Patterning Graphitic C–N Sheets into a Kagome Lattice for Magnetic Materials

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Abstract: We propose porous C–N-based structures for biocompatible magnetic materials that do not contain even a single metal ion. Using first-principles calculations based on density functional theory, we show that when patterned in the form of a kagome lattice, nonmagnetic g-C₃N₄ not only becomes ferromagnetic but also its magnetic properties can be further enhanced by applying external strain. Similarly, the magnetic moment per atom in ferromagnetic g-C₄N₃ is increased threefold when patterned into a kagome lattice. The Curie temperature of g-C₃N₄ kagome lattice is 100 K, while that of g-C₄N₃ kagome lattice is much higher, namely, 520 K. To date, all of the synthesized two- and three-dimensional magnetic kagome structures contain metal ions and are toxic. The objective of our work is to stimulate an experimental effort to develop nanopatterning techniques for the synthesis of g-C₃N₄- and g-C₄N₃-based kagome lattices.

Section: Surfaces, Interfaces, Porous Materials, and Catalysis

Magnetic materials without metals are hotly pursued for their potential applications as biocompatible magnetic materials. Unlike conventional magnetic materials where magnetism is due to d or f electrons, the magnetic materials based on nonmetal p electrons have weak spin–orbit coupling and hyperfine interaction, which are the main channels of relaxation and decoherence of electron spins. Mn atoms, because of their special electronic configuration of 3d⁵4s² and large magnetic moment of 5 μB, have been widely used as a dopant in various semiconductors such as GaAs, GaN, ZnO, AlN, and SiC. However, Mn is neurotoxic; both Mn²⁺ and Mn³⁺ can enter the brain by crossing the blood–brain barrier and cause permanent neurological disorder with symptoms similar to those of Parkinson’s disease, including tremors, difficulty in walking, and facial muscle spasms. In fact, most metal ions are toxic. Therefore, for biocompatibility, magnetic materials without metals are highly desirable. It is well-known that 3d electrons of transition-metal atoms can introduce magnetism, as do 2p electrons in some nonmetal atoms. Although 3d and 2p electrons have different orbital shapes, they share similar features in their radial distribution. Therefore, in some bonding environments, 2p electrons can display magnetism, as demonstrated in carbon nanostructures. Unfortunately, some carbon nanostructures are not biocompatible either. For example, carbon nanotubes injected into the mouse’s trachea induce severe granulomatous and lung inflammation. However, when nitrogen-doped carbon nanotubes are used, biocompatibility improves significantly, and these materials can be further used as biomembranes. These findings suggest that magnetic materials composed of C and N are highly promising for applications in spintronics as well as in biotechnology.

A great deal of experimental effort has been devoted in this direction, leading to the synthesis of graphitic C₃N₄ and C₄N₃. There are two types of structural isomers of g-C₃N₄; they consist of s-triazine units (ring of C₃N₃) or tri-s-triazine units (tri-ring of C₃N₆), respectively. We use both of them to construct kagome structures. Although increased attention has been paid to g-C₃N₄ for applications in fuel cells, photocatalysis, and hydrogen production, no study has been reported for its applications as a magnetic material. We wondered if the nonferromagnetic g-C₃N₄ can be made ferromagnetic without introducing any metal ion. Recently, g-C₃N₄ was found to exhibit ferromagnetism, providing a pathway for the design and synthesis of C–N-based magnetic materials. Can the magnetic properties of g-C₃N₄ be further enhanced by patterning it into a kagome lattice? In this study, we show that these can indeed be achieved when g-C₃N₄ (consisting of tri-s-triazine units) and g-C₄N₃ are patterned into kagome-lattice-type configurations, namely, a lattice pattern composed of interlaced triangles with shared vertices. In Figure 1, Kagome lattice, which originally means a bamboo-basket (kago) woven lattice-type conformation, namely, a lattice pattern composed of interlaced triangles with shared vertices (Figure 1). Kagome lattice, which originally means a bamboo-basket (kago) woven pattern (me), is a well-known mathematical model for frustrated magnetism. It has recently been found that this kind of structure has exceptional mechanical properties. So far, the commonly used methods for synthesis of 2D kagome structures are based on bottom-up strategies, for

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example, using metal–organic coordination or supramolecular self-assembly of specific molecules on the surface of substrates.\textsuperscript{24,25} The physical synthesis based on the top-down method is also found to be possible by using electron beam irradiation, etching techniques,\textsuperscript{26,27} lithography,\textsuperscript{28} or nano-cutting,\textsuperscript{29} as demonstrated in a graphene sheet. In the following, we present our findings of the enhanced magnetism in g-C\textsubscript{4}N\textsubscript{3} and induced magnetism in g-C\textsubscript{3}N\textsubscript{4}-based kagome structures.

All calculations were performed by using spin-polarized density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP code).\textsuperscript{30} Electronic exchange and correlation effects were treated using the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) paramatization.\textsuperscript{31} The interactions between electrons and nuclei were treated using projector-augmented wave (PAW) potentials. Hybrid functionals using the Heyd–Scuseria–Ernzerhof (HSE06) form\textsuperscript{32} were also used to achieve greater accuracy of the magnetic and electronic properties. The energy cutoff was set at 400 eV. The convergence criteria for energy and force were set to 0.01 meV and 0.001 eV/Å, respectively. The Brillouin zones were represented by Γ-centered unit cells with 11 × 11 × 1 Monkhorst-Pack special k-point mesh for a g-C\textsubscript{4}N\textsubscript{3}- and 7 × 7 × 1 mesh for a g-C\textsubscript{3}N\textsubscript{4}-based kagome lattice, respectively. The vacuum space in the nonperiodic direction is taken to be 15 Å, which is sufficient to avoid the interaction between the two neighboring images. In order to study the magnetic coupling between the two kagome sites or linking atoms, a supercell consisting of a 2 × 2 unit cell was used. The energy difference \( \Delta E \) between the ferromagnetic (FM) and antiferromagnetic (AFM) or nonmagnetic (NM) states, defined as \( \Delta E = E_{\text{AFM}}(\text{NM}) - E_{\text{FM}} \), was calculated to determine the magnetic ground state. Noncollinear spin calculations were performed to study possible spin canting, but spins were found to be collinear. Monte Carlo simulations involving 5 × 10\textsuperscript{9} steps and a (100 × 100) supercell were further carried out to study magnetism at finite temperatures.

The geometric structures of g-C\textsubscript{4}N\textsubscript{3} and g-C\textsubscript{3}N\textsubscript{4}-based kagome lattices are shown in Figure 1, where the triangular nanoflakes (TNFs) are linked by carbon or nitrogen atoms, respectively. Compared with the original g-C\textsubscript{4}N\textsubscript{3} and g-C\textsubscript{3}N\textsubscript{4} sheets, the corresponding kagome lattices are more porous. In order to investigate the stability of the kagome lattices, larger supercells consisting of 3 × 3 and 2 × 2 unit cells were used, respectively, for g-C\textsubscript{4}N\textsubscript{3} and g-C\textsubscript{3}N\textsubscript{4}-based kagome lattices, and spin-polarized ab initio molecular dynamics simulations were performed at room temperature (300 K) with a time step of 1 fs. After 5000 steps, the frameworks are still intact, and the magnetic moments remain 54 \( \mu_B \) for 3 × 3 unit cells or 12 \( \mu_B \) for 2 × 2 unit cells. When annealed from 300 to 0 K, some atoms in g-C\textsubscript{4}N\textsubscript{3} and g-C\textsubscript{3}N\textsubscript{4}-based kagome lattices exhibit slight buckling along the z direction, indicating that they are not strictly flat. The shift of some atoms in the deformed g-C\textsubscript{4}N\textsubscript{3} and g-C\textsubscript{3}N\textsubscript{4}-based kagome lattices is less than 0.20 and 0.38 Å, respectively, and the corresponding total energy is 0.082 or 0.075 eV/unit cell lower than that of the planar structures. The top and side views of fully relaxed structures with deformations are shown in Figure 1. Note that some linking atoms are shifted upward or downward from the plane (labeled with 1 and 2) and that some linking atoms remain in the plane (labeled with 0). For the deformed structures, phonon calculations at the Γ point did not reveal any unstable modes. In the following, we discuss the properties of these deformed structures.

The lattice constants of g-C\textsubscript{4}N\textsubscript{3} and g-C\textsubscript{3}N\textsubscript{4}-based kagome lattices are calculated to be 9.0 and 11.7 Å, respectively. The angle between the linking atom and its nearest two C atoms of the g-C\textsubscript{4}N\textsubscript{3}-based kagome lattice is found to be 142.2–142.4°, which is larger than that of the g-C\textsubscript{3}N\textsubscript{4}-based kagome lattice (115.1–115.3°). Figure 2a and b presents the 3D isosurface of charge distribution for g-C\textsubscript{4}N\textsubscript{3} and g-C\textsubscript{3}N\textsubscript{4}-based kagome lattices. We see that N atoms carry more charges due to their coordination number. The geometric structures of g-C\textsubscript{4}N\textsubscript{3} and g-C\textsubscript{3}N\textsubscript{4} sheets are shown in Figure 1, where the triangular nanoflakes (TNFs) are linked by carbon or nitrogen atoms, respectively. Compared with the original g-C\textsubscript{4}N\textsubscript{3} and g-C\textsubscript{3}N\textsubscript{4} sheets, the corresponding kagome lattices are more porous. In order to investigate the stability of the kagome lattices, larger supercells consisting of 3 × 3 and 2 × 2 unit cells were used, respectively, for g-C\textsubscript{4}N\textsubscript{3} and g-C\textsubscript{3}N\textsubscript{4}-based kagome lattices, and spin-polarized ab initio molecular dynamics simulations were performed at room temperature (300 K) with a time step of 1 fs. After 5000 steps, the frameworks are still intact, and the magnetic moments remain 54 \( \mu_B \) for 3 × 3 unit cells or 12 \( \mu_B \) for 2 × 2 unit cells. When annealed from 300 to 0 K, some atoms in g-C\textsubscript{4}N\textsubscript{3} and g-C\textsubscript{3}N\textsubscript{4}-based kagome lattices exhibit slight buckling along the z direction, indicating that they are not strictly flat. The shift of some atoms in the deformed g-C\textsubscript{4}N\textsubscript{3} and g-C\textsubscript{3}N\textsubscript{4}-based kagome lattices is less than 0.20 and 0.38 Å, respectively, and the corresponding total energy is 0.082 or 0.075 eV/unit cell lower than that of the planar structures. The top and side views of fully relaxed structures with deformations are shown in Figure 1. Note that some linking atoms are shifted upward or downward from the plane (labeled with 1 and 2) and that some linking atoms remain in the plane (labeled with 0). For the deformed structures, phonon calculations at the Γ point did not reveal any unstable modes. In the following, we discuss the properties of these deformed structures.

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The ground state of the g-C\textsubscript{4}N\textsubscript{3}-based kagome lattice was found to be ferromagnetic, which is lower in energy by 0.22 and 0.92 eV/unit cell than that of the AFM and NFM states, respectively. The total magnetic moment per one unit cell is 6.0 \( \mu_B \) (or 0.400 \( \mu_B \) per atom). We note that the magnetic moment of pristine g-C\textsubscript{4}N\textsubscript{3} is 1.0 \( \mu_B \) per unit cell, or 0.14 \( \mu_B \) per atom.\textsuperscript{18} The underlying reason for the enhancement of the magnetic moment is that the original g-C\textsubscript{4}N\textsubscript{3} consists of two-coordinated N and three-coordinated C, while in the kagome structure, the three-coordinated linking C atoms become two-coordinated. This change in coordination increases the magnetic moment.
especially on the linking C sites, as shown in Figure 2c, and these linking C atoms with an enhanced magnetic moment act as a mediator of the magnetic coupling between the TNFs, resulting in an enhanced magnetic stability as compared to that of the original g-C$_3$N$_4$ structure.\(^{18}\)

To get a better understanding of this system, the band structures and partial densities of states (PDOS) are given in Figure 3. We see that the system becomes an indirect band gap semiconductor with an energy band gap of 1.2 eV. The N sites are ferromagnetically polarized (see Figure 2c), and the main contribution is from the N 2p\(_z\) orbitals (labeled as T-N in Figure 3b). The p\(_x\), p\(_y\), and p\(_z\) states of the linking C sites (labeled as K-C), are highly polarized and different from those of the inner C sites (labeled as T-C), which are negatively polarized. Near the Fermi level, there are six split energy bands dominated by the p\(_z\) orbitals of T-N and the p\(_x\), p\(_y\), and p\(_z\) orbitals of K-C.

To further examine the magnetic properties of the g-C$_3$N$_4$-based kagome lattice at finite temperatures, Monte Carlo simulations are carried out by using the Ising model Hamiltonian, \(H = (−\sum_{ij}J_{ij}s_is_j)\), where \(i\) and \(j\) represent two nearest-neighbor magnetic sites. The exchange parameter \(J\) can be derived from the energy difference between the FM and AFM states. Using the Ising model, we estimate \(E_{\text{FM}} = −6Js^2\) and \(E_{\text{AFM}} = 2Js^2\) in one unit cell, where \(s\) represents the magnetic moment of the linking C atoms, which is 2 \(\mu_B\). Thus, we have \(J = (E_{\text{AFM}} − E_{\text{FM}})/8s^2 = 6.9\) meV. The variation of magnetic moment per unit cell with respect to temperature is plotted in Figure 4. We note that the magnetic moment remains in the high spin state in the low-temperature range and then drops to near zero at the Curie temperature of 520 K. This clearly indicates that ferromagnetism in the g-C$_3$N$_4$-based kagome lattice can be detected at room temperature. This is consistent with our previous molecular dynamics simulation.

The exceptional magnetic properties observed in the g-C$_3$N$_4$-based kagome lattice motivated us to explore the magnetism in the g-C$_3$N$_4$-based kagome structure. We found that the g-C$_3$N$_4$-based kagome structure, composed of s-triazine units, is nonmagnetic, while the kagome lattice consisting of tri-s-triazine units is ferromagnetic, which is lower in energy than the AFM (NM) state by 0.03 (0.33) eV/unit cell. The spin density isosurface for the FM state is given in Figure 2d. In one unit cell, the magnetic moment is 3.0 \(\mu_B\), which mainly comes from the p\(_x\) and p\(_y\) orbitals of N atoms in the TNFs (labeled as T-N in Figure 5b), while all of the C sites and the linking N atoms at the kagome sites are weakly spin-polarized. The system becomes an indirect band gap semiconductor with a small gap of 0.6 eV (see Figure 5a).

From the above, we see that the original nonmagnetic g-C$_3$N$_4$ becomes magnetic when it is patterned into the kagome lattice, but the energy difference between the FM and AFM is small (only 0.03 eV/unit cell). A similar procedure of estimating the exchange parameter can be applied here, and the kagome sites are weakly spin-polarized.
we find that $J = (E_{AFM} - E_{FM})/8s^2 = 3.8$ meV because $s = 1 \mu_0$
 in the present case. The corresponding Curie temperature is calculated to be 100 K, which is far below room temperature. In
the following, we discuss the possible approach to improve the stability of the FM state. We know that there are two main
factors affecting magnetism, coordination number and bond length. To maintain the skeleton of g-C$_3$N$_4$ and to keep the
feature of the kagome lattice, the coordination number cannot be reduced any further. However, it is possible to increase the
bond length by applying tensile strain. We define the biaxial tensile strain as $(L - L_{0})/L_{0}$, where $L_{0}$ is the lattice constants of the g-C$_3$N$_4$-based kagome lattice in equilibrium and in strained states, respectively. We
found that tensile strain can enhance the stability of the FM state. For example, when the tensile strain reaches 12.6%, the energy
difference between the FM and AFM states increases sharply from 0.03 to 0.15 eV/unit cell. During the tension, the angle between the linking atom and its nearest two C atoms of the g-C$_3$N$_4$-based kagome lattice increases significantly, but the bond length of C–N is only slightly enlarged (<0.03 Å) without breaking, which suggests that the system can endure such strain. Furthermore, the energy and in-plane tension required to reach such a biaxial strain value is found to be 1.2 eV and 1.9 GPa-nm, respectively, indicating that such a strain state can be achieved experimentally. In this strain state, the exchange parameter using the FM and AFM state energies is
expressed as $J = (E_{AFM} - E_{FM})/8s^2 = 18.8$ meV. After Monte Carlo simulations, the Curie temperature increases to 580 from 100 K. The corresponding spin density isosurface is shown in
Figure 2e. The most notable change is that the magnetic moments and the spin split orbitals, as
discussed above. Diagonalization of the Hamiltonian gives the same magnetic moment and the same spin split orbitals, as
those in the magnetic units. The main contribution to the moment is from p$_x$ and p$_y$ orbitals. The band structure and DOS (Figure 3c and d) further show that the system becomes a semimetal with semiconducting spin-up and metallic spin-down channels. This suggests that the strain manipulation can effectively modify the magnetism as well as the electronic structure.

To further confirm our main results, we used the HSE06 hybrid functional, which has been proved to be more accurate. We
found that the ground states are still ferromagnetic with the same magnetic moment and the same spin split orbitals,
but the valence bands occupied by p$_x$ orbitals are significantly enhanced, which improves the ferromagnetic coupling between
the magnetic units. The main contribution to the moment arises from N p$_2$ orbitals. The band structure and DOS (Figure 3c and d) further show that the system becomes a semimetal with semiconducting spin-up and metallic spin-down channels. This suggests that the strain manipulation can effectively modify the magnetism as well as the electronic structure.

To further confirm our main results, we used the HSE06 hybrid functional, which has been proved to be more accurate. We
found that the ground states are still ferromagnetic with the same magnetic moment and the same spin split orbitals, as
discussed above. Different from the PBE results, all conduction bands are shifted upward. Correspondingly, the band gaps of g-
C$_3$N$_4$- and g-C$_3$N$_4$-based kagome lattices are increased to 2.6 and 1.7 eV, respectively. In the g-C$_3$N$_4$-based kagome lattice with a tensile strain of 12.6%, the valence bands occupied by p$_x$ and p$_y$ orbitals are downshifted, while the spin-down p$_z$ orbitals cross the Fermi surface (as shown in Figure 6), similar to the results shown in Figure 3c and d, confirming again that the
strained state is a semimetal.

In summary, on the basis of spin-polarized DFT, we show that when patterned into kagome structures, the nonmagnetic g-C$_3$N$_4$ becomes ferromagnetic, and the magnetism of g-C$_3$N$_4$ can be enhanced, where the Curie temperature becomes 520 K and the magnetic moment per unit cell increases three-fold. These kagome structures can be fabricated using electron beam irradiation, etching techniques, lithography, or nanocutting developed for graphene. The resulting 2D kagome structures show some advantages over the existing systems synthesized by using a metal–organic coordination network or supramolecular self-assembly of specific molecules on the surface of substrates, where metal ions are used to induce

magnetism. Accordingly, its biocompatibility is compromised. Our studied systems with enhanced magnetism, porosity, and
biocompatibility are promising candidates for applications in medicine and spintronics.

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**Notes**

The authors declare no competing financial interest.

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