A scheme to fabricate magnetic graphene-like cobalt nitride CoN₄ monolayer proposed by first-principles calculations

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Based on the first-principles calculations, we propose a scheme to fabricate the cobalt nitride CoN₄ monolayer, a magnetic graphene-like two-dimensional material, in which all Co and N atoms are in a plane. Under the pressure above 40 GPa, the bulk CoN₄ is stabilized in a triclinic phase. With the pressure decreasing, the triclinic phase of CoN₄ is transformed into an orthorhombic phase, and the latter is a layered compound with large interlayer spacing. At ambient conditions, the weak interlayer couplings are so small that a single CoN₄ layer can be exfoliated by the mechanical method. © 2022 The Japan Society of Applied Physics

In 2017, two-dimensional (2D) ferromagnetism was first realized experimentally in the CrI₃ monolayer,¹ which is a milestone in the field of 2D materials. The CrI₃ monolayer is composed of three layers of atoms and it is not the thinnest material. Therefore, to fabricate magnetic 2D materials with a thickness limit is an important issue.

Graphene and the graphene-like 2D materials with a single-atom-thickness, such as borophene, boron nitride, and g-C₃N₄ are extremely promising for next-generation electronic devices.²⁻⁴ But there is no intrinsic magnetism with long-range orders in them because they are made up of the third to fifth group elements, which greatly limits the application range of these graphene-like materials. The most direct idea is to place the magnetic atoms in a sheet of graphene-like materials. When a transition metal atom is inserted in the graphene sheet or substitutes a carbon atom of graphene, it is difficult to reside in the same plane.⁵ The main reason is that the metal atom can not be bonded to the C atoms with a planar pattern. However, if we adopt nitrogen, rather than carbon, transition metal atoms may be bonded to nitrogen to form a planar monolayer. The idea is supported by the experiments of the single-atom catalyst synthesis, in which the planar geometry of the MN₄ (M = Fe, Co, Ni, etc.) moieties implanted into porous graphene sheets have been identified by the annular dark-field scanning transmission electron microscope.⁶ There are also some theoretical studies to provide evidence for the stability of the planar MN₄ (M = Cr, Mn, Co, Pt, etc.) moieties. For example, the CoN₄C₁₀, CoN₄C₂, CrN₄C₂, Mn₂N₄C₆, Pt₂N₂C₆ monolayers containing the MN₄ moieties⁷⁻¹¹ have been proved to be thermally, dynamically, and mechanically stable by the calculations of formation energy, molecular dynamics, phonon, and elastic constants. Moreover, the binary transition metal nitrides MN₄ (M = V, Cr, Mn, Fe, or Co) monolayers, which possess a similar structure to the graphene or graphene allotrope but contain the transition metal elements, have been predicted in the recent theoretical studies.¹²⁻¹³ Despite the great progress in this field, how to fabricate graphene-like magnetic two-dimensional monolayers experimentally is a crucial problem at this stage.

Very recently, the triclinic phase of beryllium tetrani tride BeN₄ was synthesized at the pressure of 85 GPa,¹⁴ and upon decompression to ambient conditions, it transforms into a layered compound with the weak van der Waals interactions. A single BeN₄ layer made up of beryllium atoms and polymeric nitrogen chains is proposed by the experiments and is confirmed by the first-principles calculations.¹⁴⁻¹⁵ The experiment of BeN₄ synthesis motivates us to think about whether the transition metal nitride MN₄ monolayers can be fabricated according to the above scheme. In experiments, FeN₄ under high pressure crystallizes into the triclinic structure with P1̅ group symmetry.¹⁶⁻¹⁸ In the theoretical studies, the CoN₄, MgN₄, and ZnN₄ structures under high pressure are predicted to be P1̅ triclinic phase through systematic structure search in the CALYPSO package.¹⁹⁻²¹ According to the above studies, the structures of FeN₄, CoN₄, MgN₄, and ZnN₄ at high pressure are definitely determined, which is a necessary prerequisite for our fabrication scheme of the magnetic monolayer. Because the structures of FeN₄ and ZnN₄ at ambient pressure are not layered materials with large interlayer spacing and there is no magnetism in MgN₄ and ZnN₄, we focus on the CoN₄ compound.

In this work, on the base of the first-principles calculations, we demonstrate that the graphene-like CoN₄ monolayer can be fabricated by the three steps, high-pressure synthesis, decompression to ambient condition, and mechanical exfoliation.

The electronic structure calculations are performed with the VASP software package, in which the plane wave pseudopotential method and the projector augmented-wave (PAW) pseudopotential with Perdew–Burke–Emzerhof (PBE) exchange-correlation functional²²⁻²⁵ are used. The plane wave basis cutoff is set to 600 eV, and the convergence thresholds of total energy and force are set to 10⁻⁵ eV and 0.01 eV Å⁻¹. The interlayer distance was set to 20 Å and a mesh with a density of 30 k-points per Å⁻¹ is used for the Brillouin zone integration. The phonon calculations are carried out with the supercell method in the PHONOPY program, and the real-space force constants were calculated using density-functional perturbation theory (DFPT) as implemented in VASP.²⁶ In the ab initio molecular dynamics simulations, the 2 × 2 × 2 supercells were employed and the temperature was kept at 1000 K for 5 ps with a time step of 1 fs in the canonical ensemble (NVT).²⁷

We first study the atomic structure of the CoN₄ compound under pressure. The structure of P1̅-CoN₄ is displayed in...
Fig. 1. (Color online) Crystal structure of $P\bar{1}$-CoN$_4$ at 40 GPa: (a) the unit cell; (b) top view of CoN$_4$ layer; (c) side view along the $c$ direction. Crystal structure of $Cmmm$-CoN$_4$ at 0 GPa: (d) the unit cell; (e) top view of CoN$_4$ layer; (f) side view along the $c$ direction. The numbers are the bond length or interlayer distance and the unit is Å.

Fig. 2. (Color online) (a)–(b) Phonon spectra of $P\bar{1}$-CoN$_4$ at 40 GPa and the Brillouin zone. (c)–(d) Phonon spectra of $Cmmm$-CoN$_4$ at 0 GPa and the Brillouin zone.

Figs. 1(a), 1(b), and 1(c), and the unit cell is marked by solid lines. One unit cell is composed of only one CoN$_4$ moiety. Due to the periodicity of the crystal structure, the CoN$_4$ moieties connect each other along the [110] lattice plane to form an infinite CoN$_4$ monolayer. The thing to notice is that at the pressure of 40 GPa the CoN$_4$ moiety in each unit cell still remains a planar configuration, which reveals the robustness of the CoN$_4$ planar configuration. The small buckling deformation occurs at the junction between two adjacent unit cells, leading to the fluctuation of the CoN$_4$ layer. The four N–Co bonds in the CoN$_4$ moiety have a length of 1.82 Å and 1.86 Å. The interlayer distance is 1.96 Å, equal to the distance of Co and N between two adjacent layers, and the distance increases gradually with the pressure decreasing.

To examine the dynamic stability of the $P\bar{1}$-CoN$_4$ structure, we perform the calculations of phonon spectra at 40 GPa. The phonon bands are shown in Fig. 2(a), and there is no imaginary frequency for their phonon modes, indicating that $P\bar{1}$-CoN$_4$ under the pressure from 40 GPa is dynamically stable. For $P\bar{1}$-CoN$_4$ at 40 GPa, the relative formation enthalpy $\Delta H$ with respect to Co metal and N$_2$ are computed in terms of the following formula,

$$\Delta H = (H_{\text{CoN}_4} - H_{\text{Co}} - 2H_{\text{N}_2})/5. \tag{1}$$

where $H_{\text{CoN}_4}$, $H_{\text{Co}}$, and $H_{\text{N}_2}$ are the enthalpies of CoN$_4$, Co metal, and N$_2$ at 40 GPa, respectively. The $\Delta H$ is $-0.45$ eV atom$^{-1}$ and the negative values indicate that the $P\bar{1}$-CoN$_4$ structure is energetically favorite at 40 GPa. The hydrostatic pressure of 40 GPa is easily achieved experimentally. Similar to the conditions for FeN$_4$ and BeN$_4$ synthesis, we can use a BX90 diamond anvil cell (DAC) to create a high-pressure environment with N$_2$ as a pressure-transmitting medium. Besides, the multianvil large-volume press (LVP), such as Kawai-type multianvil apparatus, can be used to generate the pressure of 40 GPa in a larger sample chamber.

With the decompression to 0 GPa, the triclinic $P\bar{1}$-CoN$_4$ structure will evolve into an orthorhombic structure with the $Cmmm$ group symmetry. The scenario is different from the BeN$_4$ compound, which still remains the triclinic structure when the pressure decrease from 85 GPa to ambient pressure in experiments. The $Cmmm$-CoN$_4$ structure is shown in Figs. 1(d), 1(e), and 1(f). Its unit cell is composed of only one formula cell and the CoN$_4$ moiety keeps a planar geometry. Compared with the $P\bar{1}$-CoN$_4$ structure at 40 GPa, the small buckling deformation at the junction of two CoN$_4$ moieties disappears and the whole CoN$_4$ layer becomes a perfectly planar configuration. In addition, the upper layer in the $Cmmm$-CoN$_4$ structure has an obvious translation with respect to the lower layer, causing the Co atoms in the adjacent layers to face each other. More importantly, the interlayer distance increases from 1.96 Å to 3.15 Å. Next, we verify the stability of the $Cmmm$-CoN$_4$ structure under ambient pressure. Figure 2(c) shows the phonon spectra. There is no imaginary frequency in the phonon curves, which proves that the structure is dynamically stable. The formation enthalpy $\Delta H$ with respect to Co metal and N$_2$ are computed and the value is 0.40 eV atom$^{-1}$, which is comparable to the
ones of other nitrides synthesized in experiments, such as CuN$_2$ (0.55 eV atom$^{-1}$), PtN$_2$ (0.42 eV atom$^{-1}$), and g-C$_3$N$_4$ (0.35 eV atom$^{-1}$). So, the Cmmm structure is a metastable phase similar to the above nitrides, which can exist under ambient conditions.

The variations of interlayer distance with pressure in P1-CoN$_4$ and Cmmm-CoN$_4$ structures are shown in Fig. 3(a). The blue and red solid circles are related to the P1-CoN$_4$ phase and Cmmm-CoN$_4$ phase, and the selected interlayer distances are marked in Figs. 3(b), 3(c), 3(d), and 3(e). Above 20 GPa, the CoN$_4$ retains the P1-CoN$_4$ structure, while it shifts to the Cmmm-CoN$_4$ structure below 15 GPa. A sharp increase of interlayer distance occurs at about 15 GPa, and the distance reaches up to 3.15 Å at 0 GPa, which means that there is very weak coupling between adjacent CoN$_4$ layers. The weak interlayer coupling and large interlayer space are similar to the case of triclinic BeN$_4$ compound under ambient conditions. We can imagine the following process of preparing the CoN$_4$ monolayer. The P1-CoN$_4$ phase is first synthesized under high pressure, then we gradually decompress the pressure to 0 GPa. The interlayer distance increases slowly and the Co–N bonds in the layer are not destroyed during the decompression process. At last, the Cmmm-CoN$_4$ phase with the planar CoN$_4$ layer and large interlayer spacing is obtained.

On the other hand, we compute and compare the enthalpies of P1-CoN$_4$ and Cmmm-CoN$_4$ phases at different pressures, and the data are shown in Fig. 4. When the pressures are larger than about 15 GPa for P1-CoN$_4$ or 12 GPa for Cmmm-CoN$_4$ phase, the relative enthalpies are negative, indicating that the synthesis of CoN$_4$ requires a pressure environment. With a pressure higher than 35 GPa, the P1-CoN$_4$ phase has a lower enthalpy than the Cmmm-CoN$_4$ phase, which indicates that the P1-CoN$_4$ phase does not exist under low pressure, which is consistent with the previous study. In contrast, the Cmmm-CoN$_4$ phase is a favorable structure at ambient conditions.

Since there exists a large interlayer space in the CoN$_4$ compound, one natural question is whether a single CoN$_4$ layer can be exfoliated from the bulk counterpart. Jia et al. proposed a method to assess the exfoliability of bulk crystals, in which besides cleavage energy, the mechanical integrity during the exfoliation was also taken into account.

The ratio $\sigma/Y$ is a measure to judge the exfoliability of layered compounds. $\sigma$ is the intrinsic intralayer strength of the material, a parameter to ensure the in-plane mechanical integrity during mechanical exfoliation, and $Y$ is the cleavage energy density. For simplicity, $\sigma/Y$ is represented by the in-plane Young’s modulus $Y_{in}$ and out-plane modulus $Y_{out}$, i.e., $\sigma/Y \approx Y_{in}/Y_{out}$, which makes it easier to judge the exfoliability. By computing the values of $Y_{in}/Y_{out}$ for 34 already-exfoliated 2D materials in experiments, the exfoliable threshold is determined to be 10.5. If the $Y_{in}/Y_{out}$ value is greater than 10.5, the material is regarded to be exfoliable.

For the Cmmm-CoN$_4$, we perform the calculations of the elastic constants and the Young’s modulus. The Young’s modulus $Y_{in}$ in the plane of CoN$_4$ layer varies from 600.2 to 814.6 GPa and the out-plane modulus $Y_{out}$ is 19.6 GPa. The $Y_{in}/Y_{out}$ is in the range of 30.2-41.6 GPa, greater than the threshold of 10.5. Therefore, the exfoliability of the Cmmm-CoN$_4$ compound is confirmed.

The next question is whether the free-standing CoN$_4$ monolayer is stable. In the previous study, we carried out the calculations of the phonon spectra and the molecular dynamics simulations for the free-standing CoN$_4$ monolayer. No imaginary frequency emerges in the phonon spectra and the integrity of the planar CoN$_4$ layer is not broken after 10 ps at 1000 K, which demonstrates that the CoN$_4$ monolayer has good dynamical and thermal stability. Furthermore, the stability mechanism of the CoN$_4$ monolayer is explained by the cooperation of the Co–N coordination bond, $\pi$ conjugation on the armchair N-chain, and $\pi$-d conjugation effect between the N–N $\pi$ bond and $d$ orbitals of the Co atom. By now, we have demonstrated that the graphene-like CoN$_4$ layer can be exfoliated from the bulk counterpart and can exist in the form of a single free-standing layer.

![Fig. 3](Image)

**Fig. 3.** (Color online) (a) Interlayer distance of CoN$_4$ in P1 and Cmmm phases varying with respect to the pressure. (b)–(e), At the selected pressures, the interlayer distances are marked with red numbers. Their unit is Å.
The GGA + U method is employed to investigate the magnetic properties of the CoN$_4$ monolayer. By the self-consistent calculation with the linear response method, the value of Hubbard U is determined to be 5.1 eV. Figure 5 shows the projected density of states on Co 3$d$ orbitals. We also compute the energies for ferromagnetic order (FM) and two antiferromagnetic orders (AFM-I and AFM-II), shown in Fig. 6. The FM, AFM-I, and AFM-II energies per formula cell are $-34.17$, $-34.80$, and $-34.69$ eV, respectively. The AFM-I and AFM-II orders have lower energy than the FM order, indicating that the magnetism in the ground state is antiferromagnetic.

In summary, based on the first-principles calculations, we propose a fabrication scheme of single-atom-thick magnetic 2D material, graphene-like CoN$_4$ monolayer, which is a transition metal nitride sheet with the antiferromagnetism. Under the pressure above 35 GPa, the CoN$_4$ adopts a triclinic phase with $P$1 group symmetry, while the $Cmmm$ phase is more favorite energetically with a pressure lower than 35 GPa. When the pressure decrease to 0 GPa, the interlayer spacing in the $Cmmm$-CoN$_4$ phase can reach up to 3.15 Å. The exfoliation of a single CoN$_4$ layer from the bulk counterpart is demonstrated by the ratio $Y_{in}/Y_{out}$. In addition, antiferromagnetism is determined by spin-polarized calculations. Therefore, our studies concerning the fabrication scheme of the graphene-like CoN$_4$ monolayer with intrinsic magnetism provide a new way synthesis of magnetic 2D materials in experiments.

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Fig. 5. (Color online) Partial density of states of Co 3$d$ orbitals of one Co atom in CoN$_4$ monolayer. Positive and negative values correspond to the spin-up and spin-down states.

Fig. 6. (Color online) Sketches of three magnetic orders in CoN$_4$ monolayer: (a) FM, (b) AFM-I, and (c) AFM-II.