chem2Dmat
AUGUST 31 – SEPTEMBER 03, 2021 ● ONLINE

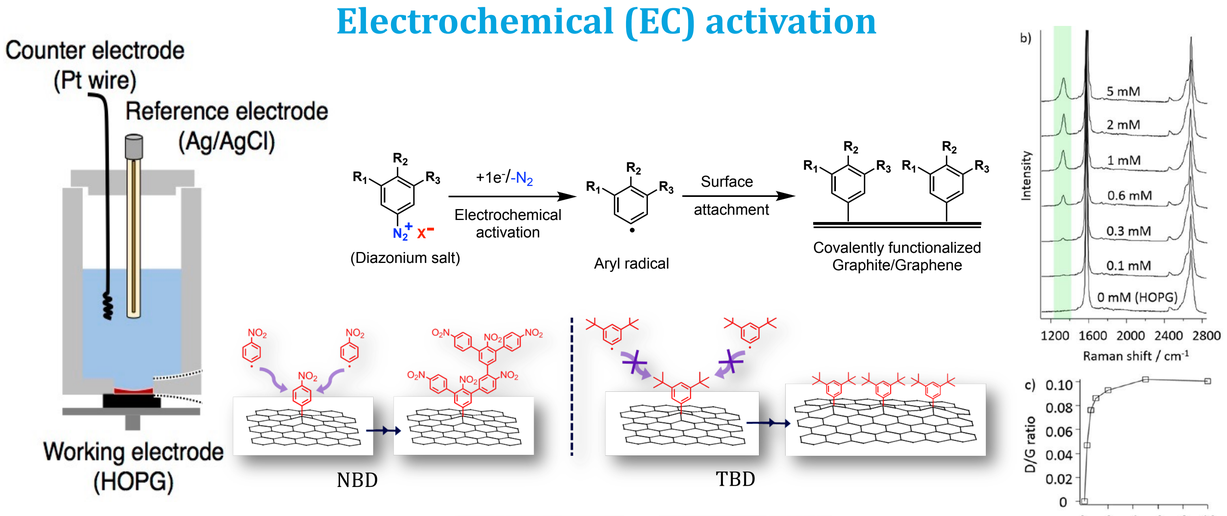
Nanostructured Covalent Functionalization of 2D Materials

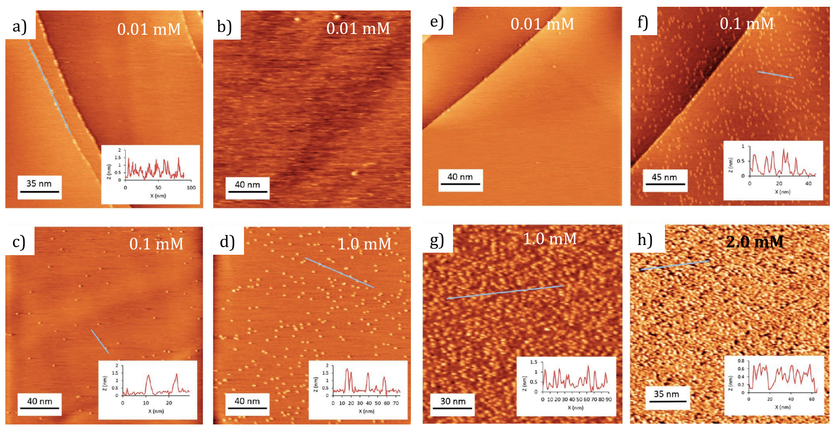
Kunal S. Mali and Steven De Feyter
Division of Molecular Imaging and Photonics, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, Leuven Belgium-3001

The 'graphene rush' that started almost a decade ago is far from over. The dazzling properties of graphene have long warranted a number of applications in various domains of science and technology. Harnessing the exceptional properties of graphene for practical applications however has proved to be a massive task. Apart from the challenges associated with the large-scale production of the material, the intrinsic zero band gap, the inherently low reactivity and solubility of pristine graphene preclude its use in several high- as well as low-end applications. One of the potential solutions to these problems is the surface functionalization of graphene using organic building blocks. The 'surface-only' nature of graphene allows the manipulation of its properties not only by covalent chemical modification but also via non-covalent interactions with organic molecules. Significant amount of research efforts have been directed towards the development of functionalization protocols for modifying the structural, electronic, and chemical properties of graphene. Here we present an overview of different experimental strategies aimed at achieving nanostructured functionalization/chemical patterning of graphite/graphene substrates using covalent functionalization protocols.

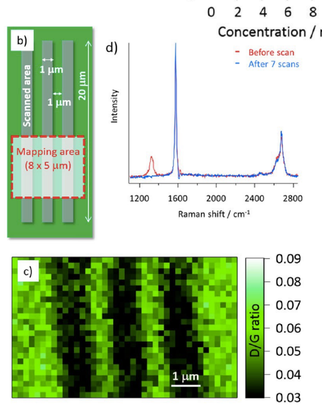
Covalent Modification using Diazonium Chemistry

Electrochemical (EC) activation





Concentration dependent covalent modification of graphite using diazonium chemistry. (a-d) NBD and (e-h) TBD. It can be readily noticed from this STM data that efficiency of covalent modification is superior for TBD

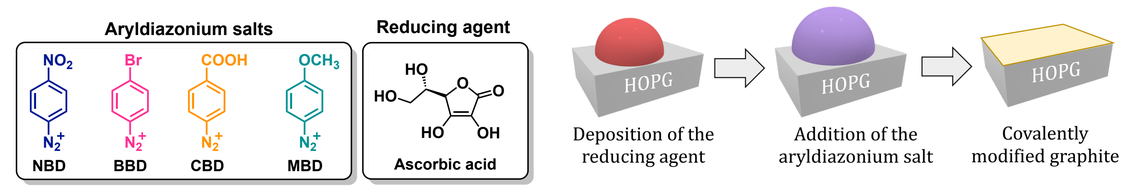


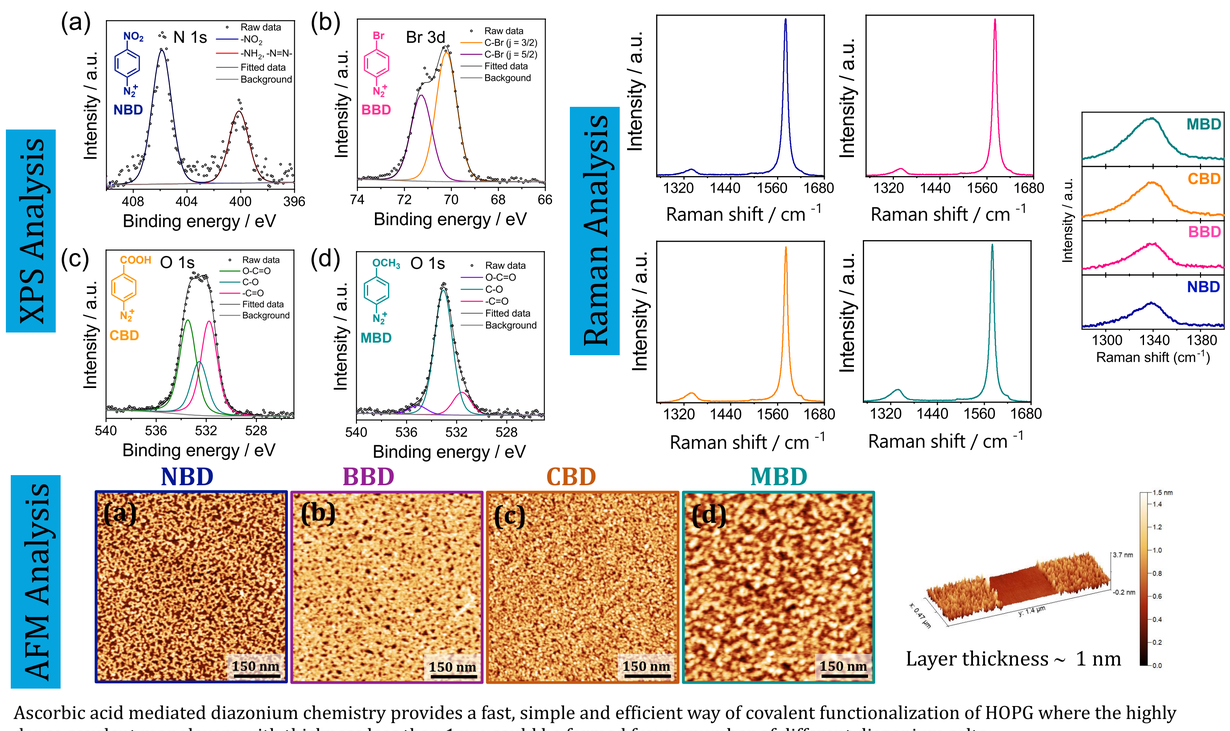
Tip-induced de-grafting of covalently modified HOPG. Raman maps show that Upon de-grafting the surface reverts back to pristine graphene.

Greenwood et al. ACS Nano, **2015**, *9* , 5520

Covalent Modification using Self-Limiting Diazonium Chemistry

Chemical activation



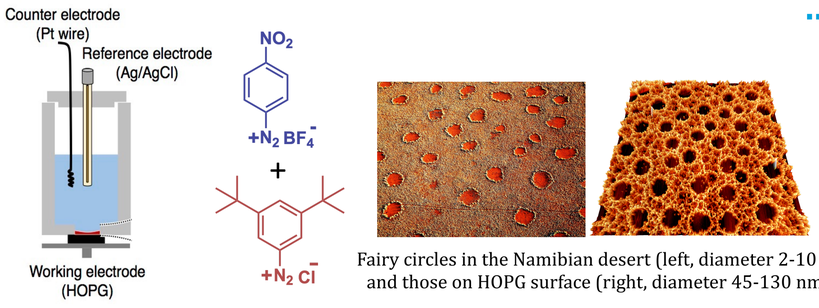


Ascorbic acid mediated diazonium chemistry provides a fast, simple and efficient way of covalent functionalization of HOPG where the highly dense covalent monolayers with thickness less than 1 nm could be formed from a number of different diazonium salts.

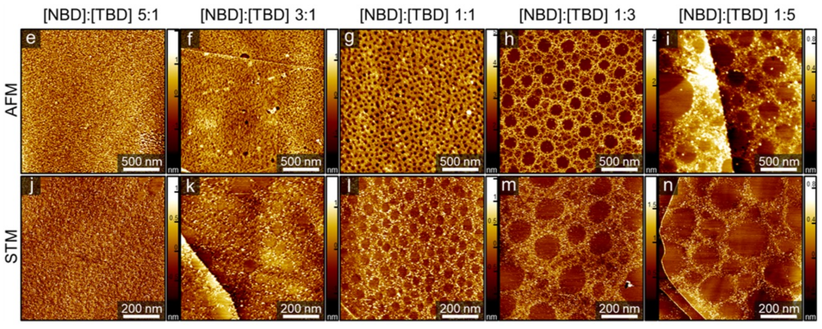
Rodríguez González et al. Nanoscale, **2020,** *12, 18782*

Covalent Chemical Patterning using Diazonium Chemistry from Micro- to Nanometer scale

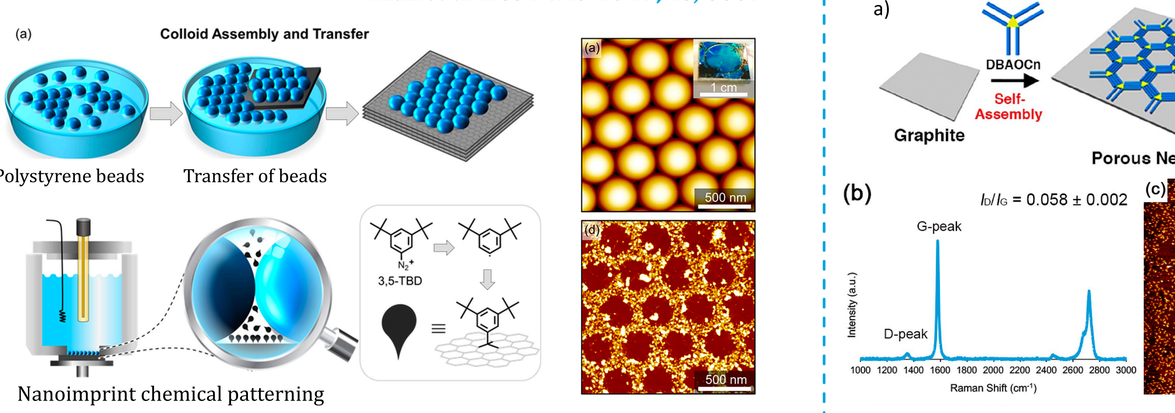
.....and from monocomponent to multicomponent



Fairy circles in the Namibian desert (left, diameter 2-10 m) and those on HOPG surface (right, diameter 45-130 nm)



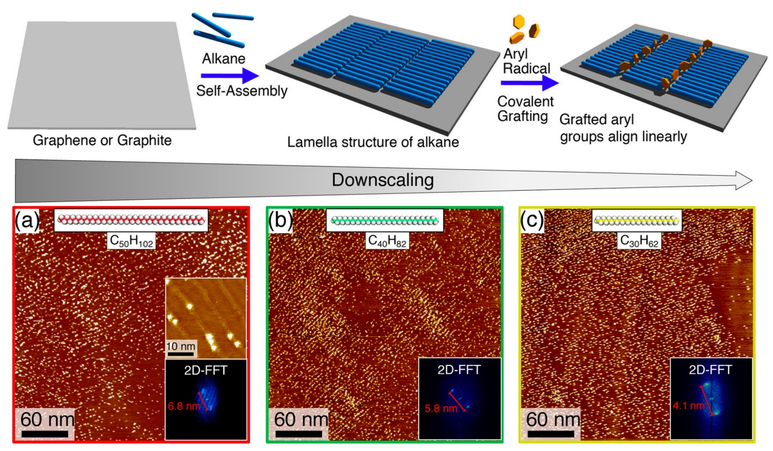
Phan *et al. ACS Nano* **2019,** *13,* 5559



Van Gorp *et al. ACS Appl. Mater. Interfaces* **2018,** *10,* 12005

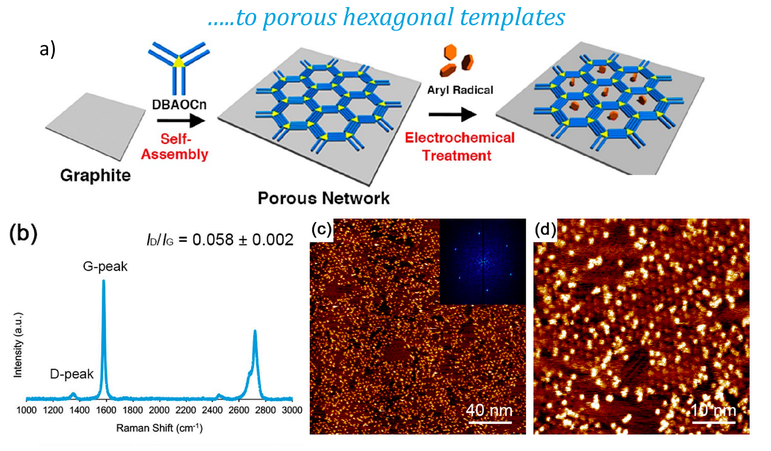
Use of self-assembled monolayers as templates for chemical patterning

From linear templates.....



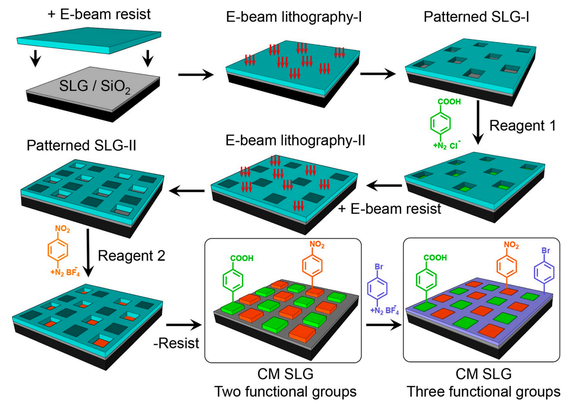
Tahara *et al. ACS Nano* **2018,** *12,* 11520

.....to porous hexagonal templates

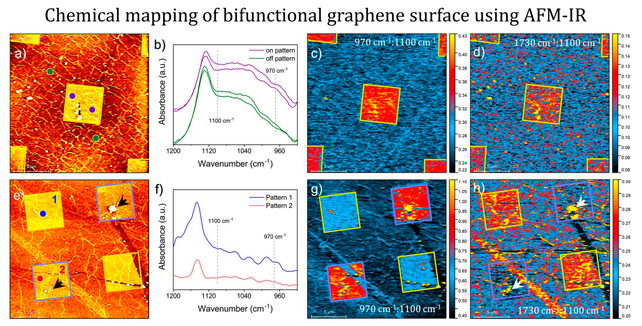


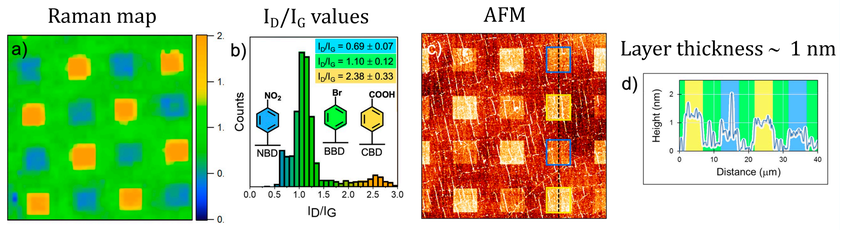
Tahara *et al. J. Am. Chem. Soc.* **2020,** *142,* 7699

Multicomponent covalent chemical patterning of single layer graphene



Chemical mapping of bifunctional graphene surface using AFM-IR





Rodríguez González et al. ACS Nano, **2021,** *15,* 10618

CONTACT PERSON

Kunal S. Mali:
Kunal.Mali@kuleuven.be

Steven De Feyter
steven.defeyter@kuleuven.be

REFERENCES

1. Greenwood *et al. ACS Nano* **2015,** *9,* 5520–5535.
2. Rodríguez González *et al. Nanoscale,* **2020,** *12,* 18782.
3. Phan *et al. ACS Nano* **2019,** *13,* 5559.
4. Van Gorp *et al. ACS Appl. Mater. Interfaces* **2018,** *10,* 12005.
5. Tahara *et al. ACS Nano* **2018,** *12,* 11520.
6. Tahara *et al. J. Am. Chem. Soc.* **2020,** *142,* 7699.
7. Rodríguez González *et al. ACS Nano* **2021,** *15,* 10618

ACKNOWLEDGEMENT

We thank all the co-authors of the original work. We also acknowledge the fruitful collaboration with the groups of Prof. Yoshito Tobe (Osaka University), Prof. Kazukuni Tahara (Meiji University) and Prof. Stefan De Gendt (IMEC, KU Leuven). Financial support from FWO under EOS 30489208.

chem2Dmat
AUGUST 31 – SEPTEMBER 03, 2021 ● ONLINE