Preserving the Edge Magnetism of Zigzag Graphene Nanoribbons by Ethylene Termination: Insight by Clar’s Rule

Yafei Li1, Zhen Zhou2, Carlos R. Cabrera1 & Zhongfang Chen1

1Department of Chemistry, Institute for Functional Nanomaterials, NASA-URC Center for Advanced Nanoscale Materials, University of Puerto Rico, Rio Piedras Campus, San Juan, PR 00931, 2Computational Centre for Molecular Science, Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Institute of New Energy Material Chemistry, Nankai University, Tianjin 300071, China.

By means of density functional theory computations, we demonstrated that C2H4 is the ideal terminal group for zigzag graphene nanoribbons (zGNRs) in terms of preserving the edge magnetism with experimental feasibility. The C2H4 terminated zGNRs (C2H4-zGNRs) with pure sp2 coordinated edges can be stabilized at rather mild experimental conditions, and meanwhile reproduce the electronic and magnetic properties of those hydrogen terminated zGNRs. Interestingly, the electronic structures and relative stability of C2H4-zGNRs with different edge configurations can be well interpreted by employing the Clar’s rule. The multiple edge hyperconjugation interactions are responsible for the enhanced stability of the sp2 coordinated edges of C2H4-zGNRs. Moreover, we demonstrated that even pure sp3 termination is not a guarantee for edge magnetism, for example, C2H2 termination can couple to the p-electron system of zGNRs, and destroy the magnetism. Our studies would pave the way for the application of zGNRs in spintronics.

Since its experimental realization in 20041–2, graphene, the first strict two-dimensional (2D) crystal with one-atomic thickness, has been a subject of great interest due to its excellent properties and promising applications3–5. Interestingly, one dimensional (1D) graphene nanoribbons (GNRs) can also be yielded by cutting graphene in the nano-scaled width. Depending on the cutting direction, two unique types of edges can be obtained: zigzag and armchair. Different from graphene which is actually semimetal, both zigzag and armchair GNRs have a nonzero band gap, which has been confirmed both theoretically6,7 and experimentally8,9. Moreover, the edge geometry also makes a huge difference in the p-electron structure at the edges. As early as in 1996, Fujita et al.10 revealed that zigzag GNRs (zGNRs) have peculiar localized edge states (completely absent in the armchair edge), which give rise to the quite flat bands near the Fermi level11. By employing the Hubbard model with the unrestricted Hartree-Fock approximation, Fujita et al.10,12 also deduced that the edge states of zGNRs are ferromagnetically (FM) coupled on each edge but antiferromagnetically (AFM) coupled between two edges. In 2006, Son et al.13 found that the edge states of zGNRs in different spin channels response oppositely to the transverse external electric field, and thus zGNRs can be half-metallic (metallic for one spin channel and insulating for the other) under a critical value of electric field. Later theoretical studies demonstrated that selective edge modification14,15 can also tune zGNRs into half-metallic. Therefore, zGNRs have very promising applications in future spintronics.

However, there is a large gap between theoretical prediction and experimental realization. The edge states of zGNRs are very reactive16, and thus cause instability, whereas armchair edges are more stable17–19. As a consequence, most synthesized nanographenes have armchair peripheries20,21, and the synthesis of GNRs with consecutive zigzag edges has been rather difficult for a long time. Encouragingly, experimental peers have achieved great progress recently in fabricating GNRs with smooth zigzag edges22–26, and the localized edge states have been vigorously confirmed by scanning tunneling microscopy (STM) and spectroscopy27–31. However, the edge magnetism of zGNRs has been scarcely detected experimentally32,33, because, to preserve the edge magnetism, the edge sites of zGNRs should have the pure sp2 coordination. Unfortunately, density functional theory
(DFT) computations by Wassmann et al. demonstrated that the pure $sp^*$ coordinated edges of hydrogen terminated zGNRs (H-zGNRs) can be stabilized only at extremely low hydrogen concentration, which is rather challenging experimentally. Under normal conditions, the edge sites tend to be fully saturated by hydrogen, which directly suppresses the edge magnetism. More seriously, zGNRs are also characterized by the nonmagnetic nature in presence of some typical atmospheric molecules, such as $O_2$, $H_2O$, $NH_3$, and $CO_2$.

Therefore, to preserve the edge magnetism of zGNRs, the first urgent thing is to find a suitable termination group for zGNRs. Recently, Chai et al. have suggested that large bulky ligands (i.e. tertiary-butyl, $C_4H_9$) terminated zGNRs favor the pure $sp^*$ termination across a broader range of thermodynamic conditions due to the strong steric effect of ligands. Though not mentioned explicitly, the hyperconjugation between the large bulky ligands and the edge states (can be seen as radicals) also contributes to the enhanced stability of the edge. Then, an interesting question arises: can we use some of some typical atmospheric molecules, such as $O_2$, $H_2O$, $NH_3$, and $CO_2$?

Models. To ascertain whether the edge magnetism of zGNRs can be preserved by $C_2H_4$ termination, we need to determine the most stable edge configuration for $C_2H_4$-terminated zGNRs. First, we computed the edge formation energy ($E_{edge}$) for each configuration, which is defined as:

$$E_{edge} = \frac{1}{2L} \left( E_{ribbon} - (N_C - 2N_{C_2H_4})E_{graphene} - N_{C_2H_4}E_{C_2H_4} \right)$$

where $E_{ribbon}$, $E_{graphene}$, and $E_{C_2H_4}$ are the total energies of the nanoribbon, one carbon atom of graphene, and one $C_2H_4$ molecule, respectively. $N_C$ and $N_{C_2H_4}$ are the numbers of carbon atoms and $C_2H_4$ groups in the supercell, respectively. $L$ is the length of one unit cell. According to this definition, the edge configurations with lower $E_{edge}$ values are more favorable energetically at 0 K. For comparison, the $E_{edge}$ of 8-H-zGNRs with pure $sp^*$ termination ($z(H)_1$) was also computed. The computed $E_{edge}$ of all the considered edge configurations and their corresponding ground states are summarized in Table 1. According to our computations, for $C_2H_4$-zGNRs, the nonmagnetic edge configuration $z_{11122}$ has the lowest value of $E_{edge}$, tightly followed by the pure $sp^*$ coordinated edge configuration $z_{11}$. Especially, the $E_{edge}$ of $z_{11}$ is lower than that of $z(H)_1$, implying that $C_2H_4$ termination could produce more stable $sp^*$ coordinated edge than hydrogen termination.

However, the content of $C_2H_4$ changes under real experimental conditions, and the chemical potential of $C_2H_4$ should be taken into account. Thus, we evaluated the relative stability of different edge configurations for 8-$C_2H_4$-zGNR under real experimental conditions by comparing their respective Gibbs formation energy ($AG_{edge}$), which is defined as:

$$AG_{edge} = E_{edge} - \frac{N_{C_2H_4}}{2L} \mu_{C_2H_4}$$

where $\mu_{C_2H_4}$ is a function of the temperature $T$ and the partial $C_2H_4$ gas pressure $P$, and can be expressed as:

$$\mu_{C_2H_4} = H^o(T) - T S^o(T) + k_B T \ln \left( \frac{P}{P^o} \right)$$

$H^o$ and $S^o$ are the enthalpy and entropy at the pressure $P^o = 1$ bar, respectively, the values of which at $T = 298$ K are obtained from the

| $z_{i1}$ | $E_{edge}$ (eV/Å) | GS |
|---------|------------------|----|
| $z_{11}$ | 0.0096 | magnetic |
| $z_{121}$ | 0.0257 | nonmagnetic |
| $z_{11121}$ | 0.0145 | nonmagnetic |
| $z_{1122}$ | 0.0170 | nonmagnetic |
| $z_{111122}$ | 0.0020 | nonmagnetic |
| $z_{57}$ | 0.2240 | magnetic |
| $z_{5711}$ | 0.4252 | nonmagnetic |
| $z_{57122}$ | 0.4401 | nonmagnetic |
| $z[H]_1$ | 0.0676 | magnetic |
textbook\textsuperscript{41}. Then, we plotted the curve of $\Delta G_{\text{edge}}$ for 8-C$_2$H$_4$-zGNRs with different edge configurations as a function of $\mu_{\text{C}_2\text{H}_4}$ in Figure 2. According to the above definition, the most stable edge configuration should have the lowest value of $\Delta G_{\text{edge}}$ within a given value of $\mu_{\text{C}_2\text{H}_4}$.

Several conclusions can be drawn from Figure 2. First, the $\Delta G_{\text{edge}}$ of $z_{1121}$, $z_{11122}$, $z(57)_{11}$, or $z(57)_{22}$ could never be the lowest at any given value of $\mu_{\text{C}_2\text{H}_4}$, indicating that these four edge configurations have no chance to be realized under real experimental conditions. Especially, the unfavorability of $z(57)_{11}$ and $z(57)_{22}$ suggests that the reconstruction of zigzag edge can be suppressed under the C$_2$H$_4$ environment. Second, the $\Delta G_{\text{edge}}$ of $z_{22}$ is the lowest when $\mu_{\text{C}_2\text{H}_4}$ is larger than 2.03 eV, indicating that $z_{22}$ can be stabilized only at extremely high C$_2$H$_4$ concentration. When $\mu_{\text{C}_2\text{H}_4}$ is in the range of [0.44, 2.03] eV, $z_{1122}$ becomes stable. $z_{111122}$, which has the lowest value of $E_{\text{edge}}$, is stable only in a rather narrow range of $[-0.11, 0.44]$. When $\mu_{\text{C}_2\text{H}_4} < -0.11$ eV, $z_{11}$ becomes the most stable edge configuration. At room temperature, $-0.11$ eV of $\mu_{\text{C}_2\text{H}_4}$ corresponds to a C$_2$H$_4$ pressure ($P$) of 2.45 bar. In other words, if the C$_2$H$_4$ pressure can be controlled to be lower than 2.45 bar at room temperature, which is experimentally rather feasible, the pure sp\textsuperscript{2} coordinated edges can be stabilized. In sharp contrast, pure sp\textsuperscript{3} coordinated edges of H-zGNRs can be stabilized only at extremely low hydrogen concentration and thus unlikely to be realized. Therefore, C$_2$H$_4$ is superior to hydrogen as a terminal group for GNRS with different edge configurations as a function of $\mu_{\text{C}_2\text{H}_4}$ in Figure 2.

According to the above definition, the most stable edge configuration should have the lowest value of $\Delta G_{\text{edge}}$ within a given value of $\mu_{\text{C}_2\text{H}_4}$.

Figure 3a presents the spatial distribution of the charge difference between $\alpha$-spin and $\beta$-spin for 8-C$_2$H$_4$-zGNRs. The magnetization per edge atom of C$_2$H$_4$-8-zGNR is 0.13 $\mu B$ (0.15 $\mu B$ for 8-H-zGNR), decaying gradually from two edges to the inner. Therefore, the stability and magnitude of edge magnetism of C$_2$H$_4$-zGNRs are comparable to those of H-zGNRs.

Then, we computed the band structure of 8-C$_2$H$_4$-zGNRs in the AFM state. As shown in Figure 3b, 8-C$_2$H$_4$-zGNR has a 0.42 eV (0.45 eV for 8-H-zGNR) band gap for both spin channels. Especially, the spin-polarized $\pi$ and $\pi^*$ bands are also quite flat near the Fermi level, a known symbol of edge states.

In lights of the above results, we conclude that C$_2$H$_4$-zGNRs can well reproduce the electronic and magnetic properties of those H-zGNRs. Therefore, C$_2$H$_4$-zGNRs may realize many fancy properties previously predicted for H-zGNRs, such as half-metallicity\textsuperscript{16}. Our computations demonstrated that under a 0.7 V/A Å transverse electric field, 8-C$_2$H$_4$-zGNR with $z_{11}$ edge configuration can be tuned into half-metallic. Here note that generalized gradient approximation (GGA) usually predicts a much higher critical value of electric filed than local density approximation (LDA)\textsuperscript{42}.

**Discussion**

Although we have determined that pure sp\textsuperscript{2} coordinated edges of zGNRs, namely, $z_{11}$, can be produced by C$_2$H$_4$ termination at rather mild experimental conditions, there is an obvious question to be explained: why does $z_{11}$ have a relatively large value of $E_{\text{edge}}$ and is unfavorable on the whole range of thermodynamics conditions? As revealed by Wassmann et al.\textsuperscript{41}, $z_{11}$ has the lowest value of $E_{\text{edge}}$ among all the edge configurations of H-zGNRs, and it is stable in a rather boarder range of thermodynamic conditions. Then, what makes the difference for C$_2$H$_4$ and hydrogen terminations? Actually this difference is simply due to the steric effect of C$_2$H$_4$ molecules. As shown in Figure 1, in a unit cell of $z_{11}$, two C$_2$H$_4$ molecules bond to an edge site of zGNR together to generate a sp\textsuperscript{3} edge site, and the rest two carbon atoms of C$_2$H$_4$ molecules bond to two edge sites of zGNR to generate two sp\textsuperscript{2} edge sites. Due to the strong steric effect, two C$_2$H$_4$ molecules are pushed up and down, respectively, at the sp\textsuperscript{2} edge sites. Thus, the strain imposed on two sp\textsuperscript{2} edge sites causes a serious edge distortion (Figure S1 of supplementary information) and consequently increases the $E_{\text{edge}}$. Here note that for $z_{111122}$ and $z_{1122}$, which continuous two sp\textsuperscript{2} coordinated edge sites are present, the edge distortion is absent. Since $z_{11}$ has the same C$_2$H$_4$ density ($\frac{N_{\text{C}_2\text{H}_4}}{2L}$) as $z_{111122}$ but a higher $E_{\text{edge}}$ than $z_{111122}$, $z_{1121}$ could never be the most stable edge configuration in any given value of $\mu_{\text{C}_2\text{H}_4}$, according to equation (2), and is hence excluded from the phase diagram.

![Figure 2](image-url)  
**Figure 2** | Gibbs formation energy ($\Delta G_{\text{edge}}$) as a function of chemical potential ($\mu_{\text{C}_2\text{H}_4}$) for different edge configurations of 8-C$_2$H$_4$-zGNR. The solid lines denote the stable edge configurations under certain $\mu_{\text{C}_2\text{H}_4}$ values. Vertical dashed lines divide the stability regions. The upper axis shows the pressure of C$_2$H$_4$, corresponding to the chemical potential at 298 K. The red dot denotes the position of saturated vapor pressure of C$_2$H$_4$ at 298 K.

![Figure 3](image-url)  
**Figure 3** | Electronic structures of C$_2$H$_4$-zGNR. (a) Spatial distribution of the charge difference between $\alpha$-spin (blue) and $\beta$-spin (red) and (b) band structure for 8-C$_2$H$_4$-zGNR with $z_{11}$ edge configuration. The red dashed line denotes the position of Fermi level.
Besides the unstability problem of z_{121}, there are still some concerns to be addressed. For example, for these stable edge configurations on the whole range of thermodynamic conditions, why are z_{11} and z_{22} magnetic while z_{111122} and z_{1122} are nonmagnetic? Moreover, why does z_{11} have a rather low \( E_{edge} \), while z_{22} has a higher \( E_{edge} \) than other stable edge configurations? Why does z_{111122} have an even lower \( E_{edge} \) than z_{11}? 

The above concerns can be satisfactorily understood by the Clar’s rule\(^{43,44} \), which has been successfully applied for accounting the \( \pi \) electron distribution and reactivity of polycyclic aromatic hydrocarbons (PAH)\(^{45-47} \) and many carbon nanomaterials\(^{48-53} \). According to the Clar’s rule, the \( sp^2 \) coordinated carbon atoms of a close-shell PAH can be formulated into two structural units that are linked by single bonds, benzenoid aromatic ring and olefinic double bond, wherever necessary. A PAH is the most stable when it has the greatest number of benzenoid rings. The unusual stability of graphene can be understood as all carbon atoms are benzenoid with a maxima density of benzenoid rings of 1/3. Without considering the steric effect of termination groups (as for H-terminated zGNRs), z_{12} should be the most stable edge configuration for zGNRs since it enables that zGNRs have the same density of benzenoid rings as graphene (Figure S2 of supplementary information). However, for C_{2}H_{4}-terminated zGNRs, the enhanced stabilization from aromaticity is overwhelmed by the steric effect; thus the z_{121} configuration is not favored anymore.

For zGNRs with density of benzenoid rings lower than 1/3, there is a competition between maximizing the density of benzenoid rings for the bulk and imposing unsaturated carbon atoms on the edges. Taking z_{11} of 8-C_{2}H_{4}-zGNR as an example, if we assume that all its carbon atoms are saturated with four chemical bonds with neighboring atoms, z_{11} will form the quinonoid structure with two double bonds in each hexagon (Figure S3 of supplementary information), and the formation of benzenoid ring in z_{11} is completely forbidden. However, the quinonoid structure is quite unstable. In this case, z_{11} would impose two unpaired electrons on each edge in a 1 \times 1 \times 3 supercell, and the resulted nanoribbon has the same density of benzenoid rings (1/3) as graphene (Figure 4a). The energy gain from the resonance favors this electronic structure as the ground state. Therefore, z_{11} has a magnetic ground state with unpaired electrons on the edges. Moreover, the unpaired electrons of z_{11} have subtle hyperconjugation interactions with neighboring C=C bonds and C=H bonds of C_{2}H_{4} which could stabilize the unpaired electrons (thus stabilizing the edge). Besides, there is also hyperconjugation interaction between C=C bonds and C=H bonds, which could also contribute to the stability of the edge. Thus, the multiple hyperconjugation interactions on the edge should be responsible for the rather favorable \( E_{edge} \) of z_{11}. In contrast, in H-zGNRs, there only exists the hyperconjugation interaction between unpaired electrons and C=C bonds, resulting in a larger \( E_{edge} \) for z(H)_{1} than z_{11}.

Similarly, by imposing four unpaired electrons to the outer \( sp^2 \) carbon atoms on each edge in a 1 \times 1 \times 3 supercell, the interior carbon atoms of z_{22} can also maximize the density of benzenoid rings (Figure 4b). In contrast to z_{11}, only half of the unpaired electrons of z_{22} can have hyperconjugation interaction with C=C double bonds while the rest are localized. Such densely localized unpaired electrons on the edges result in a very high \( E_{edge} \) for z_{22}. These analyses can also explain why the magnetization of fully saturated edges of zGNRs is larger than the \( sp^2 \) coordinated edges\(^{44} \).

In contrast to z_{11} and z_{22}, z_{111122} can achieve the maximum density of benzenoid rings without imposing unpaired electron on the edge (Figure 4c). Moreover, z_{111122} can be further stabilized by the conjugation interaction between edge C=C double bonds. It is known that generally conjugation stabilization is stronger than hyperconjugation stabilization\(^{56,57} \). As a result, z_{111122} favors the nonmagnetic ground state and has a lower \( E_{edge} \) than z_{11}. For z_{1122}, when the edge carbon atoms are all saturated, the inner carbon atoms can only be partially benzenoid (Figure 4d). However, imposing unpaired electron on edge cannot increase the number of benzenoid rings. Therefore, z_{1122} also favors the nonmagnetic ground state.

Finally, an interesting question arises: is pure \( sp^2 \) termination a guarantee for edge magnetism? Taking an example, like hydrogen and C_{2}H_{4}, C_{2}H_{2} can only form single bonds with edge carbon atoms, and intuitively may not disturb the \( \pi \) electron system of zGNR. Then, is C_{2}H_{2}, the dehydrogenation product of C_{2}H_{4}, also an ideal terminal group for zGNRs?

To address this concern, we investigated two edge configurations for C_{2}H_{2} terminated 8-zGNRs (8-C_{2}H_{2}-zGNR), including z_{11} and z_{111122}. In contrast to 8-C_{2}H_{4}-zGNR, z_{11} of 8-C_{2}H_{2}-zGNR (\(-0.205 \text{ eV/Å}\)) has a lower \( E_{edge} \) than z_{111122} (\(-0.196 \text{ eV/Å}\)). Moreover, our computations revealed that both z_{11} and z_{111122} of 8-C_{2}H_{2}-zGNR have a nonmagnetic ground state. At first glance, this is rather surprising. The nonmagnetic z_{111122} of 8-C_{2}H_{2}-zGNR can be understood in the same away as discussed above for 8-C_{2}H_{4}-zGNR. However, why is z_{11} of 8-C_{2}H_{2}-zGNR also nonmagnetic? This seemingly unexpected result can also be understood by the competition between hyperconjugation, conjugation and maximizing benzenoid rings.

In contrast to the general intuition, C_{2}H_{2} terminations significantly differ from C_{2}H_{4} terminations, since C_{2}H_{2} can couple to the \( \pi \) electron system of zGNR by forming double bonds with edge sites in the dominant resonance structure (Figure 5a): in a 1 \times 1 \times 3 supercell of z_{11} of 8-C_{2}H_{2}-zGNR, two C_{2}H_{2} molecules each form two C-C single bonds with two edge sites in each edge, but the third C_{2}H_{2} molecule forms two C=C bonds with two edge sites. With the help of newly formed C=C bonds, the carbon atoms of 8-C_{2}H_{2}-zGNR can achieve a density of benzenoid rings of 2/7 without imposing unpaired electron on the edge.

We can also get the resonance structure (Figure 5b) by imposing two unpaired electrons on each edge, in which the density of benzenoid rings can be increased to the maximum (1/3), the same as z_{11} of 8-C_{2}H_{2}-zGNR. However, this magnetic state is not favorable.

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**Figure 4** | Clar representations for 8-C_{2}H_{4}-zGNR with different edge configurations. (a) z_{11}, (b) z_{22}, (c) z_{111122}, and (d) z_{1122}. Doublet and circle denote C=C double bond and benzenoid ring, respectively. The red point represents unpaired electron.
Figure 5 | Clar representations of 8-C2H2-zGNR in z11 edge configuration. (a) and (b) represent the nonmagnetic and magnetic states, respectively.

energetically since the conjugation in the nonmagnetic state overwhelms the energy gain by maximizing the benzenoid rings. In the nonmagnetic state, the C=C bonds at edges have conjugation interaction along the zigzag direction; in the magnetic state, there exists hyperconjugation interaction between unpaired electrons and neighboring C=C bonds. The much stronger conjugation stabilization in the nonmagnetic state over the hyperconjugation stabilization in the magnetic state overcompensates the unfavorability of the nonmagnetic state with fewer benzenoid rings, which leads to a nonmagnetic ground state.

Another question is why z11 8-C2H2-zGNR has a lower Eedge than z111122. Note that z111122 has the same density of benzenoid rings as z11, and it also has the conjugation stabilization among edge C=C bonds (Figure S4 of supplementary information). However, the conjugation interaction in z111122 is not continuous in the zigzag direction while the conjugation interaction in z11 is continuous. Therefore, z111122 has a slightly lower Eedge than z11.

Overall, though C2H2 termination can produce sp2 coordinated edges with energetically very favorable Eedge, C2H2 can suppress the edge magnetism by coupling to the π-electron system of zGNR, which disqualifies C2H2 as an ideal terminal group for zGNRs. Therefore, even pure sp2 termination is not a guarantee for edge magnetism.

To summarize, by means of DFT computations, we systemically studied the energetics and electronic properties of C2H2-zGNRs with different edge configurations. The pure sp2 coordinated edges, namely z11, can be stabilized at rather mild experimental conditions. Especially, such C2H2-zGNRs with sp2 edges can well reproduce the magnetic and electronic properties of H-zGNRs. Therefore, C2H4 is an ideal terminal group for zGNRs in terms of preserving the edge magnetism. Interestingly, the edge electronic structures of C2H2-zGNRs can be well interpreted by employing the Clar’s rule. Further analysis identified multiple hyperconjugation interactions as the key factor responsible for enhanced stability of the sp2 coordinated edges. Moreover, we demonstrated that pure sp2 termination cannot guarantee edge magnetism for zGNRs, for example, C2H2 termination can couple to the π-electron system of zGNRs, and suppress the magnetism. These findings would deepen our basic knowledge of graphene electronics and provide a feasible way for realizing zGNR-based spintronics.

Methods
DFT computations were performed using the plane-wave technique implemented in Vienna ab initio simulation package (VASP). The ion-electron interaction is described using the projector-augmented plane wave (PAW) approach, GGA expressed by PBE functional and a 400 eV cutoff for the plane-wave basis set were adopted in all computations. Self-consistent field (SCF) calculations were conducted with a convergence criterion of 10−4 eV on the total energy and the electron density.

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**Author contributions**

Z.C. conceived the initial idea of this research. Y.L. demonstrated the initial idea and collected all the data. Z.Z. and C.C. participated in the discussion. Y.L. and Z.C. drafted the paper, and all coauthors revised the manuscript. Z.C. guided the work.

**Additional information**

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