Structural Transition in Oxidized Ca$_2$N Electrene: CaO/CaN 2D heterostructures

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Based on first-principles calculations we show that the oxidation of ultrathin films of Ca$_2$N electrodes, electrene, drives a hexagonal $\to$ tetragonal structural transition. The ground state configuration of the oxidized monolayer (ML) and bilayer (BL) systems can be viewed as CaO/CaN and CaO/(CaN)$_2$/CaO two dimensional (2D) heterostructures. In both systems, we found nearly free electron (NFE) states lying near the vacuum level, and the spatial projection reveals that they are localized above the oxidized CaO surface. Focusing on the magnetic properties, we find that the nitrogen atoms of the oxidized Ca$_2$N becomes spin-polarized ($\sim$1$\mu$B/N-atom); where (i) the ferromagnetic and the anti-ferromagnetic phases are nearly degenerated in the ML system, CaO/CaN, while (ii) there is an energetic preference for the ferromagnetic phase in CaO/(CaN)$_2$/CaO. We show that such a FM preference can be strengthened upon mechanical compression. Further electronic structure calculations reveal that the FM CaO/(CaN)$_2$/CaO presents half-metallicity, where the metallic channels project (predominantly) on the N-2p$_x$ orbitals. In addition to the total energy results, molecular dynamic and phonon spectra calculations have been done in order to verify its thermal and structural stabilities. Those findings suggest that CaO/(CaN)$_2$/CaO is a quite interesting, and structurally stable, 2D FM heterostructure characterized half-metallic bands sandwiched by NFE states lying on the oxidized surfaces.

I. INTRODUCTION

Two dimensional (2D) materials have been the subject of numerous studies addressing technological applications as well as fundamental issues. The seminal work on graphene $^1$ boosted the synthesis of other 2D systems. For instance, transition metal dichalcogenides. $^2$-$^8$ obtained through exfoliation processes of their layered parents, and 2D boron sheets (borophene) synthesized by bottom-up techniques on metal surfaces. $^4$-$^5$ In parallel to the experimental realizations, computational simulations have played an important role performing a virtual engineering on 2D systems; proposing new materials, and providing an atomic understanding of their physical/chemical properties. $^6$-$^8$ The combination of those efforts has contributed to the current revolution in the material science based on 2D structures. $^9$

Further control on the physical properties of those 2D materials can be done by tuning structural parameters like (i) the number of stacked layers or (ii) the equilibrium lattice structure; e.g. in (i) we have the linear/parabolic energy dispersion in graphene monolayer/bilayer. $^{10}$-$^{13}$ and in (ii) the semiconducting/metallic electronic structure of 2H/1T MoS$_2$. $^{14}$-$^{17}$ More elaborate strategies have been proposed/applied in order to tailor the electronic properties of 2D systems, as the design of van der Waals (vdW) heterostructures by stacking combinations of 2D materials. $^{18}$-$^{20}$, functionalization by foreign elements. $^{21}$-$^{23}$ and synthesis of Janus structures. $^{24}$-$^{27}$

It is worth noting that low dimensional systems, like bundles of carbon nanotubes and fullerenes host nearly free electron (NFE) states. $^{28}$-$^{30}$ In fact, NFE states have been firstly detected on metal surfaces through inverse photoemission spectroscopy experiments. $^{31}$-$^{33}$ and confirmed by first-principles calculations. $^{34}$-$^{36}$ Such NFE states are also present in 2D systems. For instance, in graphene those states were measured by near edge x-ray spectroscopy. $^{39}$ and further supported by theoretical first-principles DFT calculations. $^{40}$

Two dimensional dicalcium nitride is a layered system which hosts NFE states. Each Ca$_2$N layer unit is composed by a nitrogen atomic sheet sandwiched by calcium layers connected by Ca–N–Ca chemical bonds, whereas the Ca$_2$N layer units are stacked along the (001) direction bounded by van der Waals (vdW) interactions. Based on the oxidation states of Ca$^{2+}$ and N$^{3-}$ atoms, we can infer that each Ca$_2$N unit is positively charged, [Ca$_2$N]$^+$, and thus in order to provide electrostatic stability to the system, negative charges (anionic electron) take place between the Ca$_2$N layers. $^{41}$-$^{42}$ The NFE states are partially occupied by those anionic electrons, giving rise to metallic bands for wave-vectors on the [001] plane. $^{43}$ Meanwhile, in few layer systems, it has been predicted the presence of the anionic electrons not only embedded between the Ca$_2$N layers, but also on the surface region of the slab, giving rise to NFE surface states. $^{44}$

Few years ago, 2D nanosheet systems of Ca$_2$N electrides (electrene) have been successfully synthesized through exfoliation processes. $^{45}$ In fact, the metallic character, ruled by ionic electrons, was already pre-
dicted in the Ca$_2$N monolayer systems. Since the presence of metallic surface states makes the Ca$_2$N electrenes chemically very reactive, it has been proposed some strategies aiming to circumvent such a problem. For instance, the encapsulation of the Ca$_2$N nanosheet using 2D shields like graphene, single layer of BN, or graphane. On the other hand, NFE states make the Ca$_2$N surface a quite interesting platform to perform atomic design on 2D materials, for instance through functionalization by foreign atoms or molecules. Indeed, OH-functionalized Ca$_2$N and Y$_2$C monolayers have been proposed as new 2D materials for application in ion batteries and very recently, it has been proposed the control of the electronic and magnetic properties in Ca$_2$N monolayers through hidrogenation and oxidation processes.

Finally, it is well known that, in order to minimize the surface free energy, the surface atoms may rearrange upon incorporation of foreign elements. Such surface reconstructions may result in noteworthy electronic properties. For instance, the formation of NFE states and the nearly 1D metallic transport channels on the (single layer) indium covered silicon surface, In/Si(111)-($\sqrt{7}$×$\sqrt{3}$).

Once it is reasonable to infer that such a surface atomic rearrangements may take place in functionalized 2D systems; here, based on the density functional theory (DFT), we performed a set of first-principles calculations of the fully oxidized monolayer (ML) and bilayer (BL) Ca$_2$N electrenes. Our total energy results reveal a hexagonal $\rightarrow$ tetragonal structural transition in the oxidized Ca$_2$N-ML and -BL, resulting in 2D tetragonal heterostructures composed by stacked layers of CaO and CaN, namely CaO/CaN and CaO/(CaN)$_2$/CaO, respectively. In the sequence, the perform a detailed study of the electronic and magnetic properties of those systems. We found that both oxidized electrenes are metallic. The ferromagnetic phase is strengthened in the bilayer system; CaO/(CaN)$_2$/CaO is characterized by half-metallic bands localized within the (CaN)$_2$ layers, sandwiched by NFE states lying on the oxidized CaO surface. Molecular dynamics and phonon spectra calculation were done in order to confirm the thermal and structural stability of CaO/(CaN)$_2$/CaO. Those findings suggest that CaO/(CaN)$_2$/CaO is a potential structure for application in 2D nanodevices.

II. COMPUTATIONAL DETAILS

The calculations were performed by using the density functional theory (DFT), as implemented in the computational codes Quantum-Espresso (QE) and Vienna Ab initio Simulation Package (VASP). We have considered the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) for the exchange-correlation functional. The Kohn-Sham orbitals, and the self-consistent total charge density were expanded in plane wave basis sets with energy cutoffs of 70 and 353 Ry, respectively. The Brillouin zone sampling was performed by using a 8×8×1 k-point mesh. The Ca$_2$N-ML and -BL systems were described within the supercell approach with surface periodicties of (1×1), (2×2), and (3×3), and a vacuum region of between 22 and 28 Å. The atomic positions were relaxed until the residual forces were converged to within 5 meV/Å, and the structural relaxation (variable-cell) was performed within a pressure convergence of 0.05 Kbar. The long-range van der Waals (vdW) interactions were described using the semiempirical approaches vdW-D2 and -D3. We have also checked the validity of our results using the self-consistent vdW-DF approach. The structural stability was verified through the calculation of elastic constants and the phonon dispersion using PHONOPY code and the thermal stability was verified by ab initio molecular dynamics simulations (AIMD) at 300 K, with a time step of 1 fs using Nosé heat bath scheme.

III. RESULTS AND DISCUSSIONS

Pristine ML and BL Ca$_2$N. In Fig. we present the structural models and the electronic structure of pristine Ca$_2$N-ML and -BL. In Ca$_2$N the N atoms are
intercalated by Ca atoms, forming a triangular lattice, Fig. 2(a). At the equilibrium geometry, the Ca$_2$N-ML presents a lattice constant ($a$) of 3.56 Å, and Ca–C–a vertical distance ($d$) of 2.51 Å [Fig. 2(a)]. The Ca$_2$N-BL presents practically the same values of $a$ and $d$, and interlayer distance $h=3.62$ Å, Fig. 2(c). The energetic stability of the bilayer system is dictated by vdW interactions, where we found an interlayer binding energy of 79 meV/Å$^2$ (1.26 J/m$^2$). The electronic band structures of Ca$_2$N-ML and -BL, Figs. 2(d) and (e), reveal the formation of parabolic metallic bands for wave vectors parallel to the Ca$_2$N surface layer. The real space projection of those metallic parabolic bands within an energy interval of ±0.5 eV with respect to the Fermi level, $E_F$ ± 0.5 eV, reveals the formation nearly free electron (NFE) states spreading out on the surface of Ca$_2$N-ML and -BL, and sandwiched between Ca$_2$N layers in the BL system, Figs. 2(b) and (c).

**Oxygen adsorption.** Once we have characterized the electronic and structural properties of pristine Ca$_2$N-ML and -BL, where we found good agreement with the current literature, we examine their functionalization by oxygen adatoms. The energetic stability of the oxidized systems (O/Ca$_2$N) was inferred through the calculation of the oxygen adsorption energy ($E^a$),

$$E^a = E[Ca_2N] + E[O_2]/2 - E[O/Ca_2N],$$

where $E[O/Ca_2N]$ and $E[Ca_2N]$ are the total energies of oxidized and pristine Ca$_2$N (ML or BL), and $E[O_2]$ is the total energy of an isolated O$_2$ molecule. Positive values of $E^a$ indicate exothermic processes. In addition, in order to verify the emergence of magnetic phases, we compare the total energies of non-magnetic ($E^{NM}$) and magnetic ($E^{Mag}$) O/Ca$_2$N, $\Delta E^{mag} = E^{NM} - E^{Mag}$.

Firstly we calculate the adsorption energies of a single O adatom on the Ca$_2$N-ML. We have considered the sites A and B [Fig. 1(a)] in a (3×3) surface, and we found an energetic preference of 0.30 eV for the oxygen adatom lying on the hollow site (A), which is aligned with the Ca atom at the opposite side of the Ca$_2$N-ML. We obtained $E^a$ of 4.94 eV/O-atom, thus confirming the dissociative adsorption of O$_2$ molecules on the Ca$_2$N surface. [46, 70]

For a full coverage of oxygen adatoms, we found a structural transition of the oxidized Ca$_2$N-ML, O/Ca$_2$N-ML. We have considered the hexagonal lattice of pristine Ca$_2$N-ML as the initial configuration, and upon structural and atomic relaxations, we found (i) a metastable phase where the lattice vectors $a$ and $b$ increase by 12.5 % with respect to the pristine Ca$_2$N-ML and the planar angle between $a$ and $b$ ($\gamma$) increases from 120° to 125°, followed by (ii) a ground state tetragonal lattice with $|a|=|b|=4.72$ Å [Fig. 2(a)], and more stable than (i) by 0.97 eV/(1×1) with $E^a=4.04$ eV/O-atom, pointing out a large thermodynamic preference for (ii). As shown in Fig. 2(b), O/Ca$_2$N-ML is characterized by parallel layers of O/CaO and CaN, each one forming planar square lattices with Ca–O and Ca–N bond lengths of 2.36 Å [d in Fig. 2(b)]. Such a tetragonal phase of O/Ca$_2$N-ML can be described as a layered combination of trigonal structures of CaO and CaN crystals, forming a 2D CaO/CaN heterostructure. We can infer that the structural preference for the tetragonal phase is attributed to the larger formation energy of CaO compared with that of CaN, and also the proper stoichiometry upon the oxidation of one side of the Ca$_2$N-ML, O/Ca$_2$N-ML. On the other hand, when both sides of Ca$_2$N-ML are oxidized, O/Ca$_2$N-ML/O, the hexagonal lattice and the atomic structure of Ca$_2$N-ML have been preserved.

Focusing on the magnetic properties, there is an energy gain of $\Delta E_{mag}=68$ meV/(1×1) upon the inclusion of spin-polarization. We found a net magnetization ($m$) of 1 $\mu_B$ localized on the N atoms, a shown in Figs. 2(c) and (d) for the FM and AFM phases, respectively. The total energy comparison between the FM ($E^{FM}$) and AFM ($E^{AFM}$) phases indicates that the former is slightly more stable, with $E^{AFM} - E^{FM} = 7.6$ meV/N-atom. Electronic band structure calculations indicate the formation of metallic bands for both spin configurations (FM and AFM). The energy bands of the FM CaO/CaN [Fig. 3(a)], and the projection of the electronic states near the Fermi level [−0.15 < $E$ − $E_F$ < 0.5 eV in Fig. 3(c)] reveal a half-metallic system ruled by the N-2x,2y orbitals. Such a half-metallic behavior is suppressed in the AFM CaO/CaN. Further projection of the energy bands onto the atomic orbitals of Ca, N, and O [Fig. 3(b)] indicates that there are no atomic orbital contributions to the lowest unoccupied parabolic band $c_1$. Indeed, its spa-
FIG. 3. (a) Spin-polarized electronic band structure of the FM-CaO/CaN, (b) projection of the energy bands onto atomic orbitals; spacial projection of the metallic bands near the Fermi level ($E_F \pm 0.2$ eV) (c), and the parabolic band (c1) near the Γ-point (d). Isosurfaces of 0.001 $e/Å^3$.

Potential distribution near the Γ point, spreading out on the CaO surface [Fig. 3(d)], allow us to identify c1 as a NFE band localized at $\sim 1.6$ eV below the vacuum level ($E_{\text{vac}}$).

We next have considered the oxidation of both sides of Ca$_2$N-BL, O/Ca$_2$N-BL/O. Similarly to what we have done in O/Ca$_2$N-ML, we took the hexagonal structure of pristine Ca$_2$N-BL as the starting configuration. By performing full structural and atomic relaxations, we found a tetragonal lattice, with $|a|=|b|=4.77 Å$ [Fig. 4(a)], more stable than the hexagonal lattice by 1.97 eV/(1×1). The oxidation process is exothermic by $E_a = 4.14$ eV/O-atom, indicating that the dissociative adsorption picture has been kept for O$_2$ molecule on the Ca$_2$N-BL surface. O/Ca$_2$N-BL/O can be viewed as a combination of two CaO/CaN structures, however instead of vdW interaction, the formation of C–N chemical bonds, indicated as h in Fig. 4(b), increases the interlayer binding energy from 79 meV/Å$^2$ (pristine Ca$_2$N-BL) to 93 meV/Å$^2$. The equilibrium geometry of O/Ca$_2$N-BL/O is characterized by an inner region that mimics the atomic structure of the trigonal CaN, sandwiched by nearly planar layers of CaO, CaO/(CaN)$_2$/CaO.

In addition to the energetic stability of CaO/(CaN)$_2$/CaO, we have also examined its (i) structural, and (ii) thermal stabilities. The former [(i)], was performed by the calculation of the phonon spectra, presented in Fig. 5(a). We have considered the finite-displacement approach, with supercell sizes of (3 × 3) primitive unit cells. As we can see, there are no imaginary frequencies phonon frequencies. Those results allow us to infer that CaO/(CaN)$_2$/CaO is structurally stable. In (ii), we have performed ab initio molecular dynamics (AIMD) simulations at 300K, with a time step of 1 fs using the Nosé heating bath scheme. We have constructed a (3 × 3) supercell containing 9 formula units to minimize the constraint induced by the slab periodicity. The results of the variations of the total potential energy with respect to the simulation time, and snapshots of the last configurations are presented in Fig. 5(b). As we can observe, the atomic configuration remains nearly unaltered up to 5 ps, and no phase transition is observed in the total potential energy. These results demonstrate that the 2D CaO/(CaN)$_2$/CaO material, once synthesized, is stable and preserving its structural integrity at room temperature.

The key aspects related to the magnetic properties of CaO/(CaN)$_2$/CaO are summarized in Figs. 4(c)–(f). There is an energy gain upon the inclusion of spin-polarization of $\Delta E_{\text{mag}}=70$ meV/N-atom, practically the same values obtained in CaO/CaN. Similarly, the net magnetization is mostly localized on the N atoms, with $\sim 1 \mu_B$/N-atom. Further comparison between the FM and AFM couplings revealed that, (i) there is an energetic preference of 21 meV/N-atom for the FM configuration compared with the AFM configuration between the nitrogen atoms lying on the same CaN layer, intralayer
coupling shown in Figs. 4(c) and (d). (ii) Between the stacked CaN layers, interlayer coupling, we found the FM phase more stable than the AFM phase [Figs. 4(c) and (d)] by 32 meV/N-atom. Here, the emergence of such a magnetic phase in CaO/(CaN)$_2$/CaO can be considered as a remnant property of the (trigonal) CaN crystal. Using the mean field theory, we estimate a Curie temperature ($T_C$) in (i) of 162 K. It is worth noting that although nearly the same energy gain due to the spin-polarization ($\Delta E^{mag}$), the energetic preference for the intralayer FM configuration [(i)] has been strengthened in CaO/(CaN)$_2$/CaO; i.e., $E_{AFM} - E_{FM} = 7.6 \rightarrow 21$ meV/N-atom. Such a preference can be attributed to the FM interlayer coupling [(ii)]. In this case, we can infer that the energetic preference for the FM (interlayer and intralayer) phase can be tuned by a compressive strain normal to the CaO/(CaN)$_2$/CaO surface, and thus, increasing the Curie temperature. Indeed, as shown in Fig. 4(f), the total energy difference $E_{AFM} - E_{FM}$ of the intralayer and interlayer couplings increases upon external strain. For compression of 3% normal to the stacking direction, which corresponds to an external pressure of 17 GPa, the strength of the interlayer FM coupling increases from 32 to 46 meV/N-atom, resulting in an interlayer coupling of 27 meV/N-atom, that is, $E_{AFM} - E_{FM} = 21 \rightarrow 27$ meV/N-atom, and $T_C = 162 \rightarrow 209$ K.

The electronic band structure of the FM CaO/(CaN)$_2$/CaO characterizes a half-metallic system, where the spin-down metallic channels [purple lines in Fig. 6(a)] are (mostly) ruled by the N-$2p_{x,y}$ orbitals, Fig. 6(b). The charge density overlap of the metallic bands through the N atoms is depicted in Figure 6(c). Further energy band projections reveal that the unoccupied parabolic bands $c1$ and $c2$ in Fig. 6(b), lying at $\sim$1.1 eV (Γ-point) below the vacuum level, present no contributions from the atomic orbitals. Instead, $c1$ and $c2$ project on plane-waves characterizing NFE states spreading out (symmetrically) on the oxidized CaO surfaces as shown in Fig. 6(d). That is, the fully oxidized Ca$_2$N-BL, CaO/(CaN)$_2$/CaO, presents a combination of half-metal channels along the (CaN)$_2$ layers, sandwiched by NFE states on top of the oxidized CaO surface.

IV. SUMMARY AND CONCLUSIONS

We have performed a theoretical study, based on first-principles DFT calculations, of the oxidized Ca$_2$N electrons. The structural and atomic relaxations of the fully oxidized Ca$_2$N-ML and -BL systems reveal a hexagonal $\rightarrow$ tetragonal structural transition, giving rise to CaO and CaN (covalently bounded) stacked layers. Those oxidized systems can viewed as two-dimensional CaO/CaN and CaO/(CaN)$_2$/CaO heterostructures. Both systems are metallic, characterized by NFE states near the vacuum level, and localized above the oxidized CaO surfaces. The latter exhibits a (mechanically tunable) FM phase (strength), where the magnetic moment is mainly localized on the nitrogen atoms; giving rise to half-metallic energy bands projected mostly on the N-$2p_{x,y}$ orbitals. The structural and thermal stabilities of CaC/(CaN)$_2$/CaO have been confirmed through phonon spectra and molecular dynamic calculations. Those findings suggest that CaO/(CaN)$_2$/CaO, a half-metal intercalated by NFE states, is a promising material to the development of electronic and spintronic nanodevices based on 2D materials.
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