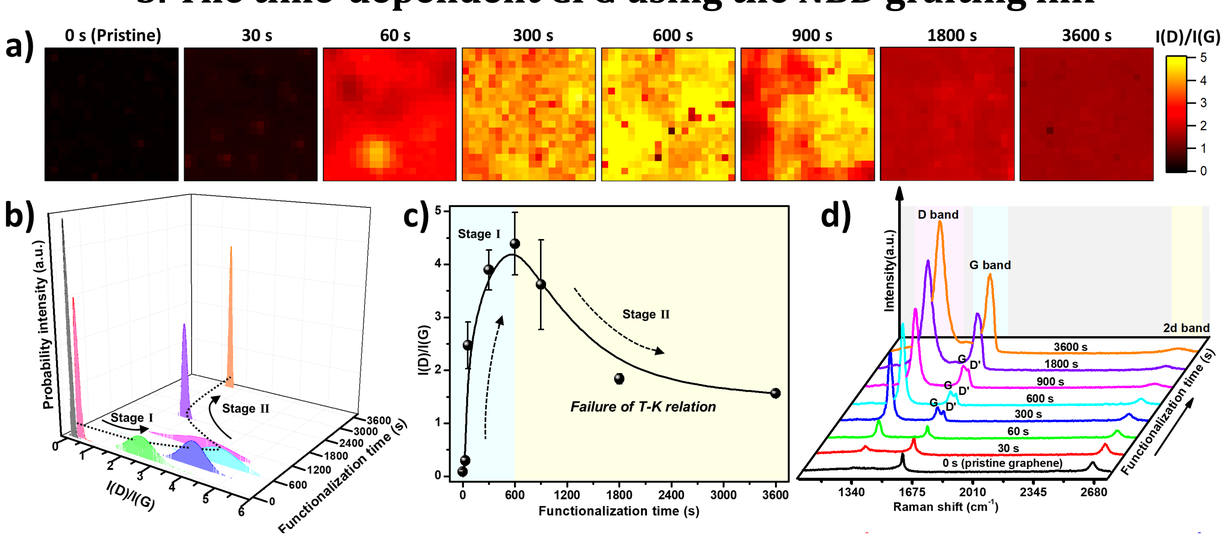
These solvents were used to prepare nitrobenzenediazonium (NBD) solutions. The grafting effect on graphene of these solutions was evaluated by the intensity of D band in the Raman spectra. Typically, the I(D)/I(G) represents the grafting density according to the T-K relation.

4. The reaction mechanism of the CFG



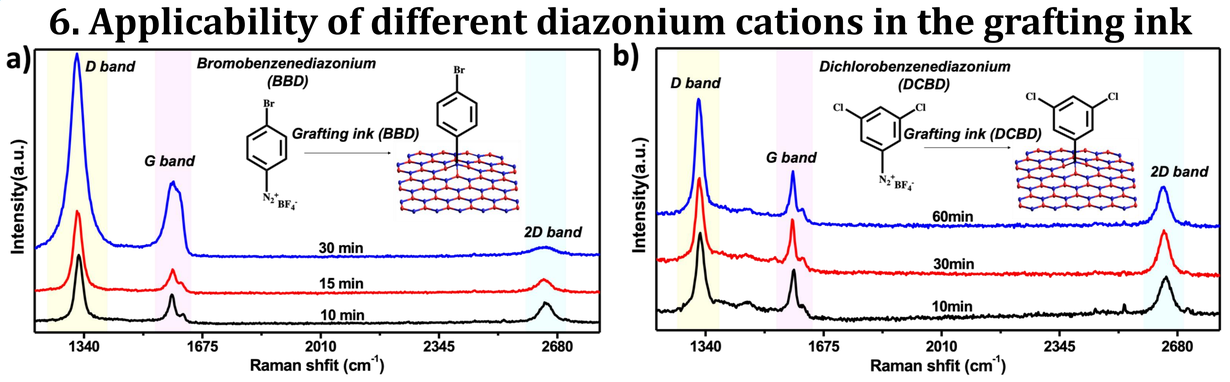
The solvation promotes ET for the CFG, I) Solvation of diazonium by DMSO; II) Solvation of graphene lattice by DMSO; III-V) The grafting ink works at the interface where the diazonium-DMSO-graphene complex formed through the synergetic solvation efficiently promotes the EF for the CFG; VI) The representation of the tentative energy evolution in the functionalization progress.

5. The time-dependent CFG using the NBD grafting ink



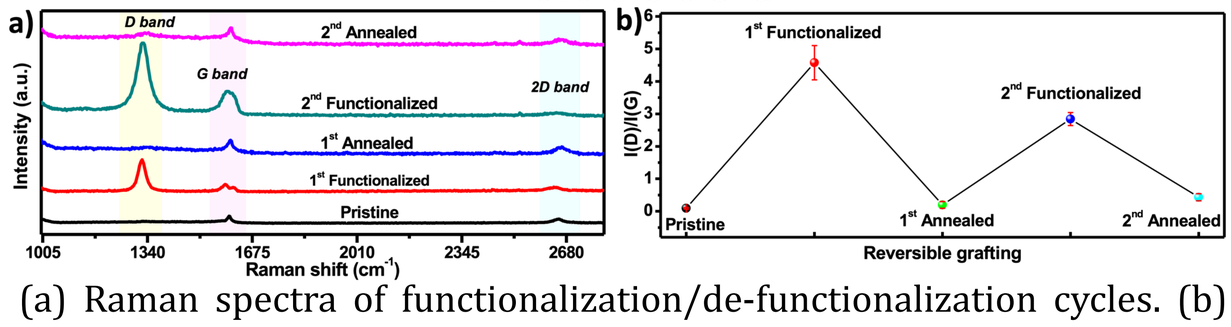
The NBD grafting ink is fixed at 80 mM NBD in DMSO. (a) Raman mappings of I(D)/(G). (b) The I(D)/I(G) distribution for every functionalized graphene for a given functionalization time. (c) The average I(D)/I(G) based on the Raman mapping versus functionalization time. (d) Raman spectra as a function of functionalization time.

6. Applicability of different diazonium cations in the grafting ink



Raman spectra of the graphene functionalized by the (a) BBD and (b) DCBD grafting ink (80mM in DMSO) with different functionalization time.

7. Reversible CFG



(a) Raman spectra of functionalization/de-functionalization cycles. (b) Average I(D)/I(G) at different functionalization/de-functionalization steps. The grafting ink allows for reversible functionalization of graphene.

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Acknowledgement

This work is supported by the Fund of Scientific Research–Flanders (FWO), KU Leuven–Internal Funds, Belgian Federal Science Policy Office (IAP-7/05), and European Research Council under the European Union's Seventh Framework Programme (FP7/2007–2013)/ERC Grant Agreement No. 340324. Y. X. acknowledges financial support from China Scholarship Council.

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