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Atomic-scale functionalization of metal-supported graphene: Towards a graphene-based catalyst

Graphitic carbon structures are usually a major obstacle for catalytic processes on transition metals. Due to their chemical inertness, carbon deposits physically block the surface active sites poisoning the catalytic reaction. In principle the effect is more pronounced as the amount of carbon increases, where an extreme scenario would be case of a complete graphene layer. However, as we demonstrated in a recent work, nanostructured graphene on Ru(0001) can be covalently functionalized employing CH2CN• radicals [1], obtaining an extremely high yield and site-selectivity down to the atomic scale [2]. On the other hand, we also know that TCNQ molecules become radicals upon adsorption on gr/Ru(0001) due to a well known charge transfer process [3]. In this work we show that TCNQ molecules can react with the previously attached -CH2CN groups on gr/Ru(0001) forming a new C-C bond, in a chemical reaction promoted by graphene [4]. We study this reaction by means of Scanning Tunnelling Microscopy (STM) and Density Functional Theory (DFT). We also demonstrate that the whole process can be reversed using STM manipulation techniques.

References

[1] J.J. Navarro et al. *Nano Lett.* **16**, 355-361 (2016)
[2] J.J. Navarro et al. *Chem. Commun.* **53**, 1041-10452 (2017)
[3] M. Garnica et al. *Nat. Phys.* **9**, 368 (2013)
[4] J.J. Navarro et al. *Sci. Adv.* 4, (2018)

Figures

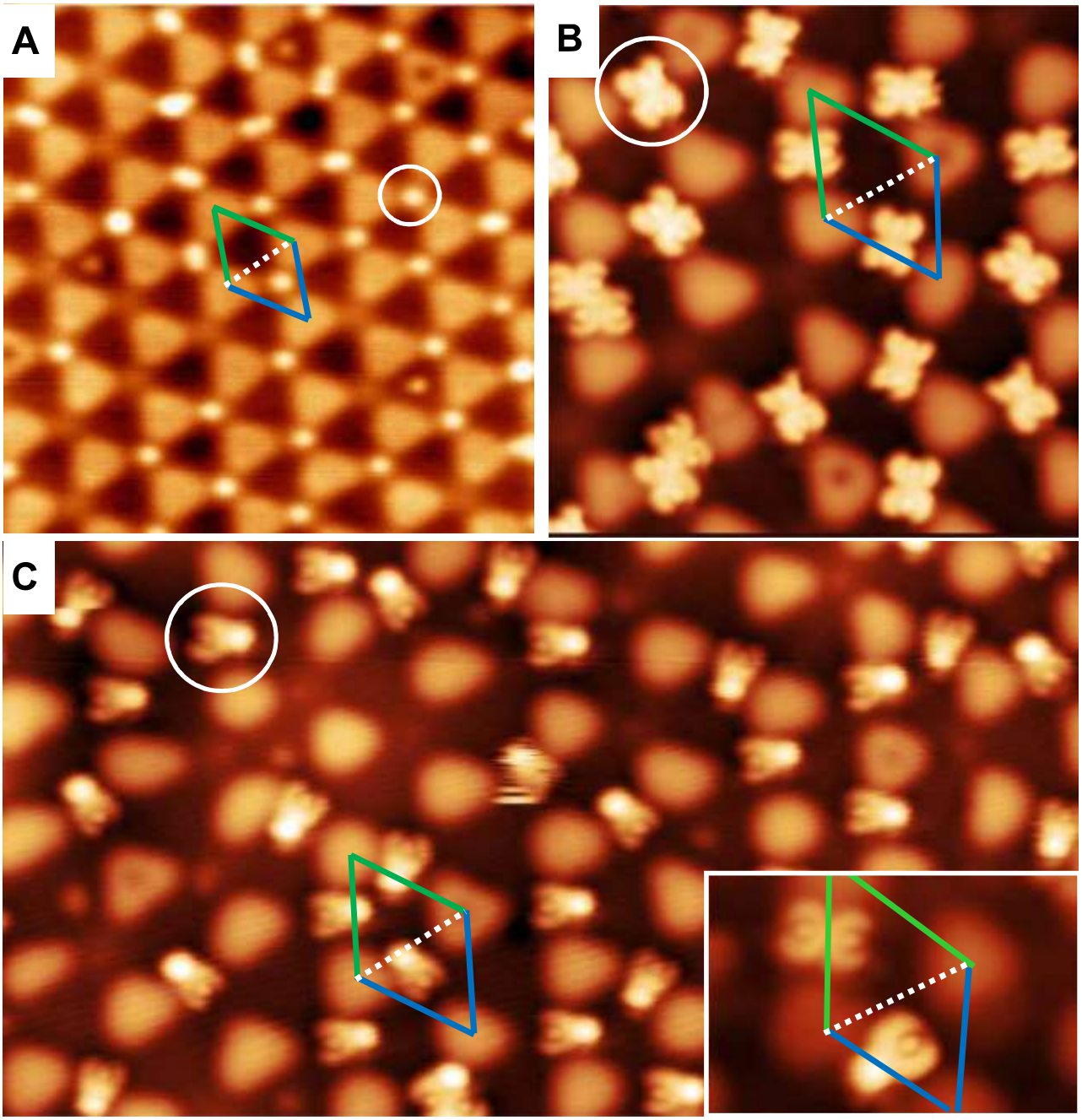

Figure 1: STM images of the gr/Ru(0001) surface functionalized with −CH2CN groups (panel A), covered by TCNQ molecules (panel B) and after the reaction between −CH2CN and TCNQ (panel C). The inset in panel C shows a small area containing a pristine TCNQ and a reacted one. In all cases the moiré cell of gr/Ru(0001) is indicated by the green-blue triangles.