Magnetic Graphene Nanohole Superlattices

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Abstract

We investigate the magnetic properties of nano-holes (NHs) patterned in graphene using first principles calculations. We show that superlattices consisting of a periodic array of NHs form a new family of 2D crystalline "bulk" magnets whose collective magnetic behavior is governed by inter-NH spin-spin interaction. They exhibit long-range magnetic order well above room temperature. Furthermore, magnetic semiconductors can be made by doping magnetic NHs into semiconducting NH superlattices. Our findings offer a new material system for fundamental studies of spin-spin interaction and magnetic ordering in low dimensions, and open up the exciting opportunities of making engineered magnetic materials for storage media and spintronics applications.

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Magnetic materials have a wide range of applications, such as being used for storage media. Magnetism is commonly associated with elements containing localized \(d\) or \(f\) electrons, i.e. the itinerant ferromagnetism\(^1\,^2\). In contrast, the elements containing diffuse \(sp\) electrons are *intrinsically* non-magnetic, but magnetism can be induced in \(sp\)-element materials extrinsically by defects and impurities. There have been continuing efforts in searching for new magnetic materials, and much recent interest has been devoted to magnetism of carbon-based\(^3\,^4\,^5\,^6\,^7\), especially graphene-based structures\(^8\,^9\,^{10}\,^{11}\,^{12}\,^{13}\,^{14}\,^{15}\,^{16}\,^{17}\,^{18}\) such as graphene nanoribbons\(^8\,^{11}\,^{18}\) and nanoflakes\(^16\,^{17}\). Here, we predict a new class of graphene-based magnetic nanostructures, the superlattices of graphene nanoholes (GNHs), using first-principles calculations.

Graphene nanoribbons\(^8\,^{11}\,^{18}\) and nanoflakes\(^16\,^{17}\) with zigzag edges have been shown to exhibit magnetism. Their magnetization is originated from the localized edge states that give rise to a high density of states at the Fermi level rendering a spin-polarization instability\(^1\). Then, for the same reason, if nanoholes (NHs) are made inside a graphene sheet with zigzag edges they may also exhibit magnetism. Furthermore, by making an array of NHs, we may expect collective "bulk" magnetism because *inter*-NH spin-spin interactions are introduced in addition to the *intra*-NH spin coupling. This allows us to go beyond the current scope limited to the spins within a single nanoribbon or nanoflake. In effect, superlattices consisting of a periodic array of NH spins form a family of nanostructured magnetic 2D crystals with the NH acting like a "super" magnetic atom.

We have investigated magnetic properties of GNHs, using first-principles pseudopotential plane-wave calculations within the spin-polarized generalized gradient approximation\(^19\). We used a rhombus supercell in the graphene plane with the cell size ranging from \(14 \times 14\) Å to \(41 \times 41\) Å and a vacuum layer of \(\sim 10\) Å. We used a \(2 \times 2 \times 1\) k-point mesh for Brillouin zone sampling and a plane wave cutoff of \(22.1\) Rd. The systems contain up to a maximum of 530 atoms. The dangling bonds on the edge atoms are saturated with hydrogen. The system is relaxed until the force on each atom is minimized to less than \(0.01\) eV/Å.

Considering first a single zigzag NH by examining the *intra*-NH spin-spin interaction, we found that individual NH can be viewed as an "inverse structure" of nanoflake or nanoribbon, like an anti-flake or anti-ribbon, with similar spin behavior. We determine the ground-state magnetism of three typical NH shapes: triangular (Fig.\[\text{I}a\]), rhombus (Fig.\[\text{I}b\]) and hexagonal (Fig.\[\text{I}c\]), by comparing the relative stability of ferromagnetic (FM), antiferromagnetic (AF)
and paramagnetic (PM) configuration as a function of NH size. Our calculations show that the ground state is FM for triangular NHs, but AF for rhombus and hexagonal NHs, and their corresponding spin densities are shown in Fig.1a, 1b and 1c, respectively. The magnetic moments are highly concentrated on the edges and decay quickly away from the edge, as shown in Fig.1d. Similar decaying behavior has been seen in nanoribbons and nanoflakes. The edge moment increases with increasing NH size (see inset of Fig.1d).

The triangular NHs have a metastable ferrimagnetic state with two edges having one spin and the other edge having the opposite spin (see supplementary Fig.1). For a 4-atom triangular NH (Fig.1a), the FM state is 52 meV lower in energy than the ferrimagnetic state, and the latter is 13 meV lower than the PM state. For a 32-atom rhombus NH (Fig.1b), the AF state is 89.2 meV lower than the PM state; for a 54-atom hexagonal NH (Fig.1c), it is 164.4 meV. The energy difference increases with increasing NH size. The triangular NHs favor FM at all sizes, whereas rhombus and hexagonal NHs only become AF when the edge contains more than five atoms, i.e. they are PM if the NH is too small. So, the triangular NHs have a stronger tendency toward magnetization.

The magnetic ordering within a single NH is consistent with both the theorem of itinerant magnetism in a bipartite lattice and the topological frustration model of the π-bonds counting the unpaired spins in the nonbonding states. For a system like graphene consisting of two atomic sublattices, each sublattice assumes one spin and the total spin $S$ of the ground state equals $\frac{1}{2}|N_B - N_A|$ where $N_B$ ($N_A$) is the number of atoms on B (A) sublattice. Because of the honeycomb lattice symmetry, atoms on the same zigzag edge belong to the same sublattice; while atoms on two different zigzag edges belong to the same sublattice if the two edges are at an angle of 0° or 60°, but different sublattices if at an angle of 120° or 180°. Consequently, the triangular NH are FM, because all three edges are 60° to each other on the same sublattice; the rhombus and hexagonal NHs are AF, because one-half the edges are on the A-sublattice and another half on the B-sublattice as the two types of edges are 120° to each other. This same argument can be applied to nanoribbons and nanoflakes.

Next, we consider GNH superlattices (a periodic array of NHs) by examining the inter-NH spin-spin interaction. In principle, one can generate four out of five possible 2D Bravais lattices of NHs (see supplementary Fig.2). Here, we focus on the honeycomb superlattices of triangular NHs (Fig.2a and 2b), in which each NH possesses a net moment acting effectively as “one” spin. The superlattice contains two sublattices of NHs, superimposed on the
FIG. 1: The ground-state magnetic configurations of different shapes of NHs. (a) FM triangular NH; (b) AF rhombus NH; (c) AF hexagonal NH. In (a-c), white and red balls indicate the up- and down-spin density isosurface at 0.02e/Å³, respectively; blue and white sticks represent C-C and C-H bonds respectively. (d) The average local magnetic moment ($\mu_B$) per atom in the triangular NH (Fig.1a) as a function of distance moving away from the center of NH, measured in atomic shells with the edge atoms as the first shell. The inset shows $\mu_B$ on the edge vs. NH size ($l$).

background of graphene containing two sublattices of atoms. We realize that the NHs on the same sublattice will be FM-coupled because their corresponding edges are at 0° to each other so that their edge atoms are on the same atomic sublattice. On the other hand, the NHs on different sublattices will be FM-coupled if they are in a parallel configuration (Fig.2a) but
AF-coupled if they are in an antiparallel configuration (Fig. 2b) when their corresponding edges are at $180^\circ$ to each other so that their edge atoms are on different atomic sublattices. These have indeed been confirmed by our first-principles calculations. Independent of NH size and supercell dimension, the FM state is favored for parallel configurations but the AF state is favored for antiparallel configurations. In both cases, the spin-polarization splits the edge states opening a gap at the Fermi energy$^{9,17}$. The total spin $S$ in one unit cell equals to $\frac{1}{2} |N_B - N_A|$; it increases linearly in the FM parallel configuration but remains zero in the AF antiparallel configuration with increasing NH size.

The collective magnetic behavior of a GNH superlattice depends on inter-NH spin-spin interaction. Particularly, there exists super exchange interaction between the NH spins, in addition to the spin coupling defined by the underlying bipartite lattice (i.e., the relative angle between the zigzag edges of GNHs). In Fig. 2c, we plot $\Delta E_{pc} = E(FM) - E(PM)$ for the FM parallel configuration and $\Delta E_{ac} = E(AF) - E(PM)$ for the AF antiparallel configuration as a function of cell dimension ($L$), i.e., the NH-NH separation. $|\Delta E_{pc}|$ increases while $|\Delta E_{ac}|$ decreases with decreasing $L$. This indicates that as the NHs getting closer, the FM state becomes relatively more stable than AF state in both configurations, i.e. the FM coupling is favored by the super exchange interaction. Also plotted in Fig. 2c are magnetic moments on the NH edges, which are found to increase in the FM but decrease in the AF configuration with decreasing $L$. This again reflects that the edge magnetization on the neighboring NHs is enhanced with the same spin when they are FM coupled but suppressed with the opposite spin when they are AF coupled by the super exchange interaction.

The above results show that long-range ferromagnetic ordering can be created by employing the parallel configuration of triangular NHs in different lattice symmetries, as illustrated in supplementary Fig. 2. The next important question is what Curie temperature ($T_c$) they can have. We have estimated $T_c$ using the mean-field theory of Heisenberg model$^{21,22,23}$,

$$T_c = \frac{2\Delta}{3k_B}$$  \hspace{1cm} (1)

Where $\Delta$ is the energy cost to flip one "NH spin" in the FM lattice, which have been calculated directly from first principles for the honeycomb lattices (Fig. 2a). Figure 2c shows that $T_c$ increases from 169 K to 1388 K when NH size ($l$) increases from 0.738 to 1.476 nm with cell dimension ($L$) fixed at 2.982 nm, and decreases from 586 K to 169 K when $L$ increases from 1.704 nm to 2.982 nm with $l$ fixed at 0.738 nm. These trends are expected since
FIG. 2: (a) Ground-state spin configurations in a FM honeycomb NH superlattice. (b) Same as (a) in an AF superlattice. All the symbols and notations for bonds and spin densities are the same as Fig.1. Yellow dashed lines mark the primitive cell. (c) $\Delta E_{pc} = E(FM) - E(PM)$ of the FM superlattice (red solid squares) and $\Delta E_{ac} = E(AF) - E(PM)$ of the AF superlattice (blue solid triangles) versus cell dimension ($L$); Edge magnetic moments, $\mu_B$ in the FM lattice with fixed hole size ($l=1.476$ nm) (red open squares) and in the AF lattice ($l=0.738$ nm) (blue open triangles) versus $L$. (d) Curie temperature of the FM superlattice as a function of NH size ($l$) and $L$.

Magnetization is stronger for larger NH size and higher NH density. Limited by computation time, some of our cell dimensions are possibly unrealistically too small (NH density too high), which gives rise to a very high $T_c$. Still, it is important to point out that our calculations suggest that it is possible to make FM GNH superlattices with $T_c$ above room temperature by using a NH size of 50 nm and a density of $10^{-4}$ nm$^{-2}$, achievable by today’s lithographic patterning technology. We note that a recent experiment has shown a $T_c \geq 350$ K in FM
FIG. 3: Illustration of DMS made from GNH superlattice. (a) A semiconductor GNH hexagonal lattice \((L = 8\sqrt{3}a, a = 2.46\,\text{Å} \) is the lattice constant of graphene.) consisting of an array of rhombus armchair NHs \((L = 8\sqrt{3}a)\). (b) GGA Band structure of (a), the inset shows the Brillouin zone. (c) TB band gap of (a)-type structures as a function of NH size \((l)\) and cell dimension \((L)\). (d) Magnetic semiconductor made by doped (a) with triangular zigzag NHs. All the symbols and notations for bonds and spin densities are the same as Fig. 1.

Since graphene-based nanostructures hold great promise for future electronics\(^{25,26,27,28}\), our discovery of GNH magnetism offers the exciting prospect of combining magnetic and semiconducting behavior in one material system. Here, we demonstrate the possibility of making diluted magnetic semiconductors (DMS) by exploiting GNHs with two different kinds of edges. Similar to superlattices of zigzag NHs, we can create superlattices of armchair NHs, which constitute a class of 2D semiconductors. Figure 3b shows the band structure
of a superlattice of rhombus armchair NHs (Fig. 3a) having a direct band gap of 0.43 eV, as obtained from first-principles calculations. Figure 3b shows the band gap as a function of NH size ($l$) and cell dimension ($L$), from tight-binding calculations. The gap increases with increasing $l$ but decreases with increasing $L$.

DMS can be made by adding triangular zigzag NHs into the semiconductor superlattice, as illustrated in Fig. 3d. To ensure the ferromagnetism, all triangular NHs must be parallel with each other acting like magnetic dopants. Usually DMS are synthesized by mixing two different materials, typically III-V semiconductors and transition-metal magnetic elements. The main challenge is to increase the magnetic dopant concentration in order to raise the Curie temperature, because the two types of materials are usually not miscible. Here, we introduce an ”all-carbon” DMS, in which combined semiconductor and magnetic behavior are achieved by structural manipulation. Consequently, room-temperature DMS are possible because the dopant concentration can be increased without the miscibility problem. One might also consider doping other magnetic elements into the semiconducting GNH superlattice.

It is very exciting to consider making engineered magnetic materials with NHs for various applications. For example, it is possible to directly pattern NHs into engineered magnetic storage media (see Fig. 4). The ground state of rhombus NHs is AF (Fig. 4b and Fig. 4 lower-left inset) and their first excited state is FM (Fig. 4 up-right inset) when the NH size is larger than 14.6 Å according to our calculation. Taking each NH as one bit, we can assign the ground state with ”$S=0$” and the excited state with ”$S=N$” to represent the '0' and '1', respectively. The switching between '0' to '1' can be done by applying a local magnetic field or energy pulse to convert between the ground and the excited state. Using a NH size of 50 nm and a density of $10^{-4}$ nm$^{-2}$, a storage density about 0.1 terabit per square inch would be achieved, much higher than the current density in use. One interesting topic of future study is the magnetocrystalline anisotropy around individual NHs, which must be larger than $k_B T$ for the proposed storage media to work.

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FIG. 4: Schematic Illustration of a magnetic storage medium consisting of a patterned array of rhombus GNHs. The insets show the detailed structure of "0" and "1" bit, represented by the ground-state AF configuration ($S=0$) and the excited FM configuration ($S=N$), respectively. Red and green balls show the spin-up and spin-down density at an isosurface value of $0.02e/\text{Å}^3$.

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Our tight-binding band structure calculations for semiconductor armchair GNH superlattices were performed using the nearest-neighbor $\pi$-band model with the hopping parameter $= 3.0$ eV.
Supplementary Fig.1 The spin-density plot of the ferrimagnetic configuration of a 4-atom triangular NH. White and red balls indicate the up- and down-spin density isosurface at 0.02e/Å³ respectively; blue and white sticks represent C-C and C-H bonds respectively.
Supplementary Fig.2 Schematic illustration of four possible types of Bravais lattice of GNHs that can be patterned in graphene. Solid arrows and lines mark the primitive cells. (a) hexagonal lattice; (b) rectangular lattice; (c) centered rectangular lattice; the dashed lines mark the conventional cell; (d) oblique lattice. Note that the square lattice is not possible.