## SUPPLEMENTARY INFO

# First-principles study of nickel reactivity under 2D cover: $\mathrm{Ni}_{2} \mathrm{C}$ formation at rotated graphene/ $\mathrm{Ni}(111)$ interface <br> (Dated: October 20, 2020) 

## I. CONSTRUCTION PROCEDURE OF THE $(6 \times \sqrt{43}) R 7.6^{\circ}$ SUPERCELL

Here we describe the construction procedure of supercell that is suitable to accomodate three different lattices, in particular (1) $\mathrm{Ni}(111)$, (2) $\mathrm{Ni}_{2} \mathrm{C}$, and (3) rotated graphene (RG), where the angle of $17^{\circ}$ is measured between the zigzag direction of graphene and $\langle 110\rangle$ direction of $\mathrm{Ni}(111)$ lattice. In this way we manage to construct $R G / N i_{2} \mathrm{C} / \mathrm{Ni}(111)$ heterostructure labeled by RGC in the paper. Despite the fact that G lattice is hexagonal and commensurate with $\mathrm{Ni}(111)$, the rotation angle introduces great challenge in the supercell construction. To tackle this problem, we fixed the mutual point of the three lattices at the origin of the coordinate system and rotated the G and $\mathrm{Ni}_{2} \mathrm{C}$ lattices around the z-axis. The construction procedure is depicted in Fig. S1.


FIG. S1: Side view of the RGC structure (the distance between its components is enlarged to improve the visibility). G and $\mathrm{Ni}_{2} \mathrm{C}$ lattices are rotated around z-axis. The lattices of $\mathrm{Ni}(111), \mathrm{Ni}_{2} \mathrm{C}$ and G with the corresponding lattice vectors are depicted on the right as viewed from above. In the G panel, the sites corresponding to $\mathrm{Ni}(111)$ lattice are denoted by small gray dots to emphasize the G rotation. The atoms coloring scheme is the same as in the Fig. 1 of the paper.

While $\mathrm{Ni}(111)$ lattice with a constant of $3.52 \AA$ is kept fixed, the structural parameters of the other two lattices are varied within a few percent interval. For every given set of structural parameters, in $(x, y)$ plane there exist the points that can be considered as the mutual points of the three lattices within a certain tolerance. Among such, two closest to the origin are used to define the supercell vectors $\left\{\mathbf{v}_{\mathbf{1}}, \mathbf{v}_{2}\right\}$. We limited our search to the supercells that contain no more than a thousand of atoms. Among the inspected candidates, the $(6 \times \sqrt{43}) R 7.6^{\circ}$ supercell, depicted in Fig. S2 (and Fig. 1 of the paper) is chosen as the most appropriate able to accommodate the RGC heterostructure. The parameters which are varied, together with their starting and final values, are as follows:

- the length of $G$ lattice vectors $\left\{\mathbf{w}_{\mathbf{1}}, \mathbf{w}_{2}\right\}$ were varied around $2.46 \AA$ while the angle between them was kept fixed at $60^{\circ}$ The lengths of $\mathbf{w}_{\mathbf{1}}$ and $\mathbf{w}_{\mathbf{2}}$ were varied independently, i.e. graphene was not kept equilateral during the procedure. The obtained values are $\left|\mathbf{w}_{\mathbf{1}}\right|=2.48 \AA$ and $\left|\mathbf{w}_{\mathbf{2}}\right|=2.42 \AA$;
- the rotation angle $\theta$ of G , measured between $\mathbf{a}_{1}$ direction of $\mathrm{Ni}(111)$ and $\mathbf{w}_{1}$ direction (zigzag) of G , was varied between $11^{\circ}$ and $20^{\circ}$. We chose $\theta=15.5^{\circ}$. It is worth noting that due to different length of $\mathbf{w}_{\mathbf{1}}$ and $\mathbf{w}_{\mathbf{2}}$ the angles $\measuredangle\left\{\mathbf{a}_{1}, \mathbf{w}_{1}\right\}$ and $\measuredangle\left\{\mathbf{a}_{2}, \mathbf{w}_{2}\right\}$ are not equal, but their difference is small. After the supercell is constructed, the structural relaxation yielded the final angles $\measuredangle\left\{\mathbf{a}_{1}, \mathbf{w}_{1}\right\}=15.5^{\circ}$ and $\measuredangle\left\{\mathbf{a}_{2}, \mathbf{w}_{2}\right\}=16.1^{\circ}$ and we here report these angles as the final ones (Fig. S 2 b ).
- starting from the values reported in Ref. [1, we varied the length of carbide lattice vectors $\left\{\mathbf{u}_{1}, \mathbf{u}_{2}\right\}$ around $4.96 \AA$ and the angle between them around $92.2^{\circ}$ (see the middle panel of Fig. S1). We chose slightly larger length of $5.06 \AA$ for both $\left\{\mathbf{u}_{1}\right.$ and $\left.\mathbf{u}_{2}\right\}$ and the angle $\measuredangle\left\{\mathbf{u}_{1}, \mathbf{u}_{2}\right\}=91.8^{\circ}$. The rotation angle of carbide lattice with respect to $\langle 110\rangle$ directions of $\mathrm{Ni}(111)$ is $\chi=33.2^{\circ}$ and it coincides with the value reported in Ref. [2].


FIG. S2: (a) EGC and (b) RGC heterostructures. Atoms coloring scheme and the image description is the same as in Fig. 1 of the paper.

## II. STM IMAGES OF RG STRUCTURE

Here we compare the STM images of RG structure modeled with the $(\sqrt{19} \times \sqrt{19}) R 23.4^{\circ}$ supercell (Fig. 5 of the paper) to the experimentally obtained one presented in Fig. S6 of Ref. [3]. The similarity of their moirée patterns


FIG. S3: (a) Experimental STM image of RG domain (rotation angle $13^{\circ}$ ) on $\mathrm{Ni}(111)$ with (b) portion of it enlarged for comparison with DFT-simulated image; $[V=-0.2 \mathrm{~V} ; I=2 \mathrm{nA}]$ (adapted from Ref. [3], Fig. S6); (c) DFT-simulated STM image of RG structure with G rotation angle of $13.2^{\circ}$, Fig. $\operatorname{S2} \mathrm{b}\left[V_{\text {bias }}=-0.3 \mathrm{eV}\right.$, ILDOS value $\left.4 \times 10^{-4}|e| / a_{0}^{3}\right]$.
and the periodicity of $\sim 1.1 \mathrm{~nm}$ are firm indications that our model of RG structure represents well the experimentally obtained RG domains on $\mathrm{Ni}(111)$ rotated by $13^{\circ}$.

## III. C1S PSEUDOPOTENTIAL GENERATION

Here we describe the details behind the construction of pseudopotential (PP) with a core-hole (missing one $1 s$ electron), which we needed to evaluate the shifts of C 1s core states in different chemical environments. Therefore, we generated PP with $1 s^{1} 2 s^{2} 2 p^{2}$ electronic configuration of C atom. One $1 s$ electron was treated as core and two $2 s$ and two $2 p$ (both spin-up) electrons as valence. Using ld1.x code of Quantum ESPRESSO distribution [4, 5] and working within the scalar-relativistic approximation, we generated the ultrasoft PP with a nonlinear core correction. The effects of exchange and correlation in the electronic gas are described with GGA-PBE xc functional [6]. The pseudization of atomic orbitals inside the core regions was performed with Troullier-Martins pseudization algorithm [7]. In particular, we used the inner and outer cutoff radii 1.0 and 1.2 a.u. for $2 s$ states and 0.9 and 1.4 a.u. for $2 p$ states.

To test the generated PP, we compared the all-electron (AE) and pseudo (PS) valence wavefunctions, their logarithmic derivatives in the energy range of interest and the atomic energy spectra at different plane wave cutoffs. As depicted in Fig. $\mathbf{S 4} 4, \mathrm{~b}$, outside the pseudization region of $\sim 1$ a.u. the PS wavefunctions reproduces well the AE wavefunctions.


FIG. S4: Radial part of all-electron and pseudo a) $2 s$ and b) $2 p$ orbitals.

The logarithmic derivatives $D^{l}(\epsilon, r)$ of AE and PS wavefunctions, defined as

$$
\begin{equation*}
D^{l}(\epsilon, r)=\frac{\mathrm{d}}{\mathrm{~d} r} \ln \psi_{l}(\epsilon, r) \tag{S1}
\end{equation*}
$$

evaluated at $r=2.0$ a.u., nearly coincide in the relevant energy range from -2.0 Ry to 2.0 Ry with differences only for $2 p$ states above 3 Ry, as depicted in Fig. S5.


FIG. S5: Logarithmic derivatives, Eq. S1 of all-electron and pseudo a) $2 s$ and b) $2 p$ wavefunctions evaluated at $r=2$ a.u..
Using the generated PP, we evaluated the eigenvalues of valence states by solving the Kohn-Sham equations at different plane wave cutoff energies in wavefunction's expansion as presented in Table S1. By rationalizing the difference between the PS and AE $2 s$ and $2 p$ eigenvalues, in all calculations involving our PP we were using the plane wave cutoff of 50 Ry .

TABLE S1: Energies of C valence states obtained at different energy cutoff in the plane wave expansion of wavefunctions. AE corresponds to eigenvalues obtained from all-electron calculations.

| cutoff $(\mathrm{Ry})$ | $\epsilon_{2 s}(\mathrm{Ry})$ | $\epsilon_{2 p}(\mathrm{Ry})$ |
| :---: | :---: | :---: |
| 20 | -2.1968 | -1.4862 |
| 30 | -2.1969 | -1.5585 |
| 40 | -2.1970 | -1.5668 |
| 50 | -2.1970 | -1.5670 |
| 60 | -2.1971 | -1.5671 |
| 80 | -2.1971 | -1.5672 |
| 100 | -2.1971 | -1.5672 |
| AE | -2.1981 | -1.5680 |

To test the transferability, we compared the differences between the AE and PS energy spectra that correspond to different valence configurations of C atom, as presented in Table S2. Errors on eigenvalues differences that do not exceed 0.005 Ry assure reasonably good transferability of generated PP.

TABLE S2: Energy difference between AE and PS eigenvalues for different electronic configurations.

| electronic configuration | $\Delta(\mathrm{AE}-\mathrm{PS})_{2 s}(\mathrm{Ry})$ | $\Delta(\mathrm{AE}-\mathrm{PS})_{2 p}(\mathrm{Ry})$ |
| :---: | :---: | :---: |
| $1 s^{1} 2 s^{2} 2 p^{2}$ | 0.00151 | 0.00024 |
| $1 s^{1} 2 s^{1} 2 p^{3}$ | 0.00264 | 0.00062 |
| $1 s^{1} 2 s^{0} 2 p^{4}$ | 0.00450 | 0.00029 |

Finally, we calculated the lattice constant and cohesive energy of graphene with our PP and compared the results to the values obtained with C.pbe-n-rrkjus_psl.1.0.0.UPF from Quantum ESPRESSO repository. The lattice constant of $2.47 \AA$ obtained with our PP is equal to the one we obtained with C.pbe-n-rrkjus_psl.1.0.0.UPF. Applying our PP, graphene displays much weaker bonding, as the cohesive energy is -6.5 eV , much lower than the value of -7.9 eV we obtained with the PP from the repository. This finding is consistent with the fact that our PP
has a core-hole and is therefore inherently unable to reproduce the most stable electronic configuration of C atom in graphene.
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