Structural stability and electronic properties of carbon star lattice monolayer*

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By means of the first-principles calculations, we have investigated the structural stability and electronic properties of carbon star lattice monolayer and nanoribbons. The phase stability of the carbon star lattice is verified through phonon-mode analysis and room temperature molecular dynamics simulations. The carbon star lattice is found to be metallic due to the large states across the Fermi-level contributed by p_z orbital. Furthermore, the nanoribbons are also found to be metallic and no spin polarization occurs, except for the narrowest nanoribbon with one C_{12} ring, which has a ferromagnetic ground state. Our results show that carbon star lattice monolayer and nanoribbons have rich electronic properties with great potential in future electronic nanodevices.

Keywords: carbon star lattice, structural stability, electronic properties, first-principles calculations

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1. Introduction

Graphene, the prototype two-dimensional (2D) inorganic honeycomb crystal in sp^2 bonding networks, possesses rather fascinating physical properties[1–4] such as 2D electron-gas behavior, anomalous quantum Hall effect, ballistic electronic conductivity, and ambipolar effect, thereby, it is regarded as a revolutionary material for post-silicon nanoelectronics. Actually, the need for miniaturization of electronic devices calls for continued development of new materials with reduced dimensionality, an intense research enthusiasm has now been shifted to the search for other promising 2D carbon allotropes inspired by the success of graphene. For instance, a family of layered carbon phases (graphyne and its substructures) containing both sp and sp^2 hybridized carbon atoms have attracted tremendous theoretical[5–8] and experimental[9,10] attention, the presence of acetylenic linkages in these materials joining hexagons C_6 together could result in non-zero band gap which is absent in graphene; another series of planar metallic carbon forms incorporating pentagons C_5, hexagons C_6, and heptagons C_7 have been studied by Terrones *et al.*,[11] furthermore, Lusk *et al.* proposed that introducing patterned defects to perfect graphene could lead to both metallic[12] and semiconducting[13] graphene allotropes. There are still other well-studied 2D carbon forms such as pentaheptites,[14] planar C_4,[15] net C,[16] net W,[17] and Kagomé lattice.[18] It seems that we would enter into the era of 2D carbon allotropes.

A novel graphene allotrope containing triangles C_3 and dodecagons C_{12} [see Fig. 1(a)] has long been proposed,[19,20] however, its fundamental properties remain largely unexplored yet, despite its significant importance. Since its geometry can be mapped to a well-known lattice model named "star lattice",[21,22] we then refer to it as "carbon star lattice" hereinafter.

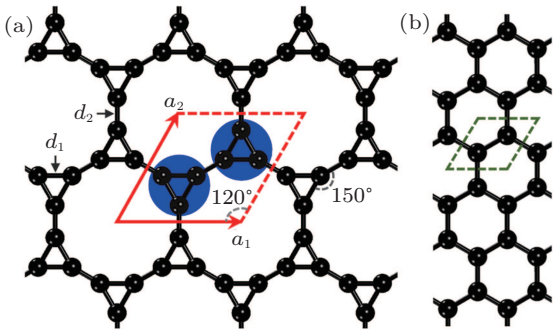


Fig. 1. (color online) (a) Geometric structure for D^1_{6h} carbon star lattice. The unit cell (containing six carbon atoms) is delineated, the Bravais lattice vectors are $|\boldsymbol{a}_1| = |\boldsymbol{a}_2| = 5.196$ Å, d_1 and d_2 are the two inequivalent bonds of 1.425 Å and 1.355 Å, respectively. In panel (a), if each C_3 triangle marked by the blue sphere is substituted by a single carbon atom, carbon star lattice transforms into panel (b) graphene.

In this work, by means of the first-principles calculations, we investigate the structural stabilities and electronic properties of carbon star lattice. Its phase stability is verified through both phonon-mode analysis and room-temperature molecular dynamics simulations. We find that carbon star lattice is metallic due to the large states across the Fermi-level contributed by p_z orbital. The nanoribbons are also found to be metallic and

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no spin polarization occurs, except for the narrowest nanoribbon with one C_{12} ring, which has a ferromagnetic ground state.

2. Computational methods

The calculations are carried out using the density functional theory (DFT) within the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE)[23] as implemented in the Vienna *ab initio* simulation package (VASP).[24–26] The projector augmented wave (PAW)[27] method is adopted with $2s^2 2p^2$ treated as valence electrons, and a plane-wave basis set with an energy cutoff of 600 eV is used. A vacuum region of 20 Å is added normal to the crystal plane to avoid the interactions between neighboring layers, the Brillouin zone (BZ) is sampled with a $27 \times 27 \times 5$ Monkhorst–Pack (MP) special k-point grid. The periodic boundary condition for nanoribbons is set with the vacuum region between neighboring ribbons larger than 20 Å. The geometries are optimized with no symmetry constraints until the remaining atomic forces are less than 0.001 eV/Å on each atom, and the energy convergence criterion is chosen as 10^{-8} eV between two ionic steps. The phonon calculations are carried out by using the package phonopy[28,29] with the forces calculated from VASP.

3. Results and discussion

We first characterize the structural and electronic properties of carbon star lattice. Its crystal structure with the space group $P6/mmm$ (D^1_{6h}) is shown in Fig. 1 versus graphene. There is a close geometrical connection between such two structures: the configuration of carbon star lattice [Fig. 1(a)] could be simply obtained by substituting each carbon atom in graphene [Fig. 1(b)] with a C_3 triangle marked by the blue spheres. Therefore, carbon star lattice possesses the same symmetry (D^1_{6h}) as graphene, but it contains six carbon atoms per unit cell. All carbon atoms in carbon star lattice are symmetrically equivalent and occupy the Wyckoff position 61 (x, $-x$, 0.5) with $x = 0.425$. The equilibrium lattice constant a of carbon star lattice is estimated to be 5.196 Å, its areal density of 0.257 atoms/Å^2 is less than 0.379 atoms/Å^2 for graphene and 0.292 atoms/Å^2 for graphyne but comparable with 0.232 atoms/Å^2 for graphdiyne, respectively.[17] There exist two distinct bonds, d_1 of 1.425 Å within C_3 triangles and d_2 of 1.355 Å between the adjacent C_3 units. Here the bond (d_2) between two adjacent C_3 units is indeed a double bond and close to the $C(sp^2)=C(sp^2)$ double bond in 1, 3-butadiene, 3-fold and 4-fold carbene.[30,31] In addition, there are two bond angles, 60° in C_3 triangles and 150° between the neighboring inequivalent bonds, both differ much from uniform 120° for graphene, implying a strained state in carbon star lattice which probably leads to an enhancement in energy. Indeed, we confirm that carbon star lattice has a total energy about 0.97 eV per atom higher than graphene at GGA–PBE level.

In order to check the dynamical stability of carbon star lattice, we thoroughly analyze its phonon modes. As shown in Fig. 2, since there is no imaginary mode in the phonon dispersions, carbon star lattice is dynamically stable at ground state. It is instructive to notice that the highest phonon frequency of carbon star lattice is estimated to be 1940 cm^{-1} locating at Γ point which corresponds to d_2 bond stretching mode. Such frequency is much larger than ~1600 cm^{-1} for graphene[32] and it could be useful in characterizing carbon star lattice in experiments. On the other hand, we perform the first-principles molecular dynamics simulations to examine whether carbon star lattice could retain its geometry at room temperature (300 K). Our simulations are carried out in canonical (NVT) ensemble with a time step of 1 fs and a relative large supercell containing 600 atoms is adopted. The configuration of carbon star lattice is well kept even after running 10000 steps, which again suggests its high phase stability.

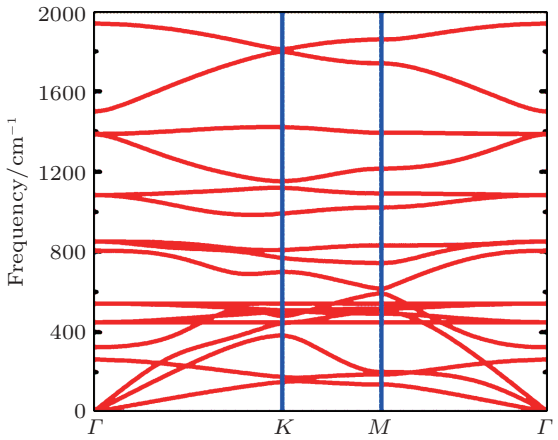


Fig. 2. (color online) Phonon dispersions of carbon star lattice.

The calculated charge density distribution, electronic band structures, and projected density of states (PDOS) of carbon star lattice are all illustrated in Fig. 3. It is shown that the electrons are more condensed around d_2 than d_1 [see Fig. 3(a)], this fact evidently indicates that carbon star lattice is not strictly sp^2 but sp^2-like hybridized. Due to the departure from perfect sp^2 hybridization, the π–π^* pseudogap locating at the Fermi level (E_F) present in graphene is filled in carbon star lattice, yielding a prominent density of states (DOS) peak of ~1.4 states/eV per atom near E_F [see Figs. 3(b) and 3(c)], indicting the metallic character for carbon star lattice. Further PDOS analysis reveals that those electronic states around E_F are dominated by the p_z orbital [see Fig. 3(c)]. The p_x and p_y states are degenerate due to symmetry and they locate over a wide energy range about 1.3 eV below E_F. Moreover, the

strong hybridization for p_x and p_y with s states can be identified through the large overlap of corresponding PDOS peaks deep below E_F.

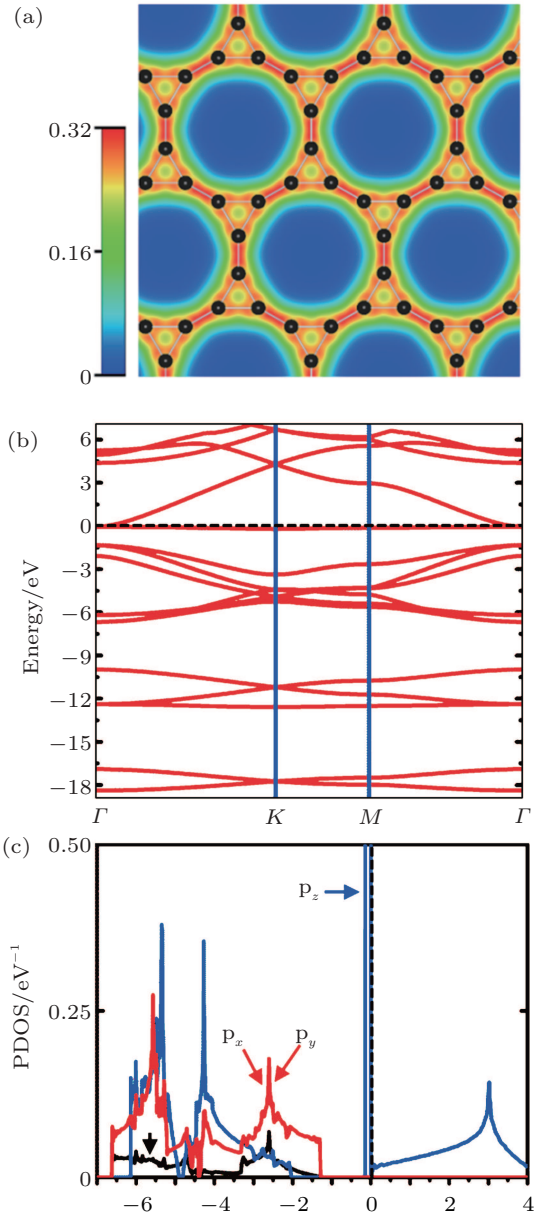


Fig. 3. (color online) (a) Charge density distribution projected on the carbon star lattice surface, the contour line represents the charge density from 0.0 to 0.32 e/Å^3. (b) and (c) Electronic band structures and PDOS of carbon star lattice. The electronic states across E_F (zero energy) are mainly contributed by the p_z orbital, p_x and p_y states are degenerate due to symmetry.

Finally, we discuss the electronic properties of carbon star lattice nanoribbons (CSLNRs). As shown in Fig. 4, cutting through an infinite sheet along the $\boldsymbol{a}_1$ or $\boldsymbol{a}_2$ directions shown in Fig. 1, we can get the CSLNRs with different widths. For simplicity, we refer to a CSLNR with width direction containing N C_{12} rings as $\boldsymbol{r}_N$-CSLNR [see Fig. 4(a)]. The dangling σ bonds at the edges are saturated by hydrogen and the geometries are all further optimized for each CSLNR calculation. Upon inclusion of the spin degrees of freedom within GGA–PBE, our calculations show that the r_1-CSLNR has a ferromagnetic (FM) ground state, and all other CSLNRs are nonmagnetic (NM) without spin polarization. The r_1-CSLNR has the total moments of 0.85 μ_B and the calculated NM–FM energy difference is only 8 meV per unit cell (containing 12 carbon atoms and 2 hydrogen atoms). The spin density distributions for r_1-CSLNR at ferromagnetic ground state are displayed in Fig. 4(b). It can be seen that the spin states are mainly distributed at the edges, and all originated from the hybrid p_z orbitals. The band structures of r_1-, r_2-, r_3-, and r_4-ACSLNRs are plotted in Fig. 5. It is clearly shown that all the CSLNRs are metallic.

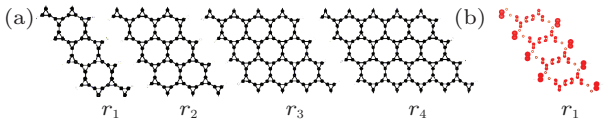


Fig. 4. (color online) (a) Nanoribbons with different widths obtained by cutting through an infinite carbon star lattice monolayer along $\boldsymbol{a}_1$ or $\boldsymbol{a}_2$ directions. (b) The spin density distributions $[\rho_{up}(r) - \rho_{down}(r)]$ of r_1-CSLNR. The isovalue is 0.01.

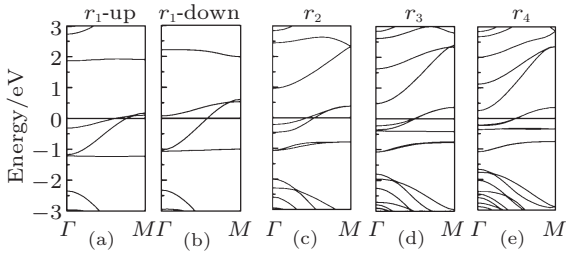


Fig. 5. The band structures for r_1- ((a) and (b)), r_2- (c), r_3- (d), and r_4-CSLNRs (e), respectively. The up-spin and down-spin states for r_1-CSLNR are separated as r_1-up and r_1-down. The Fermi level is set at zero energy. Here $M(0.0, 0.5, 0.0)$ is the same as the M shown in Figs. 2 and 3(b).

4. Conclusion

In summary, the structural stability and electronic properties of the carbon star lattice monolayer are studied by first-principles calculations. We have performed both phonon-mode analysis and room temperature molecular dynamics simulations to confirm the phase stability of carbon star lattice. Due to the large states across the Fermi-level contributed by p_z orbital, carbon star lattice is found to be metallic. Furthermore, the nanoribbons are also found to be metallic and no spin polarization occurs, except for the narrowest r_1-CSLNR, which has a ferromagnetic ground state. Because of their rich electronic properties, carbon star lattice monolayer and nanoribbons could serve as potential materials for future electronic nanodevices.

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