Topological Quadrupole Phase in Two-dimensional $C_2N$

Z. H. Li,† P. Zhou,*,‡ Q. H. Yan,¶ X. Y. Peng,*,† Z. S. Ma,¶ and L. Z. Sun*,†

†Hunan Key Laboratory for Micro-Nano Energy Materials and Devices, School of Physics and Optoelectronics, Xiangtan University, Hunan 411105, People’s Republic of China
‡Key Laboratory of Low-dimensional Materials and Application Technology, School of Material Sciences and Engineering, Xiangtan University, Xiangtan 411105, People’s Republic of China
¶Hunan Provincial Key laboratory of Thin Film Materials and Devices, School of Material Sciences and Engineering, Xiangtan University, Xiangtan 411105, People’s Republic of China

E-mail: zhoupan71234@xtu.edu.cn, xiangyang_peng@xtu.edu.cn; lzsun@xtu.edu.cn

Abstract

Quadrupole phase, as a novel high-order topological phase, exhibits nontrivial gapless states at the boundaries whose dimension is lower than bulk by two. However, this phase has not been observed experimentally in two-dimensional (2D) materials up to now. In this work, using first-principles calculations and tight-binding (TB) model, we propose that the experimentally synthesized $C_2N$ is a 2D quadrupole topological insulator with one-dimensional gapped edge states and zero-dimensional gapless corner states. $C_2N$ is found to have a large bulk gap of 2.45 eV and an edge gap of 0.32 eV, making it an excellent candidate to evidently present the nontrivial corner states in experiments. The robustness of the corner states against the edge disorders has
been explicitly identified. Moreover, another three C$_2$N-like materials are also found to
host the nontrivial quadrupole phase including an experimentally synthesized material
aza-fused microporous polymers (CMP). The four 2D quadrupole topological phases
proposed in our present work provide excellent candidates for studying the novel high-
order topological properties in future experiments.

INTRODUCTION

In recent years, topological insulators have attracted enormous attentions due to their intrin-
sic topological nature and potential applications in many fascinating areas, such as low-power
electronic devices\textsuperscript{1–4} and quantum computing.\textsuperscript{5,6} A conventional $d$-dimensional topological
insulator supports gapless states on its ($d$-1)-dimensional boundaries, and the states are
insensitive to the local perturbations that preserve the nontrivial topology of the bulk.\textsuperscript{7–9}
Recently, the notion of second-order topological insulators (SOTIs) has been proposed to
extend the bulk-boundary correspondence, in which the gapless states appear in the corners
of a 2D system or the hinges of a three-dimensional system.\textsuperscript{10–22} From a physical point of
view, the low-dimensional topological boundary states are determined by electric dipole or
quadrupole moments.\textsuperscript{10,11} So far, the topological corner states were mainly observed in arti-
ficial 2D systems,\textsuperscript{23–28} such as square, Kagome, or hexagonal lattices, in which the nontrivial
phases are mainly derived from the difference between intercell and intracell hopping param-
eters. However, the hopping in electronic materials are generally more complicated. There-
fore, we need to go beyond the simplified model to find more potential SOTIs. Moreover,
although some experimentally synthesized materials, such as monolayer graphdiyne,\textsuperscript{29,30} $\gamma$
-graphyne,\textsuperscript{31} large-angle twisted bilayer graphene,\textsuperscript{32} and honeycomb antimony,\textsuperscript{33} have been
predicted as SOTIs in their low-energy gaps. Interestingly, recent research predicts twisted
bilayer graphene and twisted bilayer boron nitride\textsuperscript{34} as SOTIs in high-energy gaps. Un-
fortunately, none of them has been experimentally verified yet. The main obstacle for the
confirmation of SOTI in a realistic system is that its bulk and edge states gaps should be large enough so that the corner states can be isolated from the bulk and edge states and not be destroyed by external perturbations. Therefore, finding a SOTI fulfilling above requirements is an urgent task in the area.

Recently, a 2D monolayer material with evenly distributed holes and nitrogen atoms, named C$_2$N-h2D (briefed as C$_2$N hereafter), has been synthesized via a bottom-up wet-chemical reaction. Because of its tremendous application prospects in electronics, gas separation, and catalysis, C$_2$N has drawn much attention from both theoretical and experimental researchers. It is generally believed that monolayer C$_2$N is just an ordinary semiconductor with an experimental band gap of 1.9 eV. In this work, using density functional theory (DFT) and TB model, we theoretically predict that the C$_2$N monolayer actually is a realistic example of 2D SOTI with non-zero bulk quadrupole moment, gapped edge states, and topological corner states. The most desirable aspects of C$_2$N are its large bulk and edge state gaps, which will facilitate the detection of the corner states in future experiments. Furthermore, we demonstrate that the topological corner states are robust against disorder and C$_6$ symmetry breaking. Similar nontrivial two-order topological phase has also been found in other three C$_2$N-like 2D monolayers and one of them was synthesized experimentally. Considering two of them have been synthesized in the experiments, C$_2$N and its analogues are excellent platforms for studying the excellent properties of SOTIs.

**RESULTS**

The 2D crystal structure of C$_2$N monolayer is illustrated in Fig. (a). It is a typical 2D porous material and can be structurally obtained from a $2\sqrt{3} \times 2\sqrt{3}$ graphene supercell by removing a carbon six ring and then replacing the C atoms on the edge of the resulted holes with N atoms. The original space group of C$_2$N is P6/mmm (No. 191) and it can be generated
Figure 1: (a) Crystal structure of C$_2$N. The grey and blue spheres represent C and N atoms, respectively. The orange and black dotted lines, respectively, represent normal primitive and Wigner-Seitz unit cell of the monolayer; (b) The 2D Brillouin zone of C$_2$N; (c) The bulk electronic band structure of C$_2$N obtained by HSE06, blue and gray bands represent the subspaces originated from p$_z$ and s+p$_x$+p$_y$ orbitals, respectively; (d) The band structure of C$_2$N obtained from TB model.
by the rotation operations $C_{3z}$, $C_{2z}$ and mirror operations $M_y$, $M_z$. The lattice constants relaxed by the first-principles calculations are $a = b = 8.333\ \text{Å}$, in good agreement with previous experiments$^{35}$ and calculations$^{37,42,43}$ Considering the negligible spin-orbit coupling of C and N atoms, $C_2N$ can be effectively treated as a spinless system. The bulk electronic band structures of $C_2N$ obtained by HSE06 and PBE are presented in Fig. S2 (b), respectively. Since the different symmetry between $p_z$ and $s$ plus $p_{x,y}$ orbitals, the bands derived from them form two independent subspaces, as shown in Fig. S2 (b). Moreover, a global band gap of 2.45 eV is formed between the valence band maximum (VBM) and conduction band minimum (CBM) at $\Gamma$ point. The VBM and CBM mainly originate from the $p_z$ orbitals of both C and N atoms.

To study the topological properties of $C_2N$, a TB model was adopted. In space group P6/mmm, the inversion operation $I$ can be considered as the product of $C_{2z}$ and $M_z$. Because the eigenvalues of $M_z$ for the $p_z$ states are odd, the eigenvalues of $C_{2z}$ and $I$ differ by a sign. Therefore, the eigenvalues of $C_{2z}$ can also be used to calculate the quadrupole moment. Under the premise of ignoring spin, there are 39 valence electrons in $C_2N$, including 9 $p_z$ orbitals. By analyzing the $C_{2z}$ eigenvalues of the occupied Bloch states at $\Gamma$ and M points, we discover that the numbers of the states with eigenvalues of -1 are 18 and 20, respectively. Furthermore, as listed in Tab. S2, this difference is entirely contributed by the $p_z$ orbital, indicating that the $p_z$ states in $C_2N$ may form a nontrivial topological phase. To simplify the analysis about the topological properties, we build a TB model with the basis of $p_z$ orbitals as follows:

$$\hat{H} = \sum_i \epsilon_i + \sum_{ij} (t_{ij} \hat{c}_i^\dagger \hat{c}_j + \text{h.c.})$$

(1)

In the model, only on-site energies ($\epsilon_C$ and $\epsilon_N$) and nearest-neighbor hopping between the $p_z$ orbitals ($t_{C-C}$ and $t_{C-N}$) are considered. By fitting the TB bands to the occupied DFT bands, we obtain the TB parameters $\epsilon_C = 0.78\ \text{eV}$, $\epsilon_N = -1.60\ \text{eV}$, $t_{C-C} = -3.20\ \text{eV}$ and $t_{C-N} = -3.21\ \text{eV}$. As shown in Fig. S2 (d), the occupied TB bands are very close to the DFT bands.
derived from $p_z$ orbitals. Furthermore, the irreducible representations (irreps) of the Bloch states at high symmetry points obtained from first-principles method and TB model match with each other well, as listed in Tab. S1. Namely, the TB model can be effectively used to investigate the electronic topological properties of $C_2N$. The irreps of the Bloch states at the high symmetry points of $\Gamma$, $K$, and $M$ are closely related to the nontrivial second-order topological phase of $C_2N$, the details will be discussed below.

Firstly, we examine the topological properties of bulk $C_2N$. Because of the coexistence of the time-reversal and spatial inversion symmetries, the Chern number of the 2D system must be zero. Moreover, the $Z_2$ is always trivial for spinless systems. Except the two topological indexes, the bulk quadrupole, which is dependent on the dipole moments, can also be taken as a topological invariant to characterize a SOTI. For 2D hexagonal materials, the bulk dipole moment $p$ can be defined as \cite{21,51}

$$p_{1,2} = \frac{1}{2} \left( \sum_n q^n \text{ modulo } 2 \right) e, \quad (-1)^{\eta^n} = \frac{\eta^n(M)}{\eta^n(\Gamma)}$$

(2)

where $p_1$ and $p_2$ are the bulk dipole moments along the two reciprocal lattice directions and the term of $\eta^n$ denotes the $C_2$ eigenvalues of the $n$th occupied band at $\Gamma$ or $M$. As for $p_z$ states, the occupied number $n$ is 9. The numbers of the negative $C_2$ eigenvalues for $\Gamma$ and $M$ points are 6 and 4 (as listed in Tab. S2), respectively, resulting in vanishing bulk dipole moments.\cite{11} The bulk quadrupole moment of $C_2N$ can be further calculated from the bulk dipole moments by \cite{11}

$$q_{12} = \sum_n p_1^n p_2^n / e \text{ modulo } e.$$  

(3)

where the terms of $p_{1,2}^n = \frac{1}{2} (q^n \text{ modulo } 2) e$. The bulk quadrupole moment of $C_2N$ from the TB model is $q_{12} = 1/2$ $e$, which is matched with the first-principles calculation with the basis set of all $s$ and $p$ orbitals. There are two origins for the appearance of SOTIs: nonzero polarization or quadrupole moment. In some lattices, the Wannier centers of the
occupied states are mainly used to analyze the polarization of the systems. For example, in the breathing kagome lattice, the mismatch between the Wannier centers and the lattice site is used to explain the nontrivial corner states. In these systems, the polarization is nonzero and their quadrupole polarization is not defined. The corner states in these systems are characterized by nonzero polarization. However, for a system with C6 rotation, the polarization must be zero, and the bulk quadrupole can also be taken as a topological invariant to characterize a SOTI. Hence, C2N is a 2D SOTI with a nontrivial bulk quadrupole moment.

The nontrivial quadrupole moment of C2N can be understood from the symmetry properties and Wannier centers of the occupied states. For a one-atom-thick 2D system, the entire two-dimensional plane is mirror-invariant, which means that all states in the plane can be classified into two groups: odd and even under the mirror operation Mz. The p_z states are odd, whereas the s, p_x and p_y states are even. In other words, all p_z states form an independent subspace and the in-plane mirror symmetry Mz can be utilized to differentiate p_z states from s, p_x and p_y states. Therefore, it is sufficient to use the subgroup P6mm (No. 183) to investigate the p_z states, and this subgroup can be generated by the operations C3z, C2z and M_y. There is a C6 rotation operation along z-axis. All Wyckoff positions of the space group are listed in Tab. S3. The C and N atoms of 2D C2N locate at the Wyckoff positions of 12f and 6d with the local point group of E and C8, respectively. The induced irreps from the p_z orbitals at the two positions can be obtained with the theory of elementary band representations (EBRs) and the results are listed in Tab. S4 and Tab. S5. However,
by summing the number of the valence electrons of C and N atoms, only half of the bands are occupied, which makes the centers of the Wannier functions of the occupied bands may not coincide with the positions of the ions. For the systems with C_6 rotation symmetry, the Wyckoff positions of 1a, 2b, and 3c are the maximal, and we only consider the irreps of the wave functions at the high symmetry points of Γ, K, and M induced from them. The 1a and 3c Wyckoff positions are labeled with green dots and red pentagrams in Fig. (a), respectively. The EBRs induced by the Wannier functions on these Wyckoff positions can be found in the Bilbao Crystallographic Server. As demonstrated in the supplemental material’s formula (1), we establish a series of linear equations using the EBRs at Γ, K, and M as the basis set and all the irreps of C_2N’s valence bands as the solutions. A set of coefficients represents a collection of possible EBRs for the valence bands. Certainly, the coefficients of these equations must be integers. After solving these equations, we discover that the nine valence bands can only be induced by the sum of the Wannier functions of A1^3c, A2^3c, and B1^3c. The mappings between them are

\[ \begin{align*} 
A1^3c & \mapsto \Gamma + \Gamma + M + M + M + K + K \\
A2^3c & \mapsto \Gamma + \Gamma + M + M + M + K + K \\
B1^3c & \mapsto \Gamma + \Gamma + M + M + M + K + K 
\end{align*} \] (4)

where A1 induces the three bands with the lowest energies, whereas the other six occupied bands with higher energies come from A2 and B1. The EBRs of the occupied bands indicate that the centers of Wannier functions locate at the Wyckoff positions of 3c that clearly deviate from the ion positions. According to their eigenvalues of symmetry operation, we can obtain the invariant indexes of the three groups of occupied states. Each index forms a free Abelian additive structure, the non-zero summation of the indexes can be taken as non-trivial criterion of the system. According to the eigenvalues of the C_2 at M and the C_3
at K, the indexes are

\[ \chi^{(6)}(A1) = (-2, 0); \quad \chi^{(6)}(A2) = (-2, 0); \quad \chi^{(6)}(B1) = (2, 0). \]  

According to the theory of the index, the above three indexes actually describe the same topological phase and they correspond to the same primitive generator \( h_{3c}^6 \). Therefore, the \( p_z \) occupied bands of \( C_2N \) can be seen as \( h_{3c}^6 \oplus h_{3c}^6 \oplus h_{3c}^6 \). If the nine bands are separated into the lowest three ones and the other six ones as shown in \( 1 \) (d), the nontrivial topological phase of \( C_2N \) can be viewed as coming from the lowest three bands because the index of other six bands is equal to \((0, 0)\). If we only consider the A1 orbitals at the 3c Wyckoff positions, the configuration of the A1 orbitals is similar with a Kagome lattice, and the three bands with the lowest energies for \( C_2N \) are similar with the occupied bands of the lattice.\(^{22}\) The \( C_2 \) eigenvalues at the \( \Gamma \) and \( M \) for the lowest three bands, as shown in \( 2 \) (b), indicate that the polarization of the bands are \( \frac{e}{2}, 0 \) and \( \frac{e}{2} \), giving rise to a zero total polarization. However, the corresponding quadrupole moments are \( \frac{e}{4}, 0 \) and \( \frac{e}{4} \), leading to a non-vanishing total quadrupole of \( \frac{e}{2} \). Moreover, the distribution of the \( C_2 \) eigenvalues is the same as the occupied bands of the Kekulé-like hexagonal lattice, thus the \( C_2N \) and the Kekulé-like hexagonal lattice\(^{21,51,58}\) share the same second-order topological nontrivial properties.

To study the edge states of \( C_2N \), we cut it into two semi-infinite structures named as termination-a and -b, respectively, as shown in \( 3 \) (a) and (c). With the help of the TB Hamiltonian, their edge density of states are calculated and the results are presented in \( 3 \) (b) and (d). The results indicate that, between the projected valence bands and conduction bands, there are two gapped edge states for termination-a, whereas there is none for termination-b. The termination dependent edge states can be explained by the filling anomaly\(^{17}\) in \( C_2N \). As discussed above, the occupied states of \( C_2N \) can only be induced from the orbitals at the Wyckoff position \( 3c \) that clearly do not match with the atomic positions of \( C_2N \). For the case of termination-a, the \( 3c \) positions just locate on the boundary, which will produce a
Figure 3: Semi-infinite C$_2$N structures of termination-a edge (a) and termination-b edge (c). The projected edge density of states for termination-a edge (b) and termination-b edge (d), respectively.

kind of charge imbalance ($\rho$). The value of the charge imbalance can be obtained based on obstructed atomic limit approximation\textsuperscript{11} as $\rho = \frac{\#\text{ions} - \#\text{electrons}}{2} |e|$, where $\#\text{ions}$ and $\#\text{electrons}$ are the number of ions and electrons per unit cell, respectively. The value of the $\rho$ is proportional to the number of the Wannier centers on one edge per unit cell. If we assume the number of unit cell along the periodic direction is $N_x$, for the termination-a edge, the $\#\text{ions}$ and $\#\text{elec}$ are $4N_x$ and $2N_x$, respectively and they are $2N_x$ and $2N_x$ for termination-b. After reducing the number of primitive cells $N_x$, we can acquire $\rho = 2|e|$ for the termination-a and $\rho = 0|e|$ for the termination-b. The value of $\rho/|e|$ is rightly equal to the number of the edge states. Interestingly, the energy gap of the two edge states, as shown in (b), reaches up to 0.5 eV. Although the energy gap of the two edge states will reduce to 0.32 eV when considering the Wannier Hamiltonian of all orbitals, as shown in Fig. S1, the energy gap of the two edge states will leave enough energy space to accommodate the corner states of C$_2$N that will be discussed below.

Besides the gapped edge states, the existence of corner states is another strong evidence for a SOTI. According to the theory of the filling anomaly, the corner charge can be obtained
Figure 4: (a) Energy spectrum of the hexagonal-shaped C$_2$N cluster with different size. S is the number of holes in C$_2$N cluster. (b) The total and (c) the individual real-space wave function distributions of six in-gap topological corner states. The radii of the spheres on each atom denotes the absolute values of square modulus of wave functions.

from the symmetry properties of the occupied bulk bands:

\[
Q^{(6)}_{\text{corner}} = \frac{e}{4} \left[ M^{(2)}_1 \right] + \frac{e}{6} \left[ K^{(3)}_1 \right] \mod e
\]  

where $[M^{(2)}_1]$ ($[K^{(3)}_1]$) is the difference of the number of the states whose C$_2$ (C$_3$) eigenvalue equal to 1 between $\Gamma$ and M (K) points. We find that the terms $[K^{(3)}_1]$ and $[M^{(2)}_1]$ are equal to 0 and 2 for C$_2$N, resulting in $Q^{(6)}_{\text{corner}} = 1/2|e|$, in consistent with the value of quadrupole moment $q_{12}$ as discussed above. To reveal the distributions of the charges, C$_2$N is cut into a hexagonal cluster with armchair edges, and its discrete energy levels are shown in (a). Remarkably, there are six in-gap states ($\psi_0$-$\psi_5$ as shown in the inset of (a)) around the Fermi energy. The results also indicate that $\psi_1$ ($\psi_2$) and $\psi_5$ ($\psi_4$) are degenerate. The real space configuration of all the in-gap states can be visualized by their wave function distributions as shown in (b). The in-gap states are well localized at the six corners. In (c), we also show the real-space wave function distributions of the six in-gap corner states.
separately. The distributions of the corner states can be well explained by the symmetry of the cluster. The point group of the hexagonal cluster is $D_6$. Thus, we can use the irreps of $D_6$ to analyze the characteristics of the eigenvalues and eigenvectors of the six in-gap states. According to $D_6$ point group, the in-gap states can be written as the linear combination of the isolated $p_z$ states at the six corners as follows:

$$
\psi_m = a + \epsilon_m b + \epsilon_m^2 c + \epsilon_m^3 d + \epsilon_m^4 e + \epsilon_m^5 f
$$

$$
\epsilon_m = e^{m\pi i/6} \quad m \in (0, 1, 2, 3, 4, 5)
$$

(7)

where $a$-$f$ denote the isolated $p_z$ states at the six corners. According to the theory of equivalence transformation, the equivalence representation of the $p_z$ states $\Gamma^{a.c.}$ can be written as the direct sum of $\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_5 \oplus \Gamma_6$. $\psi_0$ will remain unchanged under all the $D_6$ symmetry operations, that the irrep of $\psi_0$ is $\Gamma_1$. Analogous to the simple hypothetical SH6 molecule, $\psi_0$ state should be non-degenerate and its energy should be the lowest one among the six in-gap states. The irrep of $\psi_3$ is $\Gamma_3$ with anti-symmetric characteristics, it should be non-degenerate and its energy is the highest one among the six in-gap states. $\psi_1$ and $\psi_5$ states conjugate each other and the irrep of the combination of the two states is $\Gamma_6$, thus the two states should be degenerate. Similarly, $\psi_2$ and $\psi_4$ are also degenerate because they are complex conjugate each other, and the irrep of the two states is $\Gamma_5$. It is worth noting that the splitting of the energy levels of the in-gap states derives from the couplings between the corner states. The splitting will reduce with the increase in the cluster size. Namely, the corner states will become gapless in the limit of large size clusters, the results can be found in [4](a).

For a concrete C$_2$N cluster, the influence of relaxation of the chemical bonds for the boundary atoms and external atom absorptions on its electronic properties should be considered. Therefore, the robustness of the corner states against external perturbations is investigated by adding a random on-site energy to the edge atoms in TB model, and the results can be found in Fig. S3. Despite the intensity of the disorder (the difference between highest and lowest values of random on-site energies) reaches up to 1.0 eV that is much larger
Figure 5: Crystal structures of $\text{C}_3\text{N}_2$ (a), $\text{C}_4\text{N}_3$ (b), and aza-CMP (c). The blue, grey, and pink spheres represent N, C, and H atoms, respectively. (d)-(f) are the corresponding energy spectra of the hexagonal-shaped clusters, and real-space wave function distributions of six in-gap topological corner states, the radii of spheres on each atom denote the absolute values of the square modulus of wave functions.
than the gap of topological edge states, the eigenvalues of the corner states still remain in the
gap of the edge states. However, the degeneracy of the in-gap states are destroyed. More-
over, although the total real-space wave function distributions of all the corner states is very
similar to the case without disorders, its distribution symmetry is broken, as shown in Fig.
S3 (c). It means that strict symmetries of the cluster are not necessary for the appearance
of topological corner states as long as the bulk and edge band gaps are not closed. Namely,
the corner states of $C_2N$ cluster is robust against external influence, which is favorable for
experimental observation.

The Wigner-Seitz unit cell of $C_2N$ as shown in Fig. (a) indicates that the $C_2N$ monolayer
can be obtained by applying $C_6$ rotation and translational symmetries to a three-atom lig-
and (blue shadow area in the figure). Moreover, the ligand can be replace with other odd
number C-N atom chains to produce new CN monolayers, such as $C_3N_2$ and $C_4N_3$ as shown
in Fig. (a) and (b), respectively. Furthermore, partial and total N atoms in the ligand can be
replaced by the C-H atomic group to obtain CNH or CH monolayers. A well-known one
with this replacement is the experimentally synthesized aza-fused microporous polymers as
shown in Fig. (c). We take $C_3N_2$, $C_4N_3$, and $C_5N_2H$ as examples to investigate their electronic
structures and topological properties. The band structures from first-principles calculations
are presented in Fig. S4. The results reveal that these three materials are semiconductors
with the band gaps of 2.0 eV, 1.49 eV, and 1.64 eV for $C_3N_2$, $C_4N_3$, $C_5N_2H$, respectively.
The results of bulk quadrupole moments of the occupied states for all the three 2D materials
indicate that they are two-order topological insulators with the quadrupole moments of 1/2
e. With the help of TB models only considering the nearest-neighbor hopping of $p_z$ orbitals
(the detail TB model parameters can be found in Tab. S6), we find that similar corner states
appear in the three materials, as shown in Fig. (d)-(f).
CONCLUSION

In summary, the nontrivial topology of C$_2$N is revealed by the nonzero bulk quadrupole moment, gapped edge states, and in-gap topological corner states. Detailed symmetry analysis reveals that the nontrivial topological properties come from the three bands with the lowest energies. Further calculations verify that the corner states of C$_2$N are robust against edge disorders. Moreover, other three C$_2$N-like materials were found to be similar SOTIs, including the experimentally synthesized aza-CMP. Our results will promote the experimental detection of the corner states and provide realistic candidates for studying the 2D two-order topological insulators in experiments.

METHODS

Our first-principles calculations were carried out in the framework of generalized gradient approximation (GGA) for exchange-correlation potential in the form of Perdew-Burke-Ernzerhof (PBE) implemented in Vienna ab initio simulation package (VASP). A vacuum space of 15 Å was used to avoid couplings between two neighboring slabs. The first Brillouin zone was represented by the Monkhorst-Pack special k-point scheme of 7×7×1 grid meshes. The energy cutoff, convergence criteria for energy, and force were set to be 500 eV, 10$^{-6}$ eV, and 0.01 eV/Å, respectively. The bulk band structures were calculated using HSE06. The edge states of the semi-infinite structure were obtained with the tight-binding method and maximally localized Wannier functions (MLWFs) constructed with the wannier90 code.
Acknowledgement

This work is supported by the National Natural Science Foundation of China (Grant No. 11804287, 11874315, 11574260), Hunan Provincial Natural Science Foundation of China (2019JJ50577) and the Scientific Research Fund of Hunan Provincial Education Department (18A051).

References

(1) Žutić, I.; Fabian, J.; Sarma, S. D. Spintronics: Fundamentals and applications. Reviews of Modern Physics 2004, 76, 323.

(2) Kong, D.; Chen, Y.; Cha, J. J.; Zhang, Q.; Analytis, J. G.; Lai, K.; Liu, Z.; Hong, S. S.; Koski, K. J.; Mo, S.-K., et al. Ambipolar field effect in the ternary topological insulator (Bi x Sb 1–x) 2 Te 3 by composition tuning. Nature Nanotechnology 2011, 6, 705–709.

(3) Cornelissen, L.; Liu, J.; Duine, R.; Youssef, J. B.; Van Wees, B. Long-distance transport of magnon spin information in a magnetic insulator at room temperature. Nature Physics 2015, 11, 1022–1026.

(4) Lin, X.; Yang, W.; Wang, K. L.; Zhao, W. Two-dimensional spintronics for low-power electronics. Nature Electronics 2019, 2, 274–283.

(5) Moore, J. E. The birth of topological insulators. Nature 2010, 464, 194–198.

(6) Tokura, Y.; Yasuda, K.; Tsukazaki, A. Magnetic topological insulators. Nature Reviews Physics 2019, 1, 126–143.

(7) Fu, L.; Kane, C. L.; Mele, E. J. Topological insulators in three dimensions. Physical Review Letters 2007, 98, 106803.

(8) Hasan, M. Z.; Kane, C. L. Colloquium: topological insulators. Reviews of Modern Physics 2010, 82, 3045.
(9) Qi, X.-L.; Zhang, S.-C. Topological insulators and superconductors. *Reviews of Modern Physics* 2011, 83, 1057.

(10) Benalcazar, W. A.; Bernevig, B. A.; Hughes, T. L. Quantized electric multipole insulators. *Science* 2017, 357, 61–66.

(11) Benalcazar, W. A.; Bernevig, B. A.; Hughes, T. L. Electric multipole moments, topological multipole moment pumping, and chiral hinge states in crystalline insulators. *Physical Review B* 2017, 96, 245115.

(12) Schindler, F.; Cook, A. M.; Vergniory, M. G.; Wang, Z.; Parkin, S. S.; Bernevig, B. A.; Neupert, T. Higher-order topological insulators. *Science Advances* 2018, 4, eaat0346.

(13) Franca, S.; van den Brink, J.; Fulga, I. An anomalous higher-order topological insulator. *Physical Review B* 2018, 98, 201114.

(14) Geier, M.; Trifunovic, L.; Hoskam, M.; Brouwer, P. W. Second-order topological insulators and superconductors with an order-two crystalline symmetry. *Physical Review B* 2018, 97, 205135.

(15) Zeng, Q.-B.; Yang, Y.-B.; Xu, Y. Higher-order topological insulators and semimetals in generalized Aubry-André-Harper models. *Physical Review B* 2020, 101, 241104.

(16) Khalaf, E. Higher-order topological insulators and superconductors protected by inversion symmetry. *Physical Review B* 2018, 97, 205136.

(17) Benalcazar, W. A.; Li, T.; Hughes, T. L. Quantization of fractional corner charge in Cn-symmetric higher-order topological crystalline insulators. *Physical Review B* 2019, 99, 245151.

(18) Langbehn, J.; Peng, Y.; Trifunovic, L.; von Oppen, F.; Brouwer, P. W. Reflection-symmetric second-order topological insulators and superconductors. *Physical Review Letters* 2017, 119, 246401.
(19) Song, Z.; Fang, Z.; Fang, C. (d- 2)-dimensional edge states of rotation symmetry protected topological states. Physical Review Letters 2017, 119, 246402.

(20) Ezawa, M. Strong and weak second-order topological insulators with hexagonal symmetry and $Z_3$ index. Physical Review B 2018, 97, 241402.

(21) Liu, F.; Wakabayashi, K. Novel topological phase with a zero berry curvature. Physical Review Letters 2017, 118, 076803.

(22) Ezawa, M. Higher-order topological insulators and semimetals on the breathing kagome and pyrochlore lattices. Physical Review Letters 2018, 120, 026801.

(23) Xue, H.; Yang, Y.; Gao, F.; Chong, Y.; Zhang, B. Acoustic higher-order topological insulator on a kagome lattice. Nature Materials 2019, 18, 108–112.

(24) Ezawa, M. Higher-order topological electric circuits and topological corner resonance on the breathing kagome and pyrochlore lattices. Physical Review B 2018, 98, 201402.

(25) Serra-Garcia, M.; Peri, V.; Süssstrunk, R.; Bilal, O. R.; Larsen, T.; Villanueva, L. G.; Huber, S. D. Observation of a phononic quadrupole topological insulator. Nature 2018, 555, 342–345.

(26) Serra-Garcia, M.; Süssstrunk, R.; Huber, S. D. Observation of quadrupole transitions and edge mode topology in an LC circuit network. Physical Review B 2019, 99, 020304.

(27) Imhof, S.; Berger, C.; Bayer, F.; Brehm, J.; Molenkamp, L. W.; Kiessling, T.; Schindler, F.; Lee, C. H.; Greiter, M.; Neupert, T., et al. Topoelectrical-circuit realization of topological corner modes. Nature Physics 2018, 14, 925–929.

(28) Oudich, M.; Su, G.; Deng, Y.; Benalcazar, W.; Huang, R.; Gerard, N. J.; Lu, M.; Zhan, P.; Jing, Y. Photonic analog of bilayer graphene. Physical Review B 2021, 103, 214311.
(29) Sheng, X.-L.; Chen, C.; Liu, H.; Chen, Z.; Yu, Z.-M.; Zhao, Y.; Yang, S. A. Two-dimensional second-order topological insulator in graphdiyne. *Physical Review Letters* **2019**, *123*, 256402.

(30) Lee, E.; Kim, R.; Ahn, J.; Yang, B.-J. Two-dimensional higher-order topology in monolayer graphdiyne. *npj Quantum Materials* **2020**, *5*, 1–7.

(31) Liu, B.; Zhao, G.; Liu, Z.; Wang, Z. Two-Dimensional Quadrupole Topological Insulator in $\gamma$-Graphyne. *Nano Letters* **2019**, *19*, 6492–6497.

(32) Park, M. J.; Kim, Y.; Cho, G. Y.; Lee, S. Higher-order topological insulator in twisted bilayer graphene. *Physical Review Letters* **2019**, *123*, 216803.

(33) Radha, S. K.; Lambrecht, W. R. L. Buckled honeycomb antimony: Higher order topological insulator and its relation to the Kekulé lattice. *Physical Review B* **2020**, *102*, 115104.

(34) Liu, B.; Xian, L.; Mu, H.; Zhao, G.; Liu, Z.; Rubio, A.; Wang, Z. Higher-Order Band Topology in Twisted Moiré Superlattice. *Physical Review Letters* **2021**, *126*, 066401.

(35) Mahmood, J.; Lee, E. K.; Jung, M.; Shin, D.; Jeon, I.-Y.; Jung, S.-M.; Choi, H.-J.; Seo, J.-M.; Bae, S.-Y.; Sohn, S.-D., et al. Nitrogenated holey two-dimensional structures. *Nature Communications* **2015**, *6*, 1–7.

(36) Guan, S.; Cheng, Y.; Liu, C.; Han, J.; Lu, Y.; Yang, S. A.; Yao, Y. Effects of strain on electronic and optic properties of holey two-dimensional C$_2$N crystals. *Applied Physics Letters* **2015**, *107*, 231904.

(37) Zhang, R.; Li, B.; Yang, J. Effects of stacking order, layer number and external electric field on electronic structures of few-layer C$_2$N-$h$2D. *Nanoscale* **2015**, *7*, 14062–14070.

(38) Guan, Z.; Lian, C.-S.; Hu, S.; Ni, S.; Li, J.; Duan, W. Tunable structural, electronic, and optical properties of layered two-dimensional C$_2$N and MoS$_2$ van der waals het-
(39) Yang, Y.; Guo, M.; Zhang, G.; Li, W. Tuning the electronic and magnetic properties of porous graphene-like carbon nitride through 3d transition-metal doping. *Carbon* 2017, 117, 120–125.

(40) Bafekry, A.; Stampfl, C.; Ghergherehchi, M.; Shayesteh, S. F. A first-principles study of the effects of atom impurities, defects, strain, electric field and layer thickness on the electronic and magnetic properties of the C$_2$N nanosheet. *Carbon* 2020, 157, 371–384.

(41) Xu, B.; Xiang, H.; Wei, Q.; Liu, J.; Xia, Y.; Yin, J.; Liu, Z. Two-dimensional graphene-like C$_2$N: an experimentally available porous membrane for hydrogen purification. *Physical Chemistry Chemical Physics* 2015, 17, 15115–15118.

(42) Zhu, L.; Xue, Q.; Li, X.; Wu, T.; Jin, Y.; Xing, W. C$_2$N: an excellent two-dimensional monolayer membrane for He separation. *Journal of Materials Chemistry A* 2015, 3, 21351–21356.

(43) Qu, Y.; Li, F.; Zhou, H.; Zhao, M. Highly efficient quantum sieving in porous graphene-like carbon nitride for light isotopes separation. *Scientific Reports* 2016, 6, 1–6.

(44) Ma, D.; Wang, Q.; Yan, X.; Zhang, X.; He, C.; Zhou, D.; Tang, Y.; Lu, Z.; Yang, Z. 3d transition metal embedded C$_2$N monolayers as promising single-atom catalysts: a first-principles study. *Carbon* 2016, 105, 463–473.

(45) Li, X.; Zhong, W.; Cui, P.; Li, J.; Jiang, J. Design of efficient catalysts with double transition metal atoms on C$_2$N layer. *The Journal of Physical Chemistry Letters* 2016, 7, 1750–1755.

(46) Mahmood, J.; Jung, S.-M.; Kim, S.-J.; Park, J.; Yoo, J.-W.; Baek, J.-B. Cobalt ox-
ide encapsulated in C₂N–h2D network polymer as a catalyst for hydrogen evolution. *Chemistry of Materials* **2015**, *27*, 4860–4864.

(47) Hussain, T.; Searles, D. J.; Hankel, M. Insights into the trapping mechanism of light metals on C₂N–h2D: Utilisation as an anode material for metal ion batteries. *Carbon* **2020**, *160*, 125–132.

(48) Cui, X.; An, W.; Liu, X.; Wang, H.; Men, Y.; Wang, J. C₂N-graphene supported single-atom catalysts for CO₂ electrochemical reduction reaction: Mechanistic insight and catalyst screening. *Nanoscale* **2018**, *10*, 15262–15272.

(49) Cao, Y.; Deng, S.; Fang, Q.; Sun, X.; Zhao, C.; Zheng, J.; Gao, Y.; Zhuo, H.; Li, Y.; Yao, Z., et al. Single and double boron atoms doped nanoporous C₂N–h2D electrocatalysts for highly efficient N₂ reduction reaction: a density functional theory study. *Nanotechnology* **2019**, *30*, 335403.

(50) Kim, J.; Gwon, O.; Kwon, O.; Mahmood, J.; Kim, C.; Yang, Y.; Lee, H.; Lee, J. H.; Jeong, H. Y.; Baek, J.-B., et al. Synergistic coupling derived cobalt oxide with nitrogenated holey two-dimensional matrix as an efficient bifunctional catalyst for metal–air batteries. *ACS Nano* **2019**, *13*, 5502–5512.

(51) Liu, F.; Deng, H.-Y.; Wakabayashi, K. Helical topological edge states in a quadrupole phase. *Physical Review Letters* **2019**, *122*, 086804.

(52) Fang, C.; Gilbert, M. J.; Bernevig, B. A. Bulk topological invariants in noninteracting point group symmetric insulators. *Physical Review B* **2012**, *86*, 115112.

(53) Bradlyn, B.; Elcoro, L.; Cano, J.; Vergniory, M.; Wang, Z.; Felser, C.; Aroyo, M.; Bernevig, B. A. Topological quantum chemistry. *Nature* **2017**, *547*, 298–305.

(54) Aroyo, M. I.; Kirov, A.; Capillas, C.; Perez-Mato, J.; Wondratschek, H. Bilbao Crystal-
lographic Server. II. Representations of crystallographic point groups and space groups. *Acta Crystallographica Section A: Foundations of Crystallography* **2006**, *62*, 115–128.

(55) Elcoro, L.; Bradlyn, B.; Wang, Z.; Vergniory, M. G.; Cano, J.; Felser, C.; Bernevig, B. A.; Orobengoa, D.; Flor, G.; Aroyo, M. I. Double crystallographic groups and their representations on the Bilbao Crystallographic Server. *Journal of Applied Crystallography* **2017**, *50*, 1457–1477.

(56) Aroyo, M. I.; Perez-Mato, J. M.; Capillas, C.; Kroumova, E.; Ivantchev, S.; Madariaga, G.; Kirov, A.; Wondratschek, H. Bilbao Crystallographic Server: I. Databases and crystallographic computing programs. *Zeitschrift für Kristallographie - Crystalline Materials* **2006**, *221*, 15–27.

(57) Aroyo, M. I.; Kirov, A.; Capillas, C.; Perez-Mato, J. M.; Wondratschek, H. Bilbao Crystallographic Server. II. Representations of crystallographic point groups and space groups. *Acta Crystallographica Section A* **2006**, *62*, 115–128.

(58) Noh, J.; Benalcazar, W. A.; Huang, S.; Collins, M. J.; Chen, K. P.; Hughes, T. L.; Rechtsman, M. C. Topological protection of photonic mid-gap defect modes. *Nature Photonics* **2018**, *12*, 408–415.

(59) Dresselhaus, M. S.; Dresselhaus, G.; Jorio, A. Group theory: application to the physics of condensed matter. *2007*,

(60) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Physical Review Letters* **1996**, *77*, 3865.

(61) Kresse, G.; Hafner, J. Ab initio molecular dynamics for open-shell transition metals. *Physical Review B* **1993**, *48*, 13115–13118.

(62) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for met-
als and semiconductors using a plane-wave basis set. *Computational materials science* 1996, 6, 15–50.

(63) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. *The Journal of chemical physics* 2003, 118, 8207–8215.

(64) Marzari, N.; Mostofi, A. A.; Yates, J. R.; Souza, I.; Vanderbilt, D. Maximally localized Wannier functions: Theory and applications. *Reviews of Modern Physics* 2012, 84, 1419.

**AUTHOR CONTRIBUTIONS**

Z.H.L. performed tight-binding calculations, Z.H.L. and Q.H.Y. performed first-principles calculations, and P.Z., X.Y.P., and Z.S.M. did theoretical analysis. L.Z.S. supervised the project. All authors analyzed the data and wrote the paper.

**COMPETING INTERESTS**

The authors declare no competing interests.

**DATA AVAILABILITY**

The datasets generated during and/or analyzed during this study are available from the corresponding author on reasonable request.
Table of Contents