Title: Real-time imaging of adatom-promoted graphene growth on nickel[*]

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Abstract: Single adatoms are expected to participate in many processes occurring at solid surfaces, such as the growth of graphene on metals. We demonstrate, both experimentally and theoretically, the catalytic role played by single metal adatoms during the technologically relevant process of graphene growth on nickel. The catalytic action of individual Ni atoms at the edges of a growing graphene flake was directly captured by scanning tunneling microscopy imaging at the millisecond time scale, while force field molecular dynamics and density functional theory calculations rationalize the experimental observations. Our results unveil the mechanism ruling the activity of a single atom catalyst at work.

One Sentence Summary: The catalytic activity of single metal adatoms driving the growth of graphene on Ni is unveiled through a combination of real-time imaging and numerical simulations.

Main Text:

Reduced dimensionality in the catalyst structure often leads to increased chemical reactivity (*1*, *2*). More specifically, atomic steps of metal surfaces were experimentally identified as the active sites for several heterogeneous catalytic reactions (*3*, *4*), and this identification was theoretically rationalized in terms of a characteristic upshift of the d-band center (*5*). Such undercoordinated sites play also a crucial role in governing the stability of the active phase (*4*). Single atoms, representing the lowest possible coordination, can exhibit even higher specificity and efficiency compared to stepped surfaces (*1*). For example, isolated single metal atoms anchored onto oxide nanocrystallites promote CO oxidation (*6*) and the water-gas-shift reaction (*7*). Recent studies also revealed the peculiar activity of single atom alloys in boosting the selective hydrogenation of alkenes and hydrocarbons (*8*).

Mobile adatoms, commonly present on metal surfaces at elevated temperatures, are involved in several chemical processes occurring on surfaces and at the solid-liquid interface (*9*, *10*). However, the lack of direct experimental observation of the dynamics of these peculiar processes at the atomic scale, generally because of the difficulty of achieving simultaneous spatial and temporal resolution, limits the description and understanding of the surface reaction pathways. For the specific case of the chemical vapor deposition (CVD) growth of graphene on transition metals, a catalytic role of single metal atoms was predicted by theorists, but the detailed growth mechanism at the atomic scale still remains unclear (*11*).

Nickel (Ni) is one of the most used substrates to synthesize graphitic carbon single layers (*12*). We report the characterization of graphene growth on Ni(111) in real time by means of in-situ high-speed scanning tunneling microscopy (STM) measurements. By monitoring the layer formation at the atomic scale and with a time resolution down to milliseconds, we observed at the kink sites of the graphene edges single Ni atoms that are directly involved in the growth process. Simulations of possible reaction paths based on density functional theory (DFT) revealed that Ni adatoms drive the carbon (C) atom addition mechanism by substantially lowering the corresponding reaction barriers.

Islands of monolayer epitaxial graphene (EG) were synthesized on Ni(111) by subsurface C segregation at temperatures between 700 and 740 K (*13*). Three coexisting stable chemisorbed configurations of EG were observed (*14*), with the top/face-centered cubic geometry (top-fcc) as the most abundant phase. During growth, the island edges evolved too rapidly to be resolved by standard STM imaging (typical image acquisition times of ≈60 s/frame). Nevertheless, in a previous study we succeeded in identifying the top-fcc edge structure by performing high-speed STM measurements (*15*), exploiting the FAST module developed in our laboratory (*16*, *17*). The module now allows for image acquisition rates up to 100 frames/s with commercial microscopes already optimized for structural and reactivity studies. The edge terminations of EG islands on Ni(111) during growth at temperatures higher than 570 K (*15*) were identified as the zigzag (z) and Klein (k) structures shown in Fig. 1A. For both edges, kink sites obtained by interrupting the last two C rows were predicted to play an important role in graphene edge expansion (*18*, *19*).

To identify the underlying growth mechanisms during the C attachment process at both edges, we acquired STM movies with high spatial and temporal resolution and long enough for a statistically relevant analysis.

Series of consecutive images along z (Movie S1 (*20*)) and k (Movie S2 (*20*)) edges were acquired with frame rates of 36.5 and 60 Hz, respectively. The use of different frame rates (4 to 10 Hz) and tunneling current set-points (from 500 pA to 10 nA), did not yield substantial differences, indicating a negligible effect of the fast scanning tip on the observed processes. This consistency presumably resulted from the short tip-surface interaction time (typically ≈1.5 to 10 μs/ pixel), and from the thermal excitation that at elevated temperatures likely overwhelmed tip-induced effects (*21*).

Movie S1 (*20*) initially shows the formation at the z edge of two kink sites, acting as nucleation centers for graphene growth (Fig. S1 (*20*)). In the image sequence in Fig. 1B, growth proceeds from the kink site in the middle by orderly completion of the two interrupted carbon rows while moving the kink ahead. During the z edge growth, the observed structure of the kink remains always equivalent to the initial one, probably because of the preference for fcc-hollow site termination (*15*). A similar evolution was predicted by previous DFT calculations for the z edge of EG on Cu(111), where the growth would start from the hexagon forming the kink, and continuous incorporation of C atoms would form a new z chain on the graphene growth front

(*19*). The image sequence in Fig. 1C, extracted from Movie S2 (*20*), shows the growth mechanism at the k edge, similar to the one described above for the z edge, i.e. proceeding from the kink site and parallel to the edge. Our DFT calculations (Fig. S2 (*20*)) support this observation, showing that the incorporation of new C atoms takes place at the kink and that, after addition of a first C atom in a top site, the energetics favor the addition of a second C atom in a fcc-hollow site.

A closer examination of both sequences in Fig. 1, B and C, reveals the presence of bright objects at the kink sites. These features appeared and disappeared: they were present in some frames (at 27 and 82 ms in Fig. 1B, and at 17 and 50 ms in Fig. 1C) and were absent in others (at 0 and 55 ms in Fig. 1B, and at 0 and 33 ms in Fig. 1C). They were typically imaged for few scan-lines only, indicating a short residence time of the originating species (at the millisecond time scale, see supplementary text (*20*)) and their appearance did not depend on scanning parameters and tip conditions. Regarding the nature of the imaged species, one possibility would be that they are mobile C clusters, as described for graphene growth on Ru(0001) and Rh(111) (*22*, *23*). However, for Rh(111), where STM images have been acquired, the clusters have a height similar to the graphene layer, at variance with what we observe. Apparent height and lateral dimensions of the mobile species are on the other hand comparable to those of the static point-like defects observed after CVD graphene growth on Ni(111) in the same temperature range, which were previously identified as substitutional Ni atoms trapped in the graphene network during the growth process (*13*). We therefore attribute the bright features in Fig. 1, B and C, to mobile Ni adatoms, in line with previous DFT-based prediction (*24*). This hypothesis is supported by the well-known presence of diffusing adatoms on metal surfaces at elevated temperatures (*25*). Other dashed features with lower apparent height (comparable or lower than carbon atoms in graphene) were visible in some frames, and can be attributed either to Ni imaged by the tip in an off-center position (*26*), or to moving C atoms. A further confirmation of our identification of the bright features in the STM images as Ni adatoms comes from molecular dynamics (MD) simulations with state-of-the-art reactive force field (ReaxFF) performed at 710 K (Fig. 2A; details in (*20*)). Mobile Ni adatoms moved randomly over the bare metal surface until they reached a graphene edge. There, they diffused parallel to the edge, with considerably longer residence time in the kink sites.

A striking feature in the STM image series is that most of the times the presence of the Ni adatoms at the kinks is accompanied by C dimer attachment nearby (see frame at 55 ms in Fig. 1B, and frames at 33 and 50 ms in Fig. 1C) suggesting a catalytic role of the single metal atom. This observation is consistent with previous DFT calculations for graphene on Cu(111) (*19*), which showed that the barrier for C incorporation at the z edge was strongly reduced by C adatom passivation at armchair-like sites, present near a hexagon (a kink) sticking out of the edge. Our interpretation is also in line with recent in-situ transmission electron microscopy (TEM) reports of the chemical activity of single atoms in facilitating addition and removal of C atoms from the edges of suspended graphene flakes (*27*). These previous results, although significant, are not related to a real growth process, but rather to attachment-detachment events of individual C atoms, and thus cannot be directly extended to technologically relevant CVD growth processes on solid metal surfaces.

The fact that the Ni adatoms were almost exclusively imaged at the kink sites suggests that they represent a minimum energy configuration for Ni; still, the short residence time implies that the bond can be easily broken at these temperatures, avoiding the poisoning of the active kink site.

No stable Ni trapping was observed in our time-series, at variance with the defect formation pathway predicted by Wang et al. (*24*).

From the STM sequence corresponding to the k edge, two short-lived Ni adatom configurations can be identified at the kink sites (Fig. 2, B, C, F and G). DFT simulations of these configurations yielded the two stable structures shown in Fig. 2, E and I, where a Ni adatom and one/two top C atoms were added to the bare kink. The corresponding constant-height simulated images in Fig. 2, D and H, match the experimental STM data. DFT calculations indicate a remarkable mutual stabilization effect for the Ni/C configuration at the kink (from the energy comparison of configurations in Fig. S2 and S3 (*20*)). These results suggest that Ni had a strong promoting role in the addition of C atoms to the kink and hence in the edge growth, as previously predicted for Cu(111) (*19*). Similar conclusions could be drawn for the z edge, where a single intermediate state was imaged and described by DFT calculations (Fig. S4 (*20*)).

The stable configurations observed by STM and confirmed by theory can serve as a guide for a DFT description of the entire growth process, discriminating among many possible alternative paths and highlighting the catalytic role of the Ni adatom. In Fig. 3, we report the energy diagram corresponding to selected C attachment pathways to the k edge with and without the presence of the Ni adatom. The energy gain upon addition of a C atom is referred to a subsurface position far from the edge ("sub-fcc", the most stable position on a clean Ni(111) surface); for the addition of a Ni adatom, to a position on the surface far from the edge.

We take as initial configuration (labeled (0) in Fig. 3) a k edge with all terminating C atoms in fcc-hollow. The addition of a first C atom on the top site (1) involves a considerable kinetic barrier, 2.46 eV. The growth process can then follow two alternative cycles, either without (blue box) or with (red box) a Ni adatom.

Considering the process without a Ni adatom, the attachment of the second C atom in a fcc-hollow position (2) requires overcoming a barrier of 1.02 eV (see Fig. S5 (*20*) for details on energy barriers). Because of the epitaxial match between graphene and Ni(111), the edge configuration is now equivalent to the initial one. Further addition of a C top atom (3) requires again overcoming the 2.46 eV barrier, completing the cycle that can be repeated in a continuous loop, but always including this high energy barrier.

In the alternative path, a Ni adatom attaches without an energy barrier to the kink decorated by the top C atom (1), yielding an energy gain of 1.36 eV (1'). The most favorable configuration for attachment of a second C atom is again a top site, with the Ni adatom diffusing laterally, bonding to the two top C atoms (2'). In the last step of the growth cycle, another C atom attaches in the fcc-hollow position extending the graphene edge and pushing aside the Ni adatom (3'). The energy barriers involved in the two steps of this cycle are 1.61 eV and 1.19 eV, respectively. Ni adatoms, spontaneously binding to the kink site, thus reduce the rate limiting energy barrier of the cyclic process by about 35% (from 2.46 to 1.61 eV), acting as single atom catalysts for the graphene growth process.

Because the Ni attachment is barrierless, the detachment barriers from the two stable states at the kink are 1.36 eV and 1.35 eV, obtained as the DFT energy differences of the corresponding equilibrium states, i.e. configurations (1') and (2') of Fig. 3, and configurations (1) in Fig. 3 and (e) in Fig. S2 (*20*), respectively. These values yield Ni residence time values in the millisecond scale, compatible with the values extracted from the STM data (Fig. S6 (*20*)).

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Supplementary Materials:

Materials and Methods

Figures S1-S8

Movies S1-S2

References (*28-31*)

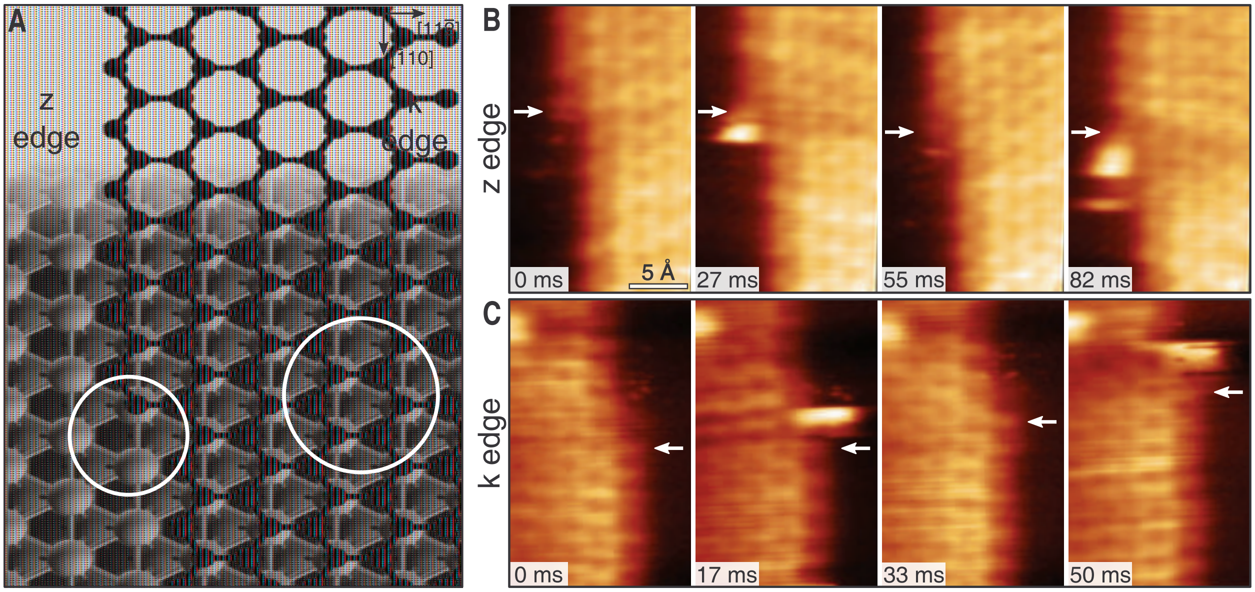

Fig. 1. Graphene growth along z and k edges. (A) Zigzag (z) and Klein (k) edges of a top-fcc EG layer on Ni (111). At both edges, the kink structures are highlighted by circles. (B) High-speed STM sequence acquired at 710 K in quasi-constant height mode at the z edge, from Movie S1 [V = 20 mV; I = 8 nA; 36.5 Hz]. White arrows indicate the position of C atoms in fcc-hollow sites near the kink. (C) Same for the k edge, from Movie S2 [V = 20 mV; I = 7 nA; 60 Hz].

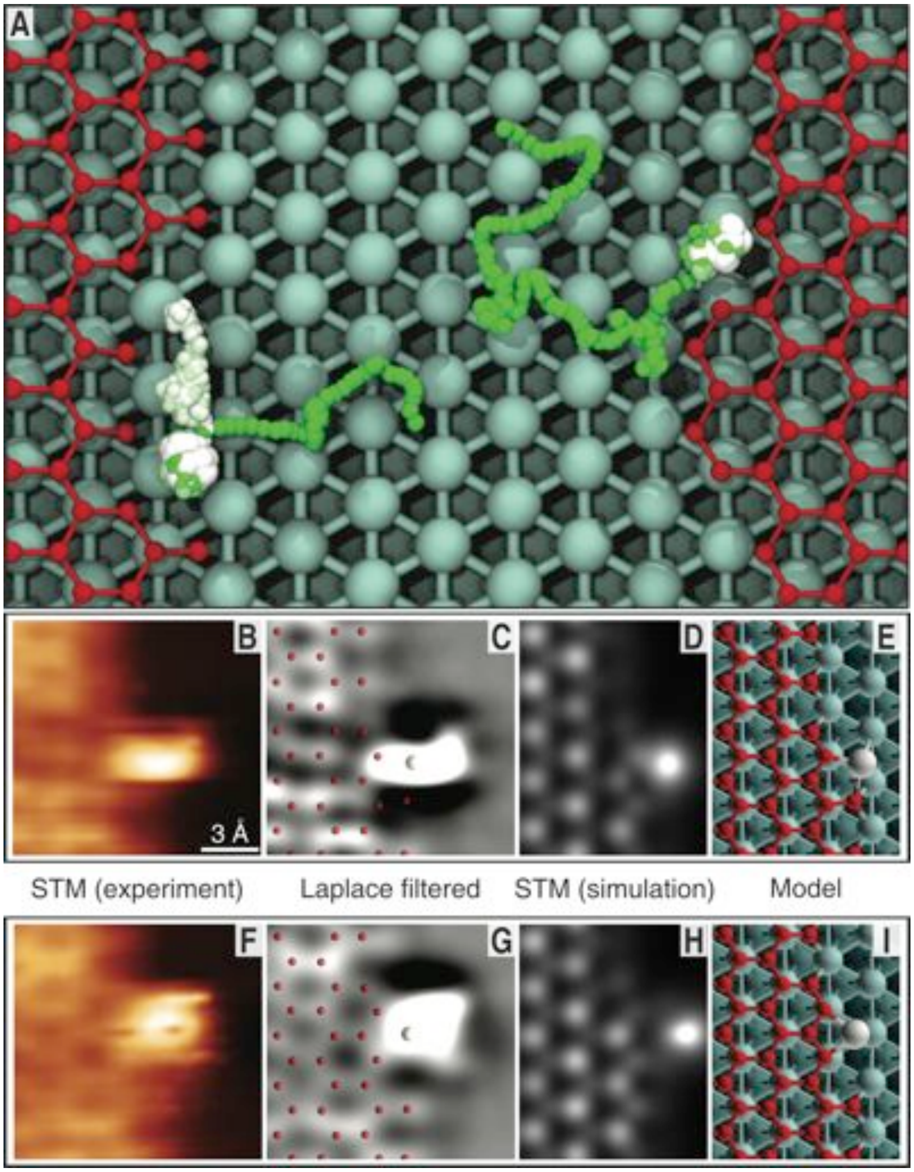

Fig. 2. Nickel adatoms at the graphene edges. (A) Ni adatom diffusing on a surface in a region delimited by graphene z (right) and k (left) edges with kinks. Two representative trajectories obtained by MD simulations with ReaxFF performed at 710 K for 100 ps are shown. Color palette for Ni trajectories: from green (initial position) to white (final position). The final steps are highlighted by increasing the ball size. (B-I) Short-lived configurations of Ni adatom at k edge kinks: (B, F) High-speed STM images from Movie S2 (*20*) [V = 20 mV; I = 7 nA], (C, G)

Laplace-filtered version of (B, F) images with superimposed ball models, (D, H) constant height STM simulated images based on the calculated geometries (E, I).

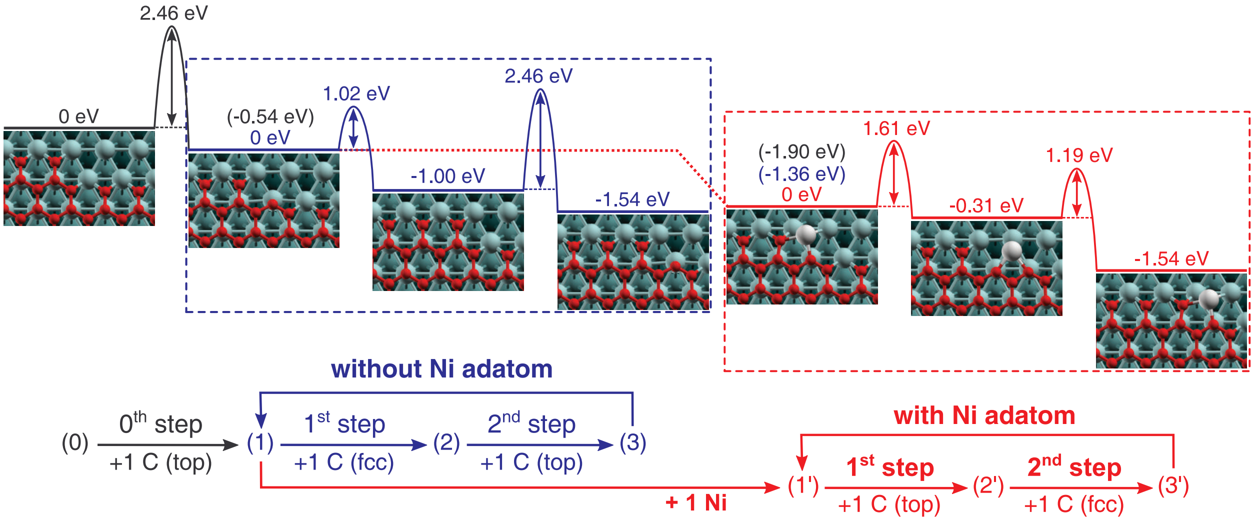

Fig. 3. Alternative graphene growth pathways as predicted by DFT. Energy zero corresponds to the bare kink configuration (0), plus one Ni adatom on the surface far from the edge and a reservoir of sub-fcc C atoms far from the edge. For clarity, the energy scale is reset for each cycle, producing the blue and red energy scales, respectively.