

SUPPORTING INFORMATION

1D selective confinement and diffusion of metal atoms on graphene

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*Computing, Big Data and Quantum Computing**

I. SIMULATION SUPERCELL

Figure S1 shows the supercell used in the simulations. The DFT equilibrium bulk Ni parameter is used, which gives a Ni(100) surface lattice with constant of 2.49 Å. Since G has a DFT equilibrium lattice constant of 2.46 Å, it is slightly stretched in the zig-zag direction. Additional strain originating from corrugation is locally different. Our choice of considering the support unstrained, letting the overlayer be strained, rather than vice-versa, is motivated by the aim of giving the most possible realistic description of the system. The specific size of the supercell was determined by the comparison with experimental STM images, as extensively discussed in Zou et al. [Carbon **130** (2018) 441].

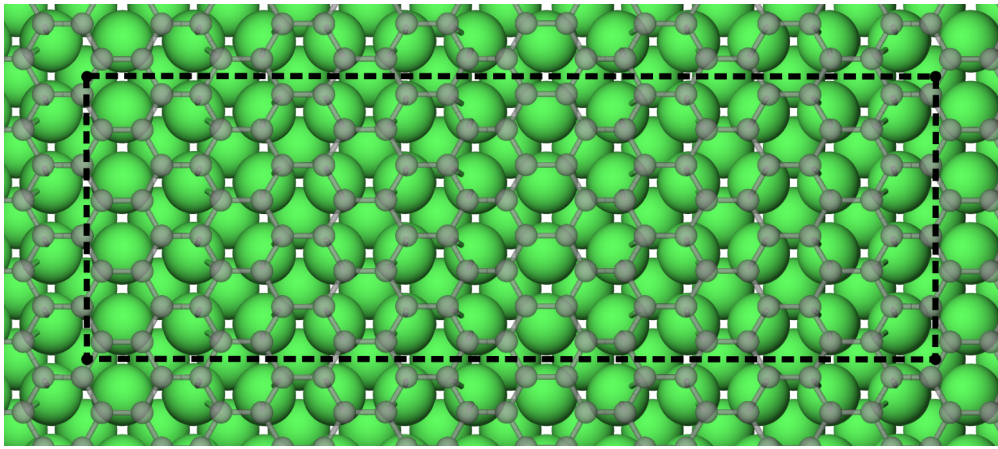


FIG. S1: The supercell used for the simulation, containing a three layer slab of Ni(100) with a 4×12 in-plane periodicity.

II. MAGNETISM OF ADSORBED COBALT ADATOMS AND CLUSTERS

We have performed spin-resolved DFT calculations, obtaining the magnetic moment of adsorbed Co adatoms and clusters: the magnetic moment of an individual atom adsorbed either on R or on V is about $1.3 \mu_B$, while atoms inside multiatomic clusters have even higher magnetic moments, ranging from 1.5 to $1.8 \mu_B$. The coupling between magnetic moments within all Co multiatomic clusters is ferromagnetic. The structures and the magnetic moments are shown in Figure S2.

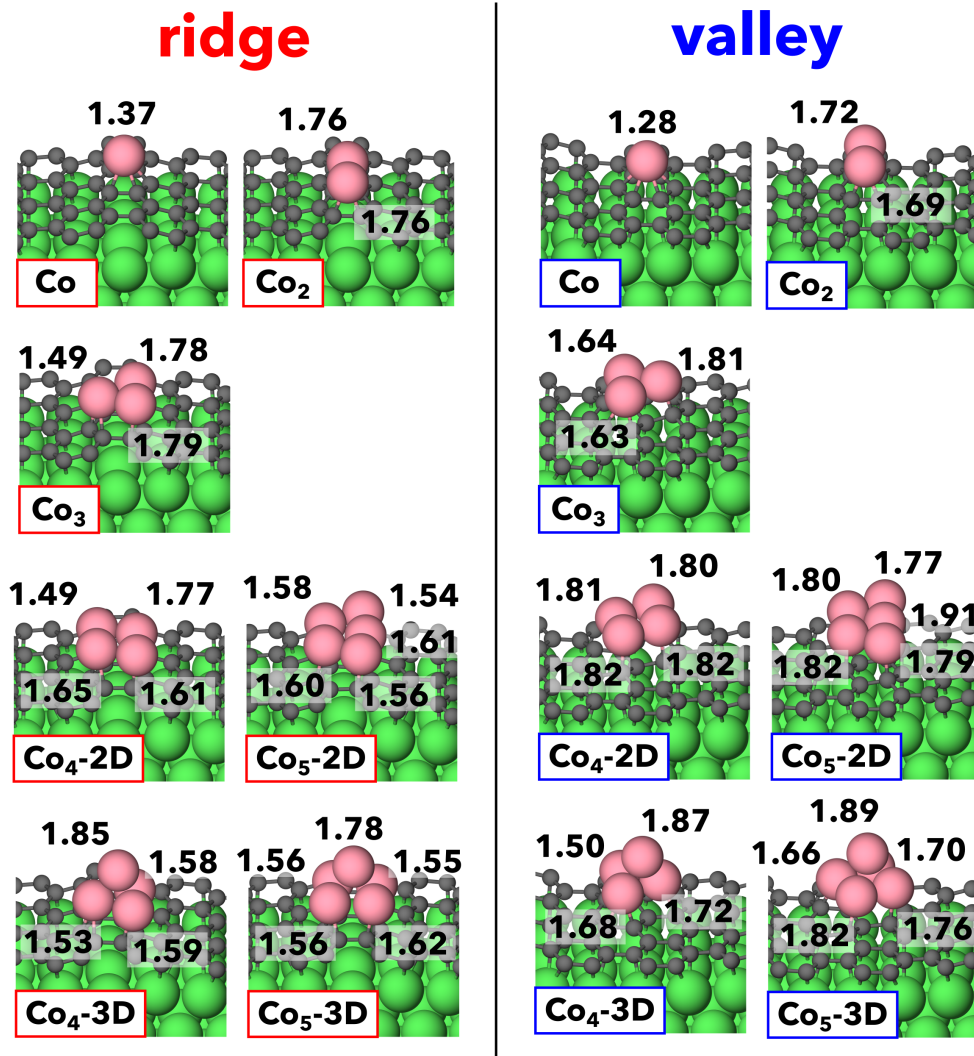


FIG. S2: The structures of Co clusters on ridge and valley with calculated magnetic moments of each atom in the cluster (in μ_B).

III. ADSORPTION OF AU ATOMS AND CLUSTERS: EXPERIMENTAL RESULTS

Figure S3 shows a STM image of Au clusters on G/Ni(100) at room temperature.

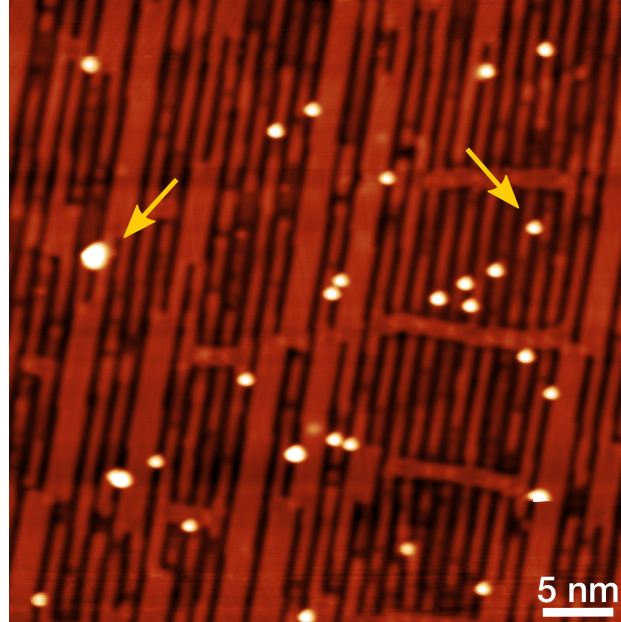


FIG. S3: STM images of Au clusters (two representative cases are highlighted by yellow arrows) on G/Ni(100) at room temperature showing, in contrast to the case of Co, the preference to occupy the valley regions of the graphene moiré. Scanning parameters: $V = -0.5$ V, $I = 0.05$ nA.

IV. ELECTROSTATICALLY-DRIVEN SORTING OF ADATOMS BETWEEN VALLEYS AND RIDGES - DETAILS OF THE DFT CALCULATIONS

For all the adsorbed elements listed in the Main Text and reported in Figure 4, we inspected all high-symmetry adsorption sites on valleys and ridges (hollow site (H), top of a C atom (T), and bridge site (B)) and found that Li, Ti, Ni, Co and Zn prefer to bind at H site, whereas F, Au, and Cu prefer T site. For all species, the adsorption site is the same on V and R, i.e. the distance from the Ni substrate has no influence on the favorable site. Furthermore, like for Co, the charge analysis revealed that even though C-2*p* orbitals of C_V atoms hybridize with Ni-3*d* more strongly than those of C_R (see Fig. 1c) and are therefore less active in forming chemical bonds, the charges transferred between the adatoms and C_V or C_R are very similar. In Table S1, we present, for all the inspected adsorbed elements, the average of the two total charges of the adsorbed atom on R and V, $q = (q_R + q_V)/2$, their differences $\Delta q = q_R - q_V$, the adsorption energies on the valley (E_V) and the ridge (E_R) of G/Ni(100), as well as the differences of the adsorption energies, $\Delta E = E_R - E_V$. The adsorption energy on free-standing G is added for comparison.

Much alike Co, other TM adatoms such as Ti and Ni strongly prefer to adsorb on R, with E_{ads} being approximately 30% higher than on V. Overall, the behavior of these two species at G/Ni(100) is very similar to Co.

In our previous studies we showed that the adsorption of a Li adatom at free-standing G is accompanied by electron transfer from the atomic Li-2*s* state to the graphene Fermi level. In that case, the DOS of G is barely unaffected by Li binding except for the rigid shift of the Fermi level towards higher energies. Li binding to G/Ni(100) does not differ much in that respect. Yet, when one compares E at V and R, the difference is evident in favor of the H_R site. Positively charged Li adatom tends to stay as far as possible from positively charged Ni atoms below the valley and thus adsorbs on R where it gains an extra E_{ads} of -0.44 eV compared to V.

Compared to Li, the binding picture of F, which is the element with the highest electronegativity in periodic table, is completely opposite. F adatom prefers to adsorb at T site, capturing a portion of C-2*p* electron. Thus, F is negatively charged and strongly prefers to adsorb at V where the electrostatic attraction with the positive nickel substrate is strongest. The E_{ads} of F on V is 0.35 eV more negative than on R.

To further clarify the role of the electrostatic interaction, we investigated the elements with a filled $3d$ shell. Those adatoms are expected to be neutral, due to their filled $3d$ configuration and very weak binding to a free-standing G. Indeed, our calculations on Zn and Cu yield very small E_{ads} that is nearly equal on V and R. Thus, if no charge transfer is involved in the adsorption process, the adatom is blind to the differences in electrostatic potential and does not show any preference for the valley or the ridge.

The last specie we consider is Au, which has the highest electronegativity among d -electron metals. Although an Au adatom displays tiny charge transfer on free-standing G, the amount of transferred charge increases substantially on G/Ni(100) due to the n -doping from Ni(100) substrate. As a consequence, E_{ads} on G/Ni(100) is substantially higher than on free-standing G (Table S1) and, choosing between V and R, Au prefers T site on V by 0.23 eV. For completeness, in Figure S4 we show the version of Figure 4 from the Main Text but with charges obtained with Bader analysis.

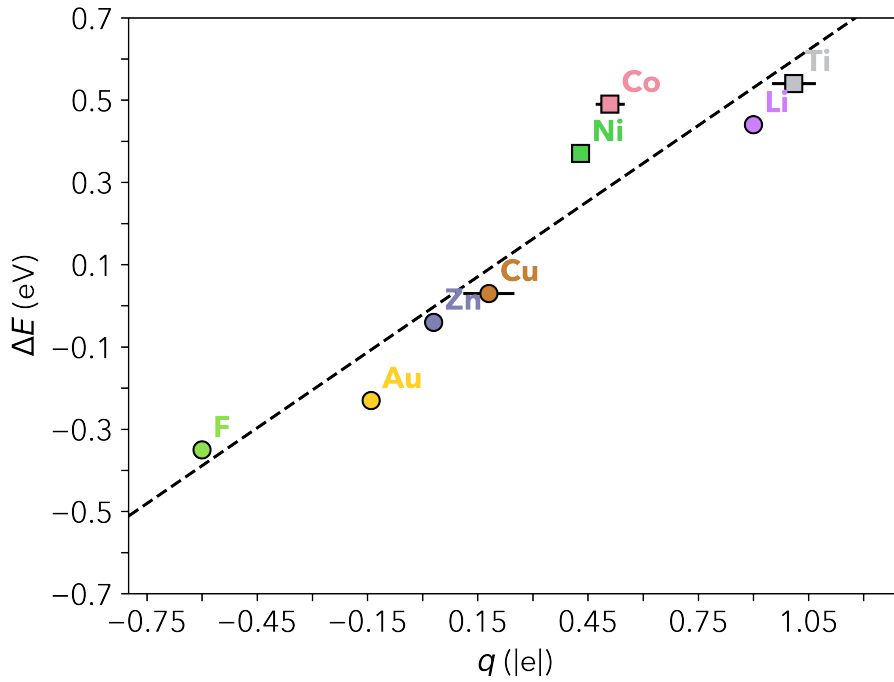


FIG. S4: See the description of Figure 4 from the Main Text. This is the equivalent figure but with charges obtained from Bader analysis.

TABLE S1: Adsorption energy of adatoms on free-standing G (E_G) and on ridge and valley of G/Ni(100) (E_R and E_V). The preferential adsorption site is indicated (H: at the center of a G hexagon; T: on top of a carbon atom). ΔE is the difference in adsorption energies, $\Delta E = E_R - E_V$, where the positive (negative) ΔE indicates the favorable adsorption on R (V). Total adatom charges on R and V are averaged ($q = (q_R + q_V)/2$) and presented together with their difference in square brackets ($\Delta q = q_R - q_V$). Charges are calculated both with Bader and Löwdin analysis (q_B and q_L).

adatom	site	E_G (eV)	E_R (eV)	E_V (eV)	ΔE (eV)	q_B [Δq_B] (e)	q_L [Δq_L] (e)
Li	H	-1.53	-1.88	-1.44	0.44	0.90[0.00]	0.62[-0.04]
F	T	-2.06	-2.96	-3.31	-0.35	-0.60[0.03]	-0.34[-0.02]
Ti	H	-1.80	-2.22	-1.68	0.54	1.01[0.12]	0.75[0.09]
Co	H	-1.40	-1.50	-1.01	0.49	0.51[0.08]	0.71[0.09]
Ni	H	-1.75	-1.72	-1.35	0.37	0.43[0.03]	0.54[0.07]
Cu	T	-0.53	-0.94	-0.91	0.03	0.18[0.14]	0.10[0.08]
Zn	H	-0.17	-0.21	-0.25	-0.04	0.03[-0.01]	-0.02[-0.03]
Au	T	-0.68	-1.32	-1.55	-0.23	-0.14[-0.02]	-0.18[0.02]

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