

Organic functionalization of Epitaxial Graphene on SiC

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A truly developed carbon-based nanoelectronics requires, among other features, low price, large production scale, large domain area and high crystalline quality. Epitaxially grown graphene on silicon carbide (SiC) can meet all of these requirements^[1]. Moreover, functionalization of graphene is expected to be an important step for development of graphene-based materials with tailored features, due to the possible control of optical and electronic properties^[2,3].

However, the high chemical inertness of graphene makes it difficult a covalent and controlled functionalization with organics. Most of the works performed until now involve either controlled adsorption of low-interacting molecular structures or unruly functionalization. In this work, we target to develop new strategies for controlled covalent anchoring of the organic molecules to the graphene lattice that can be used either to modify their properties or as a link for anchoring larger nanostructures.

In our experiment, high quality graphene was epitaxially grown on a 4H-SiC(0001) substrate with n-type doping character by chemical vapor deposition (CVD) at 1600°C under an argon (Ar) laminar flow in a hot-wall Aixtron VP508 reactor. The graphene produced by this method is much less sensitive to SiC surface defects, resulting in higher electron mobility than those grown by Si sublimation process. For epitaxial CVD growth, we formed an Ar boundary layer thick enough to prevent Si sublimation, but allowing for the diffusion of propane gas that was led into the reactor as the precursor which enables the controlled synthesis of a precisely determined number of graphene layers.

The functionalization protocols have been performed in ultra high vacuum, and we have chosen p-aminophenol organic molecules because they include two functional groups: amine and hydroxyl, allowing us to determine which one is more prone to make a bond with graphene. Prior and upon adsorption, the surfaces have been studied in-situ using several techniques, as low-energy electron diffraction (LEED), scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). Moreover, several aspects of the system have been theoretically investigated by first-principles density functional theory calculations (DFT).

Making use of atomic-resolved STM images (see figure), XPS spectra, LEED analysis and DFT calculations, we have demonstrated that we can form chemical bonding of this molecule in two different configurations. In the first the amine group loose one of the H atoms and bond by the nitrogen to the carbon. In the second the hydroxyl group dehydrogenates and reacts with the surface. We show that about 67% of the adsorbed p-aminophenol molecules were covalently bound by the nitrogen, while the other 33% by the oxygen atom.

References

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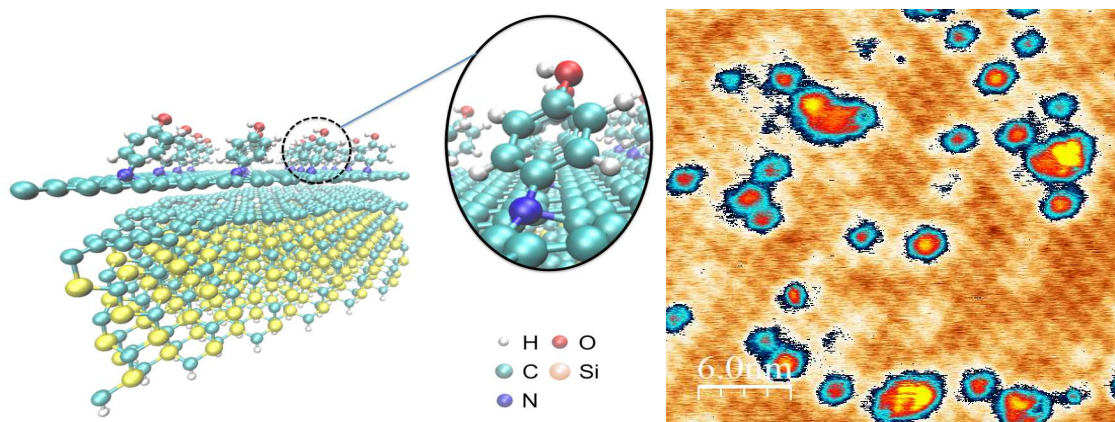


Figure 1: (left) DFT calculation of the adsorption geometry of p-aminophenol on graphene. We show the molecule on the graphene network covalently bound by a nitrogen atom. (right) STM image after our coupling protocol. We observe bumps with different heights corresponding to the molecules absorbed either by N or O on the monolayer graphene in a $(6\sqrt{3}\times 6\sqrt{3})R30^\circ$ (buffer layer) configuration.