Physics Letters A ••• (••••) •••–•••

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

# Half-metallicity in hole-doped nitrogenated honey graphene: A first-principles study

Jingzhong Zhu [a,b], Yinchang Zhao [a,b], Shuming Zeng [a,b], Jun Ni [a,b]

[a] State Key Laboratory of Low-Dimensional Quantum Physics, Department of Physics, Tsinghua University, Beijing 100084, People's Republic of China
[b] Collaborative Innovation Center of Quantum Matter, Beijing 100084, People's Republic of China

ARTICLE INFO

*Article history:*
Received 12 October 2016
Received in revised form 12 January 2017
Accepted 28 January 2017
Available online xxxx
Communicated by M. Wu

*Keywords:*
Half metal
Ferromagnetism
Phase transition

ABSTRACT

We have investigated the structural, electronic and magnetic properties of hole-doped nitrogenated honey graphene by first-principles calculations. Remarkably, there exists a stable half-metallic ferromagnetism phase with the average spin magnetic moment per carrier of near 1.0 $\mu_B$ in this monolayer system as the carrier density increases from 0 to $1.5 \times 10^{14}$ cm$^{-2}$. With further increase of carrier density, the half-metal state vanishes, while the magnetic state remains until the carrier density reaches $4.5 \times 10^{14}$ cm$^{-2}$. Our analysis reveals that the predicted itinerant magnetism arises from an exchange splitting of the electronic states at the top of the valence band, where the density of states shows a van Hove singularity. In addition, we have also studied the electron-doped nitrogenated honey graphene, and find the magnetic features are similar to those of the hole-doped system. As synthesis of monolayer nitrogenated honey graphene was reported, half-metallicity of nitrogenated honey graphene are feasible.



## 1. Introduction

Electrical current in a half-metal can be 100% spin polarized since its Fermi level is filled with the electrons of only one spin orientation [1]. Various materials have been predicted to be half-metallic ferromagnets such as Heusler alloys, zinc-blende structure compounds, manganese perovskites, transition-metal oxides and transition-metal dichalcogenides [2–9]. In these materials, half metallicity is believed to stem from transition metals. However, transition-metal-contained materials may not be designed to be fully compatible with many current matured technologies, which mainly based on semiconductor technology. Therefore much efforts have been devoted to search for metal-free half metallic materials.

Graphene has attracted much attention due to its peculiar hexangular planar configuration and abundant electronic properties [10–19]. A zigzag graphene nannoribbon shows a novel half metallic behavior when applied an in-plane homogeneous electric field [20]. This investigation has opened up a new way to the design of metal-free half metallic materials. Zigzag edged graphene nanoribbons are found to be half metallic state by chemical modification of its edges with different atoms or functional groups [21–24].

Recently, a simple wet chemical reaction was proposed to synthesized two dimensional (2D) nitrogenated honey graphene ($C_2N$) [25]. This unique 2D crystal was simply synthesized by the reaction between hexaaminobenzene (HAB) trihydrochloride and hexaketocyclohexane (HKH) octahydrate in N-methyl-2-pyrrolidone (NMP) in the presence of a few drops of sulphuric acid ($H_2SO_4$) or in trifluoromethanesulphonic acid [25]. This structure has been confirmed by various characterization techniques, such as scanning tunneling microscopy (STM) [25]. The electronic, magnetic and mechanical properties of $C_2N$, $C_2P$ and $C_2As$ were investigated by first-principles calculations [26]. The highest valence band of $C_2N$ is quasiflat and the density of states (DOS) of the $C_2N$ shows a van Hove singularity. A van Hove singularity in a material may lead to phase transitions such as superconductivity, ferromagnetism phase transitions [20]. Thus it is important to investigate whether the van Hove singularity of $C_2N$ could be tailored for designing new magnetic materials.

Here we investigate the half-metallicity of monolayer $C_2N$ via hole doping. Via hole doping, a half-metallic phase is predicted as the carrier density increases from 0 to $1.5 \times 10^{14}$ cm$^{-2}$, a ferromagnetic phase is predicted to occur for the doping density in a range of $1.5 \times 10^{14}$ cm$^{-2}$ $\sim 4.5 \times 10^{14}$ cm$^{-2}$. The magnetic moment of this system is tunable via changing the doping level. A half-metallic phase of $C_2N$ can also be realized via electron doping.

*E-mail address:* junni@mail.tsinghua.edu.cn (J. Ni).

http://dx.doi.org/10.1016/j.physleta.2017.01.050
0375-9601/

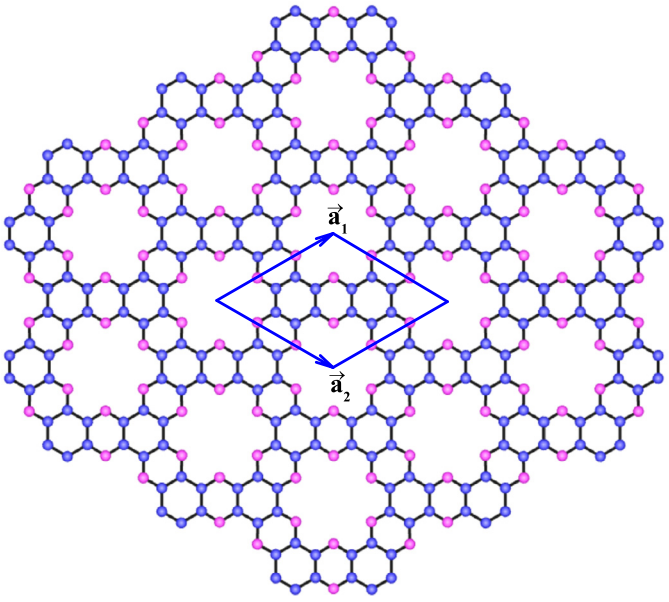


**Fig. 1.** (Color online). The relaxed structure of Nitrogenated honey graphene ($C_2N$). The unit cell is indicated by a blue parallelogram. The blue and red balls represent C and N atoms, respectively.

## 2. Methodology

All the calculations are performed within the spin-polarized density functional theory (DFT) implemented in the Vienna ab initio simulation package (VASP) [27]. We adopt the projector-augmented wave potentials to model the ion cores. A plane wave basis set with a cutoff energy of 500 eV is used for the valance electrons with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional with the inclusion of spin–orbit-coupling (SOC) [28,29]. The vacuum region between adjacent $C_2N$ layers is larger than 15 Å. The Brillouin zone (BZ) sampling is obtained using a $12 \times 12 \times 1$ Monkhorst–Pack grid for relaxation calculations and a $24 \times 24 \times 1$ Monkhorst–Pack grid for static calculations. The tolerance of the energy convergence is $10^{-5}$ eV. We relax all the structures until the force on each atom is smaller than 0.01 eV/Å. We change the carrier density by turning the total number of electrons in the unit cell of $C_2N$ with a homogeneous background-charge. Experimentally, the carrier density in graphene can be adjusted up to $4 \times 10^{14}$ $cm^{-2}$ for both electrons and holes [30,31]. In our calculations, the maximum of hole density is set to be $4.5 \times 10^{14}$ $cm^{-2}$.

## 3. Results and discussion

The geometry configuration of $C_2N$ is shown in Fig. 1, which can be considered infinite benzene rings connected by nitrogen atoms. The lattice constant of $C_2N$ is 8.33 Å. The bond lengths of C-C and C-N are 1.47 Å and 1.34 Å respectively, which is accordance with the precious result [25,26]. A primitive cell of $C_2N$ shows twelve C atoms in blue and six N atoms in red.

The Bravais lattices of Nitrogenated honey graphene and graphene are same as 2 dimensional hexagonal lattices, as shown in Fig. 2(a), thus their reciprocal lattices and Brollion zones are same, as illustrated in Fig. 2(b). The energy bands of monolayer $C_2N$ are depicted in Fig. 2(c). The band gap of $C_2N$ is about 1.67 eV, as compared with the experimental value of 1.96 eV [25], it is well known that the PBE normally underestimates the band gap of many semiconductors and insulators, typically by 30%. The conduction band minimum (CBM) and the valence band maximum (VBM) locate at the Γ point. The spin-up band and spin-down band are doubly degenerate and therefore the monolayer $C_2N$ is nonmagnetic. The VBM at the Γ point is only 0.054 eV higher than the VBM at the K point, and the VBM at the K point is only 0.046 eV higher than the VBM at the M point. Hence the VBM at the symmetry points (Γ, K, M) in the first Brillouin zone are almost degenerate. This almost degenerate dispersion gives rise to a sharp van Hove singularity in the density of states (DOS). A partial density of states (PDOS) analysis indicates that the DOS near the VBM stems mostly from the C $2p$ and N $2p$ orbitals [Fig. 2(d)]. The remaining small contribution comes from the C $2s$ and N $2s$ orbitals.

Although intrinsic monolayer $C_2N$ is nonmagnetic, our spin-polarized calculations show that it develops spontaneously a half-metallic ferromagnetic ground state even via a small density of hole doping. Fig. 3 depicts the magnetic moment and the magnetization energy (the total energy difference between the nonmagnetic and ferromagnetic state) as a function of hole density. In a large doping range of $0 \sim 4.5 \times 10^{14}/cm^2$, we find an averaged magnetic moment of about 1.0 $\mu_B$ per carrier, which is just an integer in unit of $\mu_B$. This integer spin magnetic moment is a characteristic of half-metallic magnet. The magnetization energy increases with the density of the hole doping. This illustrates that the ferromagnetic state is more stable than the nonmagnetic state for hole-doped monolayer $C_2N$.

To further understand the magnetic ground state of the hole-doped $C_2N$, we calculate its detailed electronic structure. Fig. 4 shows the detailed band structure, DOS and PDOS of the hole-doped $C_2N$. We use p to denote the hole density and three types of density are considered. At $p = 0.3$ hole/cell (i.e., $0.5 \times 10^{14}/cm^2$), as shown in Fig. 4(a), an exchange splitting of the electronic states occurs while the spin-up band shows metallic nature while the spin-down band shows insulating nature. For the same k quantum number and the j quantum number of band, the $E_j(k)$ is different for spin-up and spin-down electron. Fig. 4(a) shows the $E_j(k)$ of spin-up electron is larger than the $E_j(k)$ of spin-down electron for the same k and j. The band gap of spin-down bands is about 1.8 eV. The PDOS plots of C and N atoms show that the magnetic moment and half-metallic come mainly from the $p$ orbitals of C and N atoms. The difference of the maxima of the highest valence band and the Fermi energy is 0.012 eV. At $p = 0.6$ hole/cell (i.e., $1 \times 10^{14}/cm^2$), as shown in Fig. 4(b), the spin-up and spin-down states show metallic nature and insulating nature, respectively. The band gap of spin-down bands is 1.9 eV. The calculations based on DFT generally underestimate the band gap. This indicates that the experimental spin-down bandgap of this half metallic magnet may be wider. A wide spin-down bandgap is very important for applications of half-metallic ferromagnetic materials. The difference of the maxima of the highest valence band and the Fermi energy is 0.026 eV. With increase of the hole density, the Fermi energy becomes far from the maxima of the highest valence band. However at $p = 0.9$ hole/cell (i.e., $1.5 \times 10^{14}$ $cm^{-2}$), as shown in Fig. 4(c), both the spin-up and spin-down bands show metallic nature. This implies that the spin polarization of the carriers is not exactly 100% and this hole-doped $C_2N$ is not in a half-metallic state. However the spin-down DOS near the Fermi energy is so small that the averaged spin moment per carrier of the hole-doped $C_2N$ is still close to 1.0 $\mu_B$. The PDOS plots show that the spin-down DOS near the Fermi energy originates from the $p$ orbitals of C atoms. The monolayer $C_2N$ behaves as a half-metallic phase for the doping density in a range of $0 \sim 1.5 \times 10^{14}$ $cm^{-2}$ and becomes a ferromagnetic phase for the doping density in a range of $1.5 \times 10^{14}$ $cm^{-2} \sim 4.5 \times 10^{14}$ $cm^{-2}$.

To explore the sudden jump of the magnetic moment per carrier in Fig. 3, we also have another viewpoint to depict the bands in Fig. 4(a). The Fermi level has been set to be 0. The maxima of the spin-up valence band is 0.012 eV. The bands below



Please cite this article in press as: J. Zhu et al., Half-metallicity in hole-doped nitrogenated honey graphene: A first-principles study, Phys. Lett. A (2017), http://dx.doi.org/10.1016/j.physleta.2017.01.050