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Fundamental Research Insights

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TOWARDS SYNTHESIS AND CHARACTERIZATION OF HETEROGENEOUSLY DOPED GRAPHENE NANOSTRUCTURES

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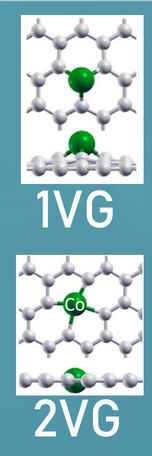
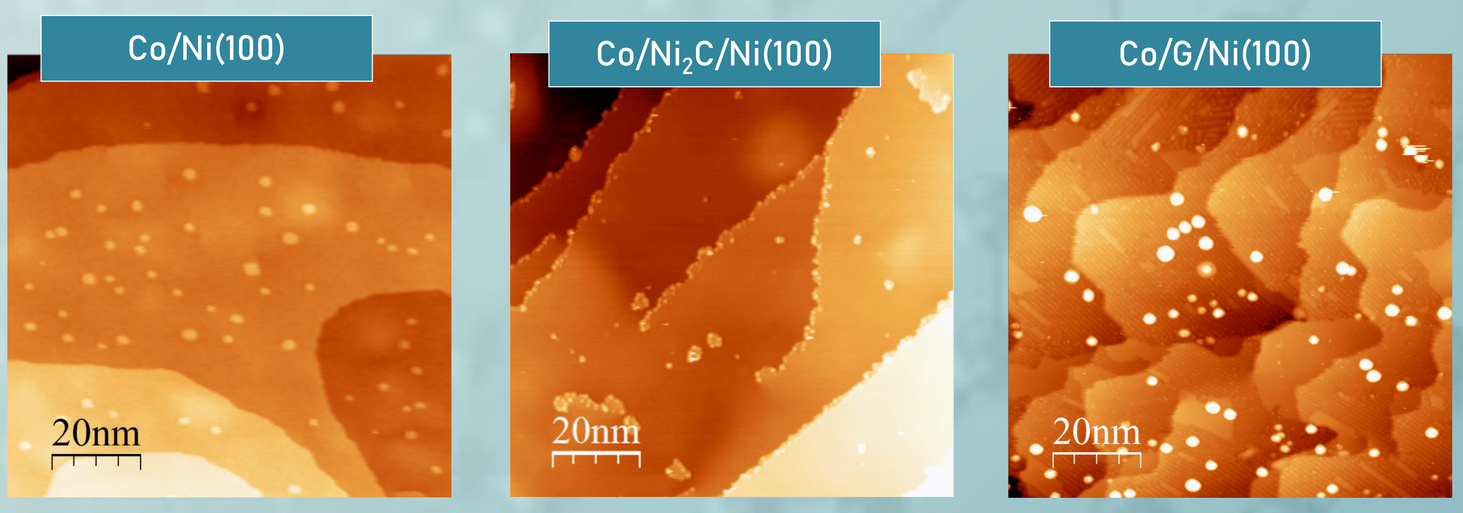
Introduction: Graphene (G) finds a variety of potential applications, such as electronic devices or catalytic 2D materials, and its functionalization with heteroatoms is one of the main routes to tune its electronic and structural properties. Among others, N and B were successfully incorporated into the graphene mesh, yet, only a few studies of transition metal (TM) doping, as Ni, Pt and Au, exist. Although theoretical calculations predict a substantial increase in the catalytic activity of such TM doped graphene, the experimental investigation is still limited. This research focuses on the understanding of the behavior of Co atoms on Ni(100) and G/Ni(100) by means of scanning tunneling microscopy, x-ray photoemission spectroscopy and density functional theory calculations in order to develop a method for Co incorporation during G formation.

Final aim is the incorporation of Co into vacancies of graphene defining a growth protocol also valid for other TMs. Theoretical calculations reported that Co could replace either a single C vacancy (1VG) or, more stable, a double C vacancy (2VG).
Co was chosen as it is expected to be the best catalyst among Fe, Ni, and Cu when incorporated in the G mesh.[1] Furthermore, the whole period from Sc to Zn as well as Pt and Au are potential dopants, exhibiting promising electronic, magnetic and catalytic properties.[2] Models adapted from Ref. [1].



Co on different surfaces

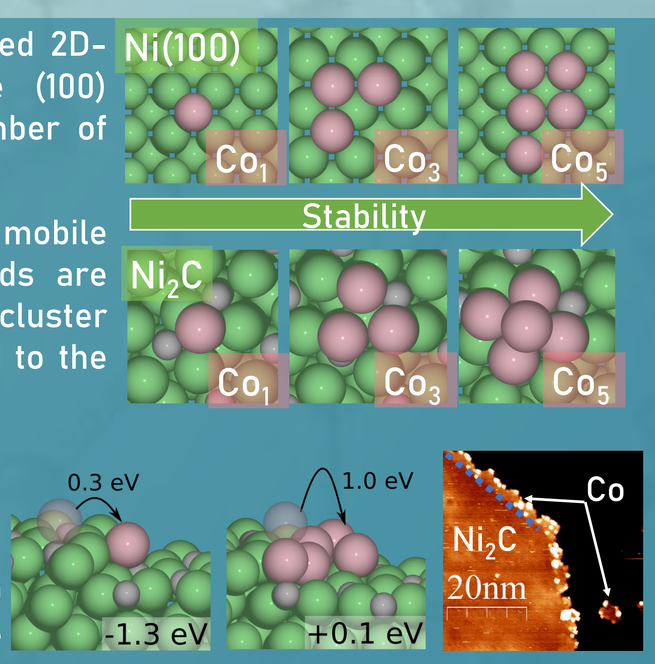


Cobalt on Ni(100): Co grows in randomly distributed 2D-islands following the 4-fold symmetry of the (100) substrate. Stability increases with increasing number of atoms.

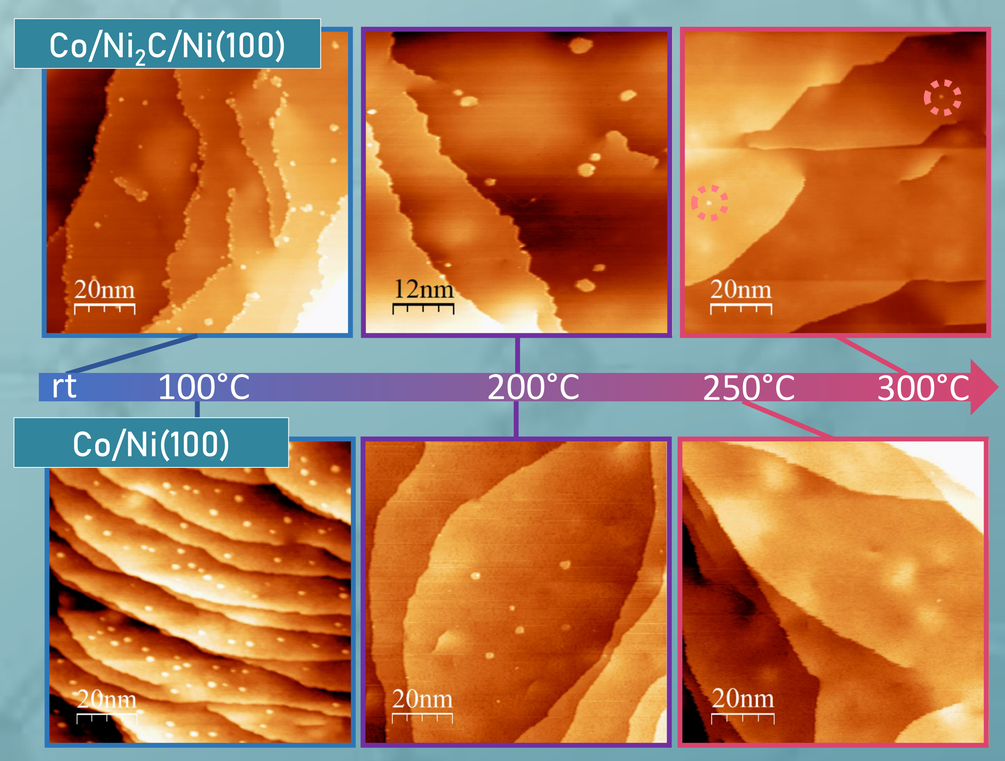
Cobalt on Ni_2C/Ni(100): Co is less stable, thus, more mobile on carbide. Steps are decorated, and less islands are observed in STM images. Energetically a 3D cluster formation from >4 atoms is more stable compared to the corresponding 2D structures.

Once a step is decorated, Co atoms from the upper terrace cannot jump to the lower one but sit on top of the decoration.

Cobalt on G/Ni(100): On graphene, spheric 3D clusters of 2-6 nm form. The clusters are stable upon annealing up to 600°C.



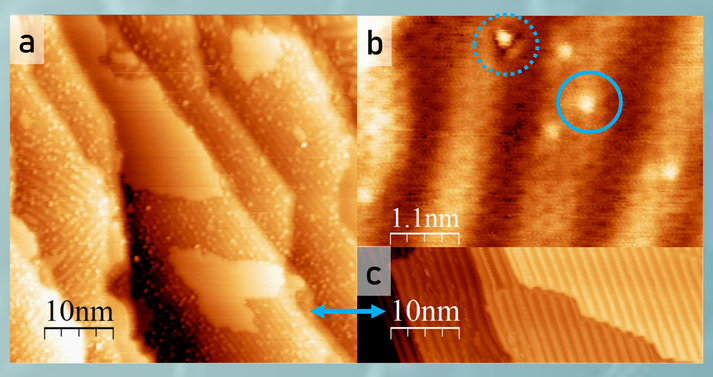
Co stability towards temperature



STM measurements at elevated temperatures (up to 500°C) allowed us to investigate Co stability on the surface. In case of Ni_2C, Co remains on the surface up to 300°C (marked in pink circles) for more than 1 h. Whereas on bare Ni, alloy formation starts at 150°C and Co islands vanish after 1 h at 250°C. Numerical simulations confirmed these observations, predicting a lower barrier for Co penetrating the Ni surface than Ni_2C.

➡ The challenge in incorporating Co into G is preventing alloy formation while reaching the temperature for G growth.

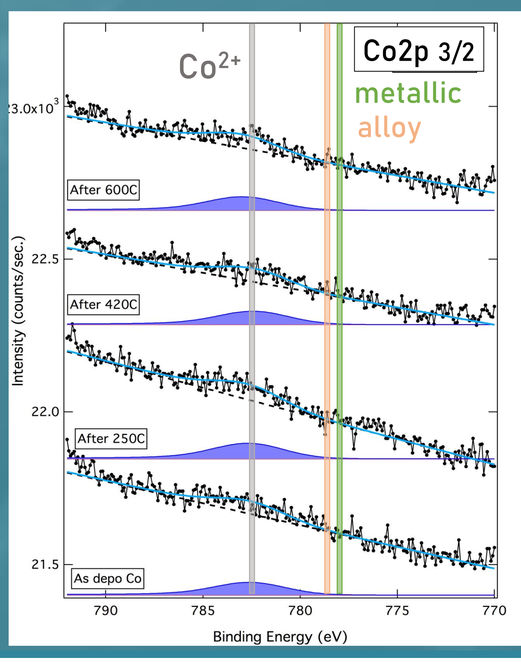
Co incorporation



Co doped graphene, a: Graphene grown during Co evaporation, b: atomic resolution suggesting two different dopant configurations, c: Graphene on Ni(100) without Co evaporation.

Route: Ni2C/Ni(100) → Graphene growth at 600°C, $p_{Ethylene}$ = 2e-6 mbar, 1h; Co evaporation for 10 minutes during growth → Doped G/Ni(100)

Based on our observations, the most promising route towards direct Co incorporation into the graphene network is the simultaneous evaporation of Co during G growth. This results in a much higher density of bright protrusions of atomic size in the STM images (a compared to c, left). Atomic resolution images of the dopants suggest two different kinds of configurations, which could be assigned to Ni and Co respectively, as it's well known that Ni adatoms get trapped during graphene formation as well.
The Co 2p 3/2 XPS spectrum indeed confirms the presence of Co in the 2+ charge state, in a stable configuration up to 600 °C, indicating that Co is more likely incorporated into G, as it would otherwise dissolve into the bulk at those temperatures. Furthermore, in the STM images no clusters or mobile adatoms were observed on top of graphene.



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REFERENCES AND AKNOWLEDGEMENTS

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