

Thermally activated chemical functionalization of graphene under ultra-high vacuum conditions

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Abstract

Although there are multiple reactions available to form carbon-carbon bonds at the graphene basal plane, many of these pathways rely on electron transfer between the graphene sheet and the reactant molecule. The distribution of electron-hole puddles in graphene grown on either SiC or metallic substrates has, consequently, been shown to have a large effect on the success of many of these reactions, in particular reactions involving diazonium salts. In an attempt to circumvent the influence of electron-hole puddles, here we introduce a thermally activated reaction, namely the decomposition of triazenes, to form carbon-carbon bonds at the graphene surface.

All experiments were conducted under ultra-high vacuum ($2E-10$ mbar) and the reaction steps were followed using a combination of scanning tunneling microscopy and mass spectrometry. Graphene samples were prepared by chemical vapor deposition upon an Ir(111) surface. Triazene molecules, prepared locally, were deposited onto the graphene surface under vacuum and heated until decomposition. This *in situ*, surface-science approach gives a unique insight into the details of the reaction between the aryl radicals and the carbon surface. Indirect evidence from the STM shows that the graphene basal plane was successfully functionalized.