

Insights into the chemical modification of graphene using diazonium salts

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Graphene is an intensively investigated material due to its engaging properties like 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 result makes graphene particularly interesting for new, highly efficient electronic devices.

Such graphene modifications will enable scientists to engineer the properties of this material in order to attend to specific purposes. However, this ambition requires a broad spectrum of tools. One of these might be the use of aryl diazonium salts as grafting agents. Generally, a diazonium salt is reduced by a one-electron reduction liberating nitrogen gas and forming a reactive aryl radical which immediately reacts with the surface [2]. The reduction of the diazonium salt is such a propitious process, that on many substrates it will appear spontaneously [3].

It has been shown, both theoretically and experimentally, that graphene, in different forms, can be grafted by the use of diazonium salts [4-7]. Thus, the conditions in which the graphene is produced will have an effect on its reactivity. Indeed, the reactivity of epitaxial graphene on different substrates might largely differ and the number of graphene layers was shown to be important [6].

In this contribution we discuss the reactivity of 4-nitrobenzenediazonium on epitaxial graphene. Epitaxial graphene was grown on single crystal silicon carbide by vacuum graphitization [8-9], and then grafted by immersion into a solution of 4-nitrobenzenediazonium salt for different grafting time periods. As a result, the surface was modified [Figure 1] by spontaneous grafting of the aryl radicals. The high resolution XPS spectrum for N1s [Figure 2] shows the presence of several types of nitrogen. Undoubtedly, the N1s peak at 406 eV corresponds to that of nitrogen in a nitro group [10]. The two minor peaks around 400 eV could originate from partially reduced nitro groups (i.e. hydroxylamino or amino groups) [10-11] or partially reduced azo groups [11-13]. Thereafter, the samples were further analyzed with STM and, considering 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].

References

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Figures

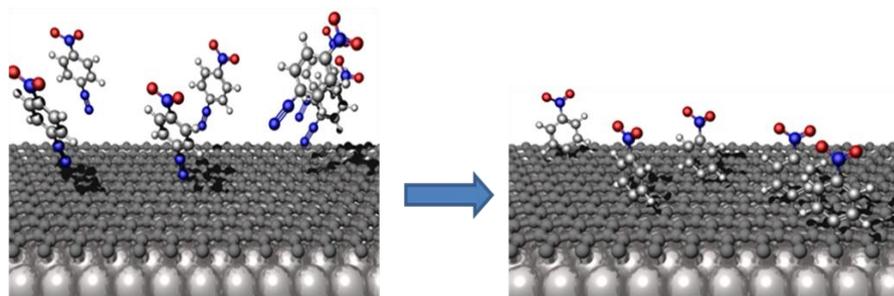


Figure 2. Schematic illustration of the grafting of 4-nitrobenzenediazonium salt on an epitaxial graphene surface.

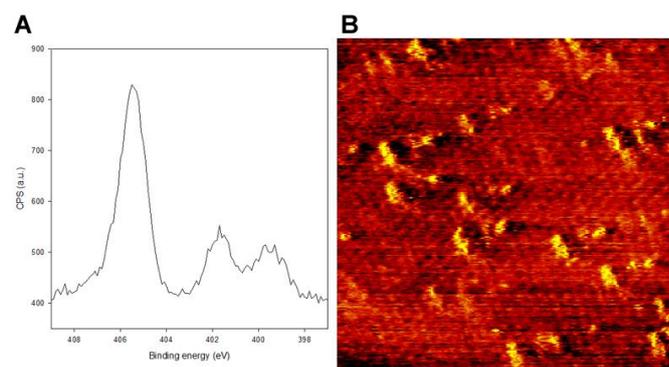


Figure 2. A: High resolution N1s XPS spectrum showing at least three nitrogen species at 406 eV, 402 eV and 399 eV. B: STM image of nitro grafted epitaxial graphene on SiC, scale 500 x 500 Å².