

First-principles study of nickel reactivity under 2D cover: Ni_2C formation at the graphene/ $\text{Ni}(111)$ interface

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Abstract

Recent experiments indicate that the reactivity of metal surfaces changes profoundly when covered with two-dimensional (2D) materials. This has been attributed to the combined electronic effect and geometry constraints imposed by the 2D cover. Nickel, the widespread catalyst choice for graphene (G) growth, displays complex structural changes during and upon G sheet formation. Following the evidence from state-of-the-art experiments, we constructed two structural models of G/ $\text{Ni}(111)$ interface (1) EG/ $\text{Ni}(111)$, where EG indicates G epitaxially aligned with nickel, and (2) RG/ $\text{Ni}(111)$ where RG indicates rotated G domains (Figure 1). Then, by applying density functional theory, we illuminated the microscopic mechanisms governing the formation of stable nickel structures rich in subsurface carbon [1]. We confirmed that nickel carbide (Ni_2C) forms under RG and revealed the essential role of the rotation in enabling high density of favorable C binding sites at the $\text{Ni}(111)$ surface. The high coverage of subsurface carbon makes the carbide phase thermodynamically advantageous over C-covered metal layers and gives rise to the formation of Ni_2C monolayer [2]. At variance with RG, the EG locks the majority of favorable C binding sites thus preventing the build-up of C density to a phase transition threshold. Therefore, we showed that the conversion of Ni surface to Ni_2C occurs exclusively under RG, in line with the strong experimental evidence [3]. This work is funded by grants from the Italian Ministry of Foreign Affairs and International Cooperation and the University of Trieste (FRA2018).

References

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- [2] L. Patera et al, *ACS Nano* **7** (2013) 7901
- [3] C. Africh et al, *Sci. Rep.* **6** (2016) 19734

Figures

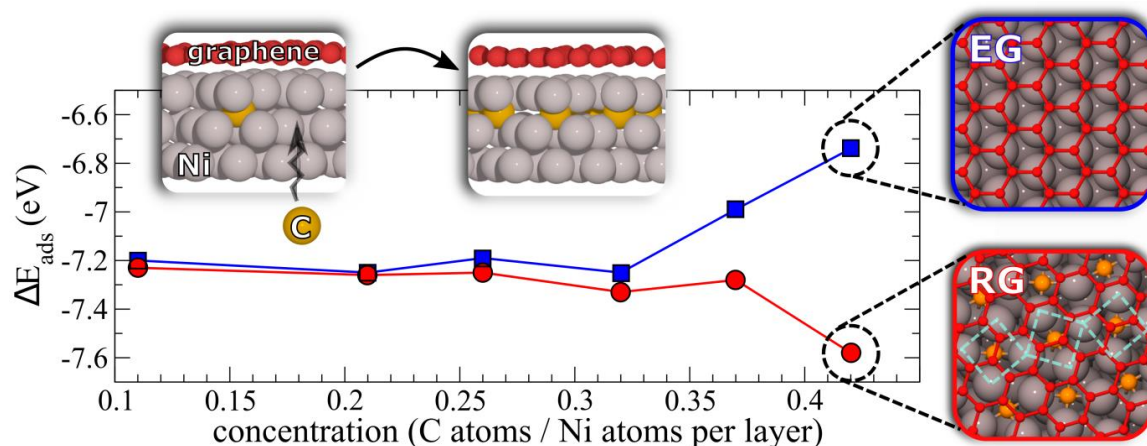


Figure 1: Differential adsorption energy (ΔE_{ads}) for the addition of subsurface C atoms in EG/ $\text{Ni}(111)$ (blue) and RG/ $\text{Ni}(111)$ (red). Carbide “clock” structure in RG/ $\text{Ni}(111)$ interface is emphasized with dashed light blue squares in the lower right corner.