

Chemical reactions on nanostructured supported graphene analyzed by DFT calculations

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A paradigmatic example in which the presence of the supporting substrate influences the properties of graphene is offered by the graphene/Ru(0001) interface. The lattice mismatch between the two systems gives rise to a strong corrugation in graphene, that exhibits a moiré pattern and dramatic variations of the graphene-metal interaction at the nanometer scale, which leads to a strong modulation of the electronic properties. Moreover, graphene has the capability to efficiently isolate further adsorbed molecules from the highly reactive metal surface. This fact has been explored in the past, when the graphene/Ru(0001) interface has been used as an adsorption template for organic molecules, at the single molecule level [1] or upon formation of a molecule monolayer [2]. A natural development is determining the role of supported graphene as a catalytic agent, studying the chemical reactions that may take place when multiple molecular species are adsorbed on the graphene/Ru(0001) surface. In this work we try to get insight into this argument, studying the adsorption of a TCNQ molecule on a graphene/Ru(0001) surface, previously functionalized with CH₂-CN radicals. By means of Density Functional Theory (DFT) calculations we determine the optimal geometric configuration of the two molecules on the surface and identify the new molecular specie found in the scanning tunneling microscopy (STM) measurements. Our calculations suggest the formation of TCNQ-CH₂CN, in which the two molecules are bonded by means of a C-C covalent bond. By a combined DFT-STM study we also characterize the newly formed system, identifying, for example, the charge transfer between the substrate and the new molecule, and assigning the scanning tunneling spectroscopy peaks to specific projected density of states features.

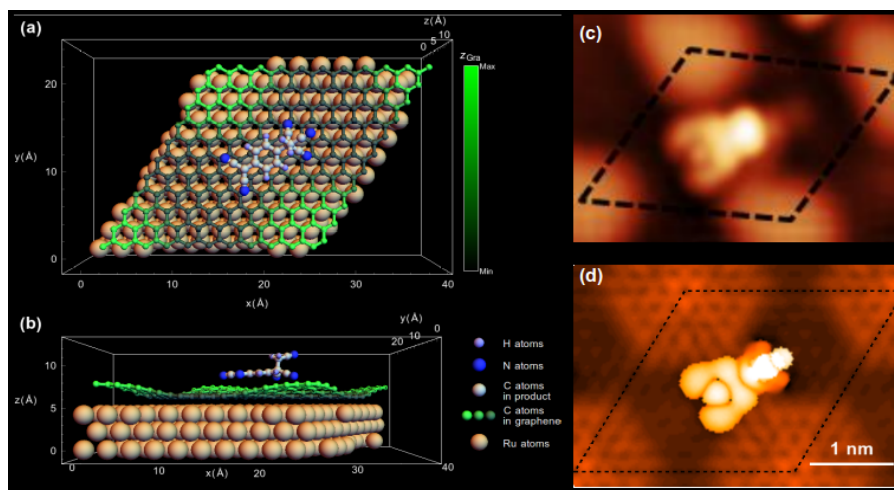


Fig. 1. (a,b) Top view (a) and side view (b) of the unit cell including the ruthenium substrate, the corrugated graphene and the TCNQ-CH₂CN molecule used in the DFT calculations. (c-d) STM images of the TCNQ-CH₂CN on the surface, as obtained in the STM measurements (c) and in the DFT simulations (d).

References:

- [1] M. Garnica et al., NanoLett. 14, 4560 (2014)
- [2] M. Garnica et al., Nature Phys. 9, 368 (2013)