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Metallic and Magnetic 2D Materials Containing Planar Tetracoordinated C and N

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Supporting Information

ABSTRACT: The top monolayers of surface carbides and nitrides of Co and Ni are predicted to yield new stable 2D materials upon exfoliation. These 2D phases are p4g clock reconstructed, and contain planar tetracoordinated C or N. The stability of these flat carbides and nitrides is high, and ab initio molecular dynamics at a simulation temperature of 1800 K suggest that the materials are thermally stable at elevated temperatures. The materials owe their stability to local triple aromaticity (π, σ-radial, and σ-peripheral) associated with binding of the main group element to the metal. All predicted 2D phases are conductors, and the two alloys of Co are also ferromagnetic, a property especially rare among 2D materials. The preparation of 2D carbides and nitrides is envisioned to be done through surface deposition and peeling, possibly on a metal with a larger lattice constant for reduced affinity.

I. INTRODUCTION

Usually tetracoordinated carbon has a tetrahedral spatial arrangement due to its sp3 hybridization. However, Hoffmann et al.1 suggested that planar tetracoordinated carbon (ptC) could be stabilized (i) electronically, by using strong σ-donors or π-acceptors, (ii) mechanically, by constraining the ptC into a rigid steric framework, or (iii) by a combination of the two. Since then, several molecules containing this atypical ptC have been predicted and synthesized.2-10 Planar tetracoordinated nitrogen, ptN, also has been predicted to have kinetic stability and nitrides is high, and ab initio molecular dynamics at a simulation temperature of 1800 K suggest that the materials are thermally stable at elevated temperatures. The materials owe their stability to local triple aromaticity (π, σ-radial, and σ-peripheral) associated with binding of the main group element to the metal. All predicted 2D phases are conductors, and the two alloys of Co are also ferromagnetic, a property especially rare among 2D materials. The preparation of 2D carbides and nitrides is envisioned to be done through surface deposition and peeling, possibly on a metal with a larger lattice constant for reduced affinity.

Inspired by this finding, penta-B2C was designed, consisting of pentagons containing two ptCs and a three-coordinated B.20 It has a wide indirect band gap of 2.28 eV, and according to the DFT calculations, it can be switched to a metallic semiconductor under certain biaxial strains. Panchanatna et al. proposed a number of hypothetical extended networks containing ptC constructed from the C22- unit.21 In addition, Wang et al. have recently reported the design of a BeC2 monolayer on the basis of density functional theory calculations. This new 2D material contains quasi-planar pentacoordinated C and it is predicted to be stable, with moderate cohesive energy, positive phonon modes and high melting point, and delocalized bonding.22 For periodic systems with ptN, Be-decorated BN, or BC2N nanoribbons,23,24 in which ptC and ptN coexist, were also predicted.

Upon exposure to hydrocarbons under catalytic conditions, ptC also forms on metal surfaces: on Co,25-29 on Ni(100),30,31 and on stepped Ni(111).32,33 There, ptC plays a major role in defining surface morphology and as an initiation site for coking in catalysis. Surface carbides of Co and Ni show a p4g reconstruction, namely, a rotation of the two neighbor squares, along with a small expansion of the metal—metal distance, as shown in Figure 1. They are extremely stable, competing with graphite on these metals, and with stability driven by the local...
aromaticity. On the basis of this bonding principle, we further proposed that analogous aromatic p4g carbides should also form on the surfaces on Rh and Pd, and p4g nitrides should form on Co, Ni, and Rh.

This previous work showed that the bonding effects leading to special stability are largely confined to the top monolayer in the surface alloys. Subsurface layers retain the geometric and electronic structures of the bulk metals. Intrigued by these observations, we now probe if the top monolayers forming on metal surfaces can be stable 2D materials.

II. COMPUTATIONAL METHODS

Plane-wave PAW-DFT calculations were done using VASP,[35–37] with GGA rPBE,[38,39] and an empirical dispersion correction (D2).[40] In optimizations, both atomic positions and lattice constants were relaxed, until the forces were smaller than 0.05 eV Å/atom. Plane-wave energies were bonded by a 450 eV cut-off. The Brillouin zone was sampled with a (5 × 5 × 1) Monkhorst-Pack k-point grid. A more accurate (25 × 25 × 1) grid was used for the projected density of states (PDOS). A vacuum distance of ∼15 Å was set between monolayers to avoid interlayer interactions. We tested the influence of increasing the vacuum distance between monolayers up to ∼20 Å and found it has no impact on the results, suggesting that 15 Å is enough of a distance to avoid the interaction between layers. The six-layer fcc (100) slabs of Co, Ni, and Ag were built from the experimental bulk lattice parameters. Phonon calculations were carried out on a 2 × 2 supercell containing 24 atoms, with PBEsol,[41] using the Phonopy software.[42] Born–Oppenheimer molecular dynamics simulations, BO-MD, were performed using PBE[43] and ultrasoft pseudopotentials, as implemented in Quantum Espresso.[44]

Simulations were carried out at 300 K and every 200 K within simulations, the lattice vectors to change. This resulted in a more rapid exploration of the configurational space. After ca. 3 ps of

III. RESULTS AND DISCUSSION

We computationally characterized M2X monolayers (M = Co, Ni, and X = C, N). After the monolayers were lifted off of the metal surfaces and optimization, the p4g reconstruction and planarity of M2X persisted (Figure 1, Table 1). The carbides and nitrides are composed of XM4 squares, where X is located at the center of the metallic void, and M4 rhombuses. The computed phonon spectra of these p4g phases, with no imaginary modes in the entire Brillouin zone, confirm their kinetic stability (Figure S1). Co2N, Ni2N, and Ni2C materials are completely planar and feature a p4c or pTn. Co2C is slightly buckled, with the shift of 0.14 Å above and below the plane (Figure 1). The Co2C monolayer with enforced planarity has three imaginary modes (Figure S2). It is observed that the less electron-rich systems (Co over Ni, carbides over nitrides) are more strongly reconstructed, in agreement with the previous description of surface alloys.[44] Differences in bond lengths are in line with the radii of the constituting elements.

To evaluate the energetic stability of these structures, we calculated the cohesive energy per atom:

\[ E_{coh} = \frac{(E_{\text{UnitCell}} - 2E_X - 4E_M)}{6} \]

where \( E_X \) is the energy of a C or N atom, \( E_M \) is the energy of a Co or Ni atom, and \( E_{\text{UnitCell}} \) is the energy of one unit cell used in calculations. \( E_{coh} \) (Table 1) are between ca. −4.2 and −5.0 eV. Despite the absence of interactions in the z-direction, the monolayers compete in stability with the bulk Co and Ni fcc, calculated to be −5.04 and −4.65 eV per atom, respectively. Furthermore, the binding energies of the gas phase C/N to the most stable M(111) monolayers, \( BE(X) \), are −4.7 to −9.7 eV. Overall, the stability of the monolayers is very high, and it is the highest for the most electron poor Co2C.

The binding energies of the monolayers to the parent metallic fcc slab (BE*, Table 1) are rather large too, indicating that the monolayers could be hard to obtain through exfoliation of the parent slabs. However, we find that on (100) fcc silver (whose lattice constant of 4.09 Å is larger than that for Co, 3.35 Å, and Ni, 3.52 Å), the binding energies (BE**) are very small. Thus, we hypothesize that 2D carbides and nitrides could be prepared on, and peeled from, a silver slab. Note that on Ag the monolayers adopt the unreconstructed structure (Supporting Information, Figure S3). This fact will be the subject of our future studies.

To further probe the thermal stability of the proposed 2D alloys, ab initio molecular dynamics (MD) simulations at different temperatures were performed, for Ni3N as a selected case. We stress that Ni3N is actually the least stable, judging by \( E_{coh} \) values (Table 1). After 8 ps, the structure remained p4g up to a striking \( T \) of 1800 K. During the simulations, the monolayer buckles, with \( \Delta z \) being proportional to \( T \) (300 K, 0.3 Å; 800 K, 0.8 Å; 1000 K, 0.9 Å; 1200 K, 1.1 Å; 1400 K, 1.2 Å; 1600 K, 1.2 Å; 1800 K, 1.2 Å). For comparison, snapshots taken at the end of the MD at 300 K and 1800 K can be found in the Supporting Information (Figure S4). Overall, the system exhibits robust thermal stability and at least strong kinetic trapping.

Even though the system never exits the p4g phase in high-\( T \) MD, we further checked for its possible reorganization, for the Co2C case. First, we performed MD simulations at 800 K, with the mass of the metal nucleus artificially reduced, and allowing the lattice vectors to change. This resulted in a more rapid exploration of the configurational space. After ca. 3 ps of

![Image](https://example.com/fig1.png)
Our results taken together allow us to infer that the 2D p4g systems via the maximal possible localization of the full electron density, using SSAdNDP (Figure 3). We find this method to produce meaningful results only for closed-shell systems, and therefore we focus the analysis on Ni2N, as a representative case. In total, there are 50 valence electrons. SSAdNDP localizes four d-AO lone pairs on each Ni atom (occupation numbers, ON = 1.98 and 1.63 lel). The absence of any classical 2 centers–2 electrons (2c–2e) bonds suggests that the rest of the electrons are delocalized over more than 2c. Four 3c–2e bonds with ON = 1.89 lel are found, and they arise from the mixing of the 2s atomic orbital (AO) of N with d-AOs of the metal. The remaining 10 electrons are delocalized 5c–2e bonds, shared between all the atoms in the Ni4N square. Three 5c–2e bonds (ON = 1.99−1.97 lel) are σ-radial, where 2s-, 2p-, and 2p- AOs of N are mixed with the d_{yz},d_{xz},d_{xy} AOs of Ni. With six delocalized electrons populating these states, the system obeys the (4n + 2) Hückel’s rule for local σ-aromaticity in the Ni4N cycle, with n = 1. In addition, there is a completely bonding 5c–2e AOs of the metal with an insignificant participation of AOs on N. Two electrons in this state make the system additionally σ-peripherally aromatic, with n = 0. Note that the difference between σ-radial and peripheral is the orientation of the atomic orbitals: they point inward in the cycle, i.e., radially, in the σ-radial states, and along the periphery of the cycle in σ-peripheral states. A single π-state (ON = 1.68 lel) formed by the p_y AO on N and d_{xz},d_{yz} AOs on Ni makes the system locally π-aromatic, with n = 0. Overall, the system is 3-fold aromatic: σ-radial, σ-peripheral, and π. This strong stabilizing effect of aromaticity explains the marked preference for the p4g 2D structure. For Ni2C we found the same bonding pattern (Figure S7). For all alloys, the C/N-binding states lay deep below the Fermi level, E_F, as can be seen in Figure 4. From our previous work,34 we infer that they are identical for all considered 2D carbides and nitrides, and all of them are stabilized by triple aromaticity. In the work by Yang et al.,46 the SSAAdNDP for the buckled phase showed a different bonding pattern from the 2D phase, but also buckling was significant, and accompanied by a large change in charge distribution. This is not the case with our slightly buckled Co2C. The buckling seems to drive the structure toward somewhat higher compactness, for the enhancement of the bonding overlap (Table 1). In fact, among the considered materials, Co2C needs to accommodate the elements of the largest relative sizes (atomic radii: C 0.67 Å vs N 0.56 Å; Co 1.52 Å vs Ni 1.49 Å).

The states at E_F remain delocalized. Essentially, some of the d-states of the metal get consumed by the binding of the main group element, but other d-states remain delocalized as in the parent metallic monolayer. In accord with these modest changes in the wave functions, the structures of the monolayers are perturbed minimally. DFT suggests that all carbides and nitrides are metallic. This can be seen from the projected density of states (PDOS) plots (Figure 4). This result was indicative of the high preference of nitrides for the p4g reconstructed phase. Carbides are the most stable in the “hexagonal” but highly buckled phase (Figure 2B), with the corresponding planar monolayers being kinetically unstable (Figure S6). The highly buckled “pentagonal” phase of Co2C is also slightly more stable than p4g. The 2D nature of these buckled phases, however, can be questioned, as they likely tend toward the 3D bulk, and cannot be considered 2D anymore. Our results taken together allow us to infer that the 2D p4g phase prepared on top of a metal slab and exfoliated should be stable even at high T.

What electronic effects govern the structures of the found p4g 2D phases of Co and Ni carbides and nitrides? The bonding between Co/Ni and C/N is ionic, q(C/N) ~ −1, as is the case with all systems where the presence of ptC is governed electronically.10 We examined the chemical bonding in our systems via the maximal possible localization of the full electron density, using SSAdNDP (Figure 3). We find this method to produce meaningful results only for closed-shell systems, and therefore we focus the analysis on Ni2N, as a representative case. In total, there are 50 valence electrons. SSAdNDP localizes four d-AO lone pairs on each Ni atom (occupation numbers, ON = 1.98 and 1.63 lel). The absence of any classical 2 centers–2 electrons (2c–2e) bonds suggests that the rest of the electrons are delocalized over more than 2c. Four 3c–2e bonds with ON = 1.89 lel are found, and they arise from the mixing of the 2s atomic orbital (AO) of N with d-AOs of the metal. The remaining 10 electrons are delocalized 5c–2e bonds, shared between all the atoms in the Ni4N square. Three 5c–2e bonds (ON = 1.99−1.97 lel) are σ-radial, where 2s-, 2p-, and 2p- AOs of N are mixed with the d_{yz},d_{xz},d_{xy} AOs of Ni. With six delocalized electrons populating these states, the system obeys the (4n + 2) Hückel’s rule for local σ-aromaticity in the Ni4N cycle, with n = 1. In addition, there is a completely bonding 5c–2e AOs of the metal with an insignificant participation of AOs on N. Two electrons in this state make the system additionally σ-peripherally aromatic, with n = 0. Note that the difference between σ-radial and peripheral is the orientation of the atomic orbitals: they point inward in the cycle, i.e., radially, in the σ-radial states, and along the periphery of the cycle in σ-peripheral states. A single π-state (ON = 1.68 lel) formed by the p_y AO on N and d_{xz},d_{yz} AOs on Ni makes the system locally π-aromatic, with n = 0. Overall, the system is 3-fold aromatic: σ-radial, σ-peripheral, and π. This strong stabilizing effect of aromaticity explains the marked preference for the p4g 2D structure. For Ni2C we found the same bonding pattern (Figure S7). For all alloys, the C/N-binding states lay deep below the Fermi level, E_F, as can be seen in Figure 4. From our previous work,34 we infer that they are identical for all considered 2D carbides and nitrides, and all of them are stabilized by triple aromaticity. In the work by Yang et al.,46 the SSAAdNDP for the buckled phase showed a different bonding pattern from the 2D phase, but also buckling was significant, and accompanied by a large change in charge distribution. This is not the case with our slightly buckled Co2C. The buckling seems to drive the structure toward somewhat higher compactness, for the enhancement of the bonding overlap (Table 1). In fact, among the considered materials, Co2C needs to accommodate the elements of the largest relative sizes (atomic radii: C 0.67 Å vs N 0.56 Å; Co 1.52 Å vs Ni 1.49 Å).

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confirmed using the Hubbard U correction (Supporting Information). It is even more exciting that Co$_2$C and Co$_2$N have magnetic properties. We characterized the antiferromagnetic, ferromagnetic, and nonmagnetic states of cobalt compounds, and the relative energies are summarized in Table 3. Although for Co$_2$C, the ferromagnetic state is clearly favored (with a magnetic moment of the unit cell being 4.0 μB), for Co$_2$N the ferromagnetic (with a magnetic moment 2.6...
Table 3. Relative Energies (eV) of Ferromagnetic (FM), Antiferromagnetic (AFM), and Nonmagnetic (NM) States of p4g Reconstructed Co2C and Co2N

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<thead>
<tr>
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<th>FM</th>
<th>AFM</th>
<th>NM</th>
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<tbody>
<tr>
<td>Co2C</td>
<td>0.0</td>
<td>0.19</td>
<td>0.76</td>
</tr>
<tr>
<td>Co2N</td>
<td>0.0</td>
<td>0.002</td>
<td>0.27</td>
</tr>
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μB) and antiferromagnetic states are degenerated. The spin density in all cases was found to be largely localized on the metal atoms.

To the best of our knowledge, magnetism is exceedingly rare among stable 2D materials. Applications, for example, in memory devices can therefore be envisioned. Of another notice is the p2-AO on ptC/ptN: it is involved in the delocalized π-state but essentially remains occupied but uncoordinated. This may indicate its reactivity, affinity for small molecules with accessible vacant MOs for dative bonding, or interesting electronic properties (to-be-discovered in the future).

IV. CONCLUSIONS
To summarize, we propose a new class of metallic, and in some cases magnetic, 2D materials: carbides and nitrides of Co and Ni. These phases feature ptC and ptN coordination, rare in extended systems. 2D phases are predicted to be stable at elevated temperatures. The structure and stability are governed by 3-fold local aromaticity of the M2X (M = Co, Ni, X = C, N) unit that binds the main group elements. The possible method of preparation of these materials could involve exfoliation off of a slab with a larger lattice constant metal, such as Ag.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b07612.

Phonon spectra of all studied materials, structures of the monolayers supported on the parent slabs and on the surface of Ag, snapshots from MD trajectory taken at different temperatures, structures and phonon spectra of the planar p4g, “pentagonal”, and “hexagonal” Co2C monolayer, SSAdNDP results for Ni2C, and calculated DOS with and without Hubbard U (PDF)

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Notes
The authors declare no competing financial interest.

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REFERENCES


