

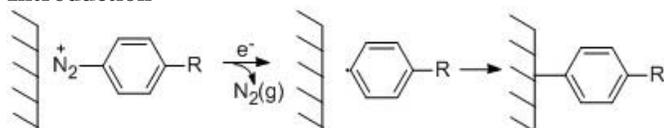
## Chemical modifications of graphene using diazonium chemistry

Mikkel S Kongsfelt<sup>1</sup>, Marcel Cecato<sup>1</sup>, Louis Nilsson<sup>2</sup>, Bjarke Jørgensen<sup>2</sup>, Liv Hornekær<sup>2</sup>, Steen U. Pedersen<sup>1</sup> and Kim Daasbjerg<sup>1</sup>

<sup>1</sup>Department of Chemistry, Aarhus University, 8000 Aarhus C, Denmark

<sup>2</sup>Department of Physics and Astronomy and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, 8000 Aarhus C, Denmark

### Introduction



**Scheme 1.** General scheme for the grafting of aryl diazonium salts on a substrate.

Graphene is being intensively investigated due to its interesting properties such as high mechanical strength, conductivity and optical transparency. Modifications of graphene resulting in defects in the otherwise perfect  $sp^2$ -character of the graphene have been shown to open up a bandgap[1]. This makes graphene really interesting for new electronic devices with higher efficiency.

These types of modifications of graphene will enable scientists to engineer the properties of graphene to a specific purpose, but this will require a broad spectrum of tools to modify graphene. One of these tools might be the use of aryl diazonium salts as grafting agents.

Aryl diazonium salts are grafted according to the general Scheme 1[2]. The diazonium salt is reduced by a one electron reduction liberating nitrogen gas and forming a reactive aryl radical that will immediately react with the surface. The reduction of the diazonium salt is so favorable a process that on many substrates it will happen spontaneously[3].

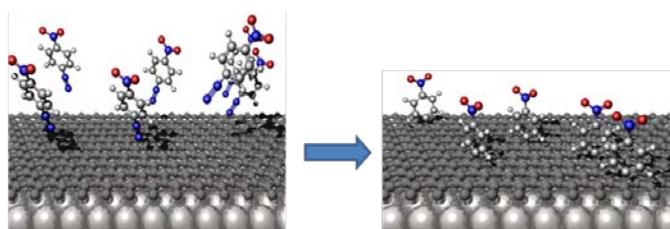
It has been shown both theoretically and experimentally that graphene in different forms can be grafted by the use of diazonium salts[4-6]. It is clear though that the conditions on which the graphene is produced will have an effect on the reactivity. The reactivity of epitaxial graphene on different substrates might differ highly in reactivity and the number of graphene layers has clearly been shown to be important[6].

### Experimental

Epitaxial graphene was grown on single crystal silicon carbide by vacuum graphitization.[7-8]

The epitaxial graphene was grafted by immersion into a 10 mM solution of nitro phenyl diazonium salt and 0.1 M tetrabutyl ammonium tetrafluoroborate for several hours. As a

result the surface was modified as shown in Scheme 2 by spontaneous grafting of the aryl radicals.

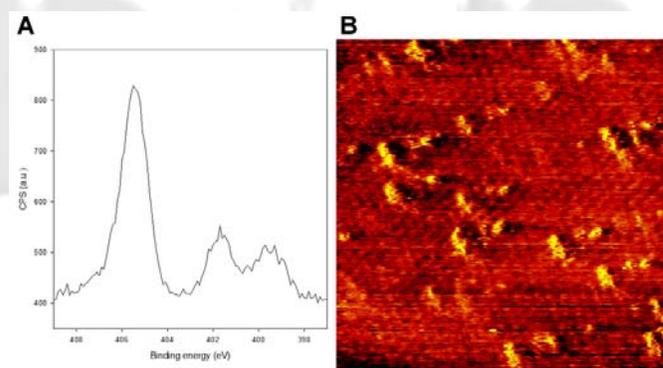


**Scheme 2.** Grafting of nitro phenyl diazonium salt on an epitaxial graphene surface.

### Results and discussion

The high resolution XPS spectrum for N1s in Fig. 1 shows the presence of several types of nitrogen. Undoubtedly, the N1s peak at 406 eV corresponds to that of nitrogen in a nitro group[9-10]. The two minor peaks around 400 eV could originate from partially reduced nitro groups (i.e. hydroxylamino or amino groups)[9-10] or azo groups[11-13].

The samples were further analyzed by STM and with the grafting times applied it was evident that only a moderate coverage of the graphene in small islands was achieved in agreement with earlier results on HOPG surfaces[14]. These results indicate that the grafting of graphene is initiated randomly, maybe at defects or by dimer formation as depicted by Jiang et al. [5].



**Fig. 1** A: High resolution N1s XPS spectrum showing at least three nitrogen species at 406 eV, 402 eV and 399 eV. B: STM image of nitro grafted epitaxial graphene on SiC, scale 500 x 500  $\text{\AA}^2$ .

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