New Spiral Form of Carbon Nitride with Ultrasoftness and Tunable Electronic Structures

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ABSTRACT: The structural diversity and multifunctionality of carbon nitride materials distinct from pure carbon materials are drawing increasing interest. Using first-principles calculations, we proposed a stable spiral structure of carbon nitride, namely spiral-C3N, which is composed of sp2-hybridized carbon and pyridine nitrogen with a 60° helical symmetry along the z-direction. The stability was verified from the cohesive energy, phonon spectrum, and elastic constants. Despite the strong covalent bonds of the spiral framework, the spiral-C3N exhibits a hardness lower than 12.00 GPa, in sharp contrast to the superhardness of cubic carbon nitrides reported in previous literature, which can be attributed to the unique porous configuration. The softness of the spiral-C3N was also confirmed by the small ideal strengths, which are, respectively, 33.00 GPa at a tensile strain of 0.22 along the [1̅21̅0] direction and 18.00 GPa at a shear strain of 0.52 in the (0001)[1̅21̅0] direction. Electronic band structure of spiral-C3N exhibits metallic features. A metal–semiconductor transition can be triggered by hydrogenation of the pyridine nitrogen atoms of spiral-C3N. Such a new three-dimensional spiral framework of sp2-hyperdized carbon and nitrogen atoms not only enriches the family of carbon nitride materials but also finds application in energy conversion and storage.

1. INTRODUCTION

As the neighbor element of carbon, nitrogen can form abundant allotropes with carbon. The structural diversity and multifunctionality of carbon nitride materials are drawing increasing interest because of their unique properties distinct from pure carbon materials. To date, a large number of carbon nitride materials with different stoichiometries, such as C3N,1−9 C2N,10 C2N3,11 CN,12,13 C3N4,14−19 and CN2,20,21 have been theoretically proposed or successfully synthesized, exhibiting potential application in energy conversion and storage, electronic devices, and so on. Carbon-rich carbon nitrides have been demonstrated to be more readily synthesized.22 For example, C3N materials have been fabricated via different approaches in the experiments.2,3−7 Bulk C3N flakes were synthesized from m-phenylenediamine (1,3-(NH2)2C6H4) by thermolysis under a static vacuum2 and small particles with hollow sphere-like configurations were produced at a temperature of 400 °C.5 The C3N powders synthesized from CaCN2 and C2Cl6 using a solvothermal method have a graphitic-like structure.7 The controllable and large-scale synthesis of C3N from polymerization of 2,3-diaminophenazine generated a hole-free 2D honeycomb lattice.7 Additionally, superhard C3N with C2221 and C2/c phases has also been predicted based on first-principles calculations.8,9 The entire question of the existence of C3N4 in relation to other nanocrystalline to polymeric carbon nitride materials has been reviewed recently.23,24

Notably, most of the carbon nitrides prefer graphite-like layered configurations because of the stable sp2-hybridization of carbon and nitrogen atoms. The strong covalent bonds involved in these carbon nitrides lead to high energy stability and excellent mechanical and electronic properties superior to graphene. For example, the two-dimensional (2D) C3N monolayer shows ultrahigh stiffness and thermal conductivity and high carrier mobility,25 and can serve as a promising anode material for Na- and K-ion batteries.26 C2N with a natural band gap has been employed in fabricating field-effect transistor devices with a high on/off current ratio of 107.10 C3N4 has shown great potential applications in photocatalysis,27 hydro-
gen generation,28 and energy storage.29 The porous configurations of C2N and C3N4 are also implementable for water desalination and gas separation.30,31 The C6N7 monolayer was predicted to be a promising candidate for water splitting under visible light.32 Suter et al. indicate that a range of graphitic carbon nitride (gC3N4) solid solutions or nanocomposite materials with tunable electronic properties might be produced using scalable thin film production techniques, by adjustment of the synthesis and deposition conditions.33 However, a three-dimensional covalent bond framework of all-sp2 hybridized carbon and nitrogen atoms has never been reported. Compared with the covalent bonds formed between sp3-hybridized atoms in cubic carbon nitrides, sp2-hybridized carbon and nitrogen atoms form a stronger covalent bond and the resulted 3D framework may have superhardness.34

As a unique morphology in crystals, the spiral structure has been drawing increasing interest because of the fascinating mechanical, electronic, and optical properties.35–40 The spiral structures of carbon materials can act as ideal nanosprings to store and release energy35 or potential nonlinear optical materials.36 Some spiral structures of carbon nitrides have also been synthesized in recent experiments, such as coiled carbon nanotubes with nitrogen dopants for supercapacitor applications,41 and tripod ligands containing star-shaped tris-terpyridines with 60° bis-terpyridines.39 However, the spiral structure of carbon nitrides has been rarely reported.

Here, based on first-principles calculations, we propose a stable 3D spiral framework of sp2 carbon and nitrogen atom carbon (spiral-C3N) with a 60° helical symmetry along the z-direction. The spiral covalent bond framework exhibits unexpected softness with the hardness lower than 20 GPa, in sharp contrast to the superhardness of cubic carbon nitrides reported in previous literature. We attributed the ultrasoftness of spiral-C3N to the unique porous configuration, which renders a large critical strain of 0.22 (tensile) and 0.52 (shear). Different from the semiconducting nature of 2D carbon nitrides, the electronic band structure of spiral-C3N exhibits metallic features with several bands across the Fermi level. A metal–semiconductor transition can be triggered by hydrogenation of the pyridine nitrogen atoms of spiral-C3N. The unique spiral structure, mechanical, and electronic properties hold great promise for application in energy conversion and storage.

2. RESULTS AND DISCUSSION

The energy-optimized atomic structure of spiral-C3N can be constructed by spirally stacking zigzag carbon nitride nanoribbons along the z-direction with a rotation angle of 60°, as shown in Figure 1. C–C covalent bonds are formed between adjacent benzene rings along the z-direction. Each unit cell contains three arrays of nanoribbons (18 C and 6 N atoms) and exhibits a triple-propeller-like shape along the z-direction, as shown in Figure 1a. A 60° helical symmetry around the z-direction is evident. The spiral framework possesses the P61222 symmetry of a hexagonal crystal system (D6h, No. 180). Two nonequivalent C atoms occupy the 12k (0.742, 0.744, 0.278) and 6e (0, 0, 0.222) Wyckoff positions, while one non-equivalent N atom occupies the 6f (0.500, 0.500, 0.226) Wyckoff positions in each primitive cell. The optimized lattice constants are a = b = 4.75 Å and c = 13.12 Å. The length of the C–C bond between adjacent nanoribbons along the z-direction is about 1.46 Å, which is slightly longer than that of the bonds in graphene (~1.42 Å) but shorter than that of the single bond in diamond (~1.53 Å). We attributed it to the rotation between the nanoribbons, which breaks the π conjugation. The distance between adjacent nanoribbons on the x–y plane is 4.37 Å as shown in Figure 1a, which is larger than the layer distance of graphite 3.35 Å. In contrast to the cubic carbon nitrides, spiral-C3N possesses a porous structure with a density of only 1.94 g/cm3, which is slightly lower than that of graphite (2.06 g/cm3). Within the benzene ring, the lengths of the C–C bonds are 1.46 and 1.42 Å, resulting in a slight deformation relative to the standard benzene ring. The C–C bond length is 1.34 Å, which is similar to that of the bonds in a similar chemical environment (1.35 Å).21 and slightly shorter than the bonds of 2D carbon nitrides (1.38–1.43 Å).25,26,41 These bond lengths are between single bonds and double bonds, indicating that the electrons are well delocalized in the rings. The bond angles deviate slightly from the corresponding standard values of sp2-hybridized bonds (120°). For example, the angles in the benzene ring have a slight difference of 0.34° and 0.81°, and the benzene ring of C3N4 is 1.52° shorter than the benzene ring of spiral-C3N. The unique spiral structure, mechanical, and electronic properties hold great promise for application in energy conversion and storage.

Figure 1. Atomic structure of spiral-C3N (a) side view, (b) Top view, and (c) base formation unit of spiral-C3N. The red broken line indicates the axis of rotation and gray and blue balls represent C and N atoms, respectively.
energetic favorability of the framework. Notably, the formation energy of spiral-C\textsubscript{3}N is only slightly higher than that of the graphene-like C\textsubscript{3}N (0.20 eV/atom).\textsuperscript{c} The rotation between adjacent nanoribbons breaks the π conjugation in the spiral framework compared with the planar configuration of graphene-like C\textsubscript{3}N and thus increases the energy of the system.

The dynamic stability of spiral-C\textsubscript{3}N can be confirmed from the phonon spectrum shown in Figure 2. The phonon spectrum is free from imaginary frequency modes except the long wavelength acoustic vibration with tiny imaginary frequencies near the Γ point. Similar tiny imaginary frequencies have also been found in other stable structures\textsuperscript{b2,b3} and won’t affect the stability of spiral-C\textsubscript{3}N. To further prove the thermal stability of spiral-C\textsubscript{3}N, we performed a molecular dynamics simulation on a large supercell within Nose–Hoover thermostat at 500 K and a time step of 1.0 fs. After 5000 cycles, the total energy of the supercell of spiral-C\textsubscript{3}N was converged without any structure collapse, as shown in Figure 2c.

The elastic constants of the spiral-C\textsubscript{3}N demonstrated the mechanical stability of the spiral framework. The symmetry of spiral-C\textsubscript{3}N leads to five independent elastic constants: \( C_{11}, C_{12}, C_{13}, C_{44}, \) and \( C_{66} \), which were evaluated to be 343.684, 394.183, 58.663, 120.130, and 52.660 GPa, respectively. These elastic constants satisfy the Born criteria of mechanical stability:\textsuperscript{c5} \( C_{44} > 0 \), \( C_{11} > |C_{12}| \), \( (C_{11} + 2C_{12}) \times C_{33} > 2C_{13}^2 \), all of which imply the stability and plausibility of spiral-C\textsubscript{3}N.

Having verified the stability of spiral-C\textsubscript{3}N, we turned to the mechanical properties of this spiral framework of covalent bonds. The elastic constant along the \( x \)- (or \( y \))- direction (\( C_{11} \)) is slightly lower than that along the \( z \)-direction (\( C_{33} \)). The elastic constant of \( C_{44} \) is only 58.663 GPa, suggesting a low shear modulus of the material. Young’s modulus \( (E) \) can be correlated with bulk \( (B) \) and shear \( (G) \) moduli using the formula\textsuperscript{c6}:

\[
E = \frac{9BG}{(3B + G)}
\]

while \( B \) and \( G \) can be obtained from the elastic constants according to Voigt–Reuss–Hill (VRH) approximations.\textsuperscript{c6} The Young’s moduli along three directions \( (Y_x, Y_y, \text{ and } Y_z) \) were determined from the strain–stress method.\textsuperscript{c7} The moduli of spiral-C\textsubscript{3}N are listed in Table 1. For comparison, the data of some typical carbon and nitride materials and graphite are also presented. Young’s modulus along the \( Z \)-direction (axial-direction) is larger than the corresponding values of \( X \)- and \( Y \)-directions (radial direction), which is consistent with the elastic constants. The Young’s moduli along the radial directions \( (X \)- and \( Y \)-directions) are almost equal and are comparable to the corresponding values of graphite. The Young’s modulus, bulk modulus, and shear modulus of spiral-C\textsubscript{3}N are far lower than those of C\textsubscript{2}/c-C\textsubscript{3}N, O–C\textsubscript{3}N, and \( \text{Pnnm-CN} \) and were predicted to be superhard.\textsuperscript{c5,c9,c12}

Frameworks of strong covalent bonds are always correlated with superhardness.\textsuperscript{c8} The lengths of the covalent bonds in spiral-C\textsubscript{3}N are shorter than those of C–C and C–N bonds in superhard carbon or carbon nitride materials.\textsuperscript{c8,c9,c10} We, therefore, evaluated the hardness of spiral-C\textsubscript{3}N from first-principles calculations. In view of the porous structure of spiral-C\textsubscript{3}N, we adopted the strategy proposed by Chen et al.\textsuperscript{c53} which has been validated for porous structures.\textsuperscript{c54,c56} According to this strategy, the Vickers hardness (\( H_v \)) can be correlated with the Pugh’s modulus ratio \( k = G/B \) and bulk modulus \( B \) by an empirical formula: \( H_v = 2(kG)^{0.55} - 3 \). The Vickers hardness of spiral-C\textsubscript{3}N was evaluated to be only 11.44 GPa, suggesting that it is an ultrasoft material in spite of the strong covalent bonds.

Notably, many factors are relevant for the hardness of materials, such as elastic modulus, bond length, bond density, degree of covalent bonding, strength, and so on. Among these factors, strength is often positively correlated with hardness and well reflects the material’s ability to resist fracture and deformation. To further confirm the ultrasoftness of spiral-C\textsubscript{3}N and reveal the unexpected mechanical properties, we evaluated the ideal strength of the system. Ideal strength corresponds to the maximum stress at which a perfect crystal begins to collapse or undergoes phase transition along the specific direction and thus is more suitable for describing the mechanical strength than elastic constants\textsuperscript{c57,c58}. As a benchmark, we first calculated the ideal tensile strengths of diamond and c-BN along the [1\{1\}0] direction. Our results 90.91 GPa (diamond) and 64.80 GPa (c-BN) agree well with those reported in previous literature.\textsuperscript{c57,c61} Using the same strategy, we evaluated the ideal tensile strength of spiral-C\textsubscript{3}N along different directions and planes. As shown in Figure 3, the ideal tensile strengths along the [1\{0\}10], [1\{2\}10], and [0\{0\}1] directions were 50.20, 33.00, and 41.77 GPa with strains of 0.42, 0.22, and 0.18, respectively. At the critical states, the C–

![Figure 2](https://dx.doi.org/10.1021/acsomega.0c04997)

**Figure 2.** (a) Phonon spectrum of spiral-C\textsubscript{3}N along the high-symmetry direction of the first Brillouin zone (b), and (c) total energy fluctuations with respect to the simulation time at 500 K.

**Table 1.** Young’s Modulus Along the Three Axes \( (Y_x, Y_y, \text{ and } Y_z) \), Young’s Modulus \( (E) \), Bulk Modulus \( (B) \), Shear Modulus \( (G) \), Hardness \( (H_v) \), and Pugh Modulus \( (k) \) of Spiral-C\textsubscript{3}N, C\textsubscript{2}/c-C\textsubscript{3}N, O–C\textsubscript{3}N, \( \text{Pnnm-CN} \), and Graphite at Zero Pressure

| Material       | \( Y_x \)  | \( Y_y \)  | \( Y_z \)  | \( E \)    | \( B \)    | \( G \)    | \( H_v \)  | \( k \)     |
|----------------|------------|------------|------------|-----------|-----------|-----------|------------|------------|
| spiral-C\textsubscript{3}N | 297.84     | 298.15     | 370.43     | 239.74    | 170.24    | 94.738    | 11.44      | 0.56       |
| C\textsubscript{2}/c-C\textsubscript{3}N\textsuperscript{c12} | 997.30     | 406.70     | 457.00     | 502.70    | 300.00    | 94.738    | 11.44      | 0.56       |
| O–C\textsubscript{3}N\textsuperscript{c13} | 905.04     | 406.00     | 401.00     | 400.00    | 300.00    | 94.738    | 11.44      | 0.56       |
| \( \text{Pnnm-CN} \)\textsuperscript{c21} | 753.60     | 347.90     | 330.80     | 347.90    | 240.00    | 94.738    | 11.44      | 0.56       |
| graphite\textsuperscript{c8} | 286.00     | 286.00     | 36.30      | 286.00    | 440.00^0^c50^0^ | 94.738    | 11.44      | 0.56       |

\(^{a}\)All parameters except Pugh modulus and behavior are in GPa. \(^{b}\)Individual layer plane. \(^{c}\)Parallel to basal planes in any direction.
C bond along the zigzag direction within the nanoribbons breaks first, followed by the C–C bond between the adjacent nanoribbons. This trend is inconsistent with lengths of the corresponding C–C bonds, i.e., former is shorter than the longer by 0.04 Å. The shear strengths in the (0001)[1010], (0001)[1210] and (1010)[1210] slip systems are 24.00, 18.00, and 22.33 GPa at strains of 0.66, 0.52, and 0.27, respectively.

The strength of the materials is determined by the weakest strength component. Clearly, spiral-C3N has the lowest ideal tensile and shear strength of 33.50 GPa at a strain of 0.22 along the [0001][1010], (0001)[1210] and (1010)[1210] slip systems. The relatively small shear strength and larger strain mean the low hardness and good ductility of the material. Although the covalent bonds between the sp2-hybridized C and N atoms are stronger than those of the superhard carbon or carbon nitride materials, the large void and anisotropic distribution of covalent bonds reduce their strength. The Pugh modulus ratio $k = 0.56$ further proves the ductility of spiral-C3N. In a recent work, density of a material was proposed as an indicator of the mechanical properties. The density of spiral-C3N, which is close to the value of graphite, may have similar mechanical properties.

Finally, we investigated the electronic structure of spiral-C3N. The electronic band structure of spiral-C3N, as shown in Figure 4a, exhibits metallic features with several bands across the Fermi level. This differs significantly from the semi-metallic features of 2D carbon nitride materials, such as the C3N monolayer, graphene-like C3N4, and C2N-h2D, and so forth.

To reveal the origins of the electronic band structures, the orbital-resolved electron density of states (PDOS) projected onto different C and N atoms as labeled in Figure 1d. The Fermi level was set to zero. Isosurfaces of the Kohn–Sham wavefunctions near the Fermi surface of (c) top view and (d) side view of a single rotation layer in spiral-C3N.

![Figure 3](https://example.com/fig3.png)

**Figure 3.** Orientation-dependent stress–strain relations for tensile and shear deformation of spiral-C3N.

![Figure 4](https://example.com/fig4.png)

**Figure 4.** (a) Band structures of spiral-C3N along the high-symmetry directions in the first Brillouin zone. (b) Orbital-resolved electron density of states (PDOS) projected onto different C and N atoms as labeled in Figure 1d. The Fermi level was set to zero. Isosurfaces of the Kohn–Sham wavefunctions near the Fermi surface of (c) top view and (d) side view of a single rotation layer in spiral-C3N.

![Figure 5](https://example.com/fig5.png)

**Figure 5.** (a) Atomic structure of spiral-C3N-adsorbed one H, (b) band structures from the PBE functional, and (c) isosurfaces of the Kohn–Sham wavefunctions near the Fermi surface of spiral-C3N adsorbed one H. Gray, blue, and white balls represent C, N, and H atoms, respectively.
the CBM state is contributed by C$_2$ atoms. The spiral conduction channel along the z-direction is blocked completely. These features were further confirmed by the PDOS plotted in Figure 6. In the region near the Fermi level, the states arise mainly from the P$_x$ and P$_y$ orbitals of the C and N atoms, whereas the contribution from H atoms and s and P$_z$ orbitals of C and N atoms can be ignored. The VBM and CBM states show π-binding and anti-π-binding features, respectively. Tunable electronic properties of spiral-C$_3$N hold great promise for the relevant applications, such as electronic devices and sensors.

3. CONCLUSIONS

Using first-principles calculations, we proposed a new stable form of carbon nitride material (spiral-C$_3$N) with a unique spiral framework, ultrasoftness, and tunable electronic properties. The spiral framework of the strong covalent bonds between sp$^2$-hybridized carbon and nitrogen atoms exhibits ultrasoftness with the hardness lower than 11.40 GPa and a low ideal shear strength of 18.00 GPa, in sharp contrast to the superhardness of cubic carbon nitrides reported in previous literature. It has a metallic electronic band structure with several bands across the Fermi level. The π-conjugation in the spiral framework contributes to the metallic features of spiral-C$_3$N. The helical channel along the z-direction will make the electron transport more fascinating. A metal-semiconductor transition can be triggered by hydrogenation of the pyridine nitrogen atoms. Such a new three-dimensional spiral framework contributes to the metallic features of spiral-C$_3$N. The spiral-C$_3$N will make the electron transport more fascinating. A metal-semiconductor transition can be triggered by hydrogenation of the pyridine nitrogen atoms. Such a new three-dimensional spiral framework contributes to the metallic features of spiral-C$_3$N.

4. METHODS AND COMPUTATIONAL DETAILS

Our first-principles calculations were performed by using density functional theory (DFT) implemented in the Vienna Ab initio simulation package. The exchange–correlation functional was described by using the generalized gradient approximation of the Perdew–Burke–Ernzerhof (GGA-PBE) functional. The energy cutoff of plane wave was set to be 520 eV. The Brillouin zone was sampled using a $12 \times 12 \times 6$ Monkhorst–Pack k-point grid. To describe long-range weak interaction in the porous structure, van der Waals interactions were taken into account using a corrected PBE functional (DFT-D3). Atomic positions and lattice constants were fully optimized using a conjugate gradient method until the remaining forces acting on each atom became less than $10^{-2}$ eV Å$^{-1}$. Phonon calculations were carried out by using a supercell approach in the Phonon code. Elastic constants, Young’s moduli along three directions (Y$_x$, Y$_y$, and Y$_z$), and ideal strength were calculated by the strain–stress method in the CASTEP package. To obtain the ideal strength, the equilibrium structure was transformed into an orthogonal structure. Then, the target-stress is applied on the structure along a specific direction, while the stresses of other directions were kept zero. The lattice vectors and atomic positions were then relaxed simultaneously to obtain the final structures and the corresponding strain. The polycrystalline bulk, shear, and Young’s moduli were estimated by using the Voigt–Reuss–Hill averaging scheme. Vickers hardness was calculated using the strategy proposed by Chen et al.

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Notes
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