

Adatom Defect Induced Spin Polarization of Asymmetric Structures

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The spin polarization of carbon nanomaterials is crucial to design spintronic devices. In this paper, the first-principles is used to study the electronic properties of two defect asymmetric structures, Cap-(9, 0)-Def [6, 6] and Cap-(9, 0)-Def [5, 6]. We found that the ground state of Cap-(9, 0)-Def [6, 6] is sextet and the ground state of Cap-(9, 0)-Def [5, 6] is quartet, and the former has a lower energy. In addition, compared with Cap-

(9, 0) CNTs, the C adatom on C₃₀ causes spin polarization phenomenon and Cap-(9, 0)-Def [6, 6] has more spin electrons than Cap-(9, 0)-Def [5, 6] structure. Moreover, different adsorb defects reveal different electron accumulation. This finding shows that spin polarization of the asymmetric structure can be adjusted by introducing adatom defects.

Introduction

Carbon nanotubes (CNTs) have attracted much attention since their discovery in 1991.^[1–3] Studies have shown that the magnetic phenomenon of CNTs is related to edge effects.^[4] Compared to symmetrical structures, asymmetrical structures are related to the design of directional transport,^[5] electro-magnetic switches^[6–7] and other devices. Studies on hetero-junction CNTs with different radii exhibit spin ferromagnetic or antiferromagnetic coupling phenomenon, which are related to the number of carbon atoms at two zigzag edges. In addition, our research on cap-(9, 0)/(10, 0) CNTs shows that the carbon atoms at zigzag edges have spin polarization but do not at the cap end, and increasing or decreasing charges affect the spin density.^[8–9] And cap-(5, 5)/(9, 0) CNTs adsorbed with alkali-metal atoms demonstrate that electrons transfer from the alkali atom to the CNTs.^[10] So can we adsorb non-metallic atoms on cap-CNTs to affect the distribution of spin density, thereby adjusting the spin density?

The spin-polarized behavior of electrons is closely related to the design of magnetic materials, spintronic device and so on.^[11–12] Previous studies on graphene and CNTs have shown that p electrons at zigzag edges exist spin polarizations.^[13–14] These spin-polarized electrons have spin ferromagnetic or spin antiferromagnetic coupling because of the same or different spin arrangement orientations.^[15–18] But armchair graphene and CNTs do not have spin polarization phenomenon.^[15] Further studies show that eliminating the armchairs edges between the

zigzag edges improves their spin-polarized properties.^[19–20] In addition, defects such as vacancies, doping, and adsorbed atoms affect the spin polarization phenomenon,^[18,21–24] and these defects inevitably exist in carbon materials. Therefore, it is necessary to study the spin polarization behavior of the defect structures.

In this paper, based on the cap-(9, 0) CNTs, the defect for adsorbed atoms that may cause spin polarization is introduced on the surface of C₃₀. We used the first-principles density functional theory method (DFT)^[25–27] to study it. The calculation results show that C adatom induces the generation of spin density, and the spin density distribution is different for different adsorption positions. This work will provide help for the research of spintronic injection and other devices.

Materials and Methods

Based on the asymmetric structure of cap-(9,0) CNTs previously studied,^[8] we adsorbed C atoms on it to form asymmetric defect structure. Similar to C₆₀,^[28] C₃₀ also has [6, 6] bond (connecting two hexagons) and [5, 6] bond (connecting a pentagon and a hexagon), which means that only two adatom defects can be formed on the surface of C₃₀. Therefore, in this paper, we adsorbed a C atom on the [6, 6] and [5, 6] bond at cap end to form Cap-(9, 0)-Def [6, 6] and Cap-(9, 0)-Def [5, 6] structures, respectively, as shown in Figures 1a and 1b.

For carbon-based materials, the DFT methods deal with spin polarizations caused by various defects and edge unsaturation.^[29–31] We used the screened exchange hybrid density functional HSE06 method proposed by Heyd, Scuseria and Ernzerhof.^[32–33] Because the maximum Milliken spin density values calculated by it are more reliable than those obtained using the local spin density approximation (LSDA) and semi-local gradient corrected functional of Perdew, Burke and Ernzerhof (PBE).^[15] Moreover, all calculations were performed using the Gaussian 09 program^[34] with the 6-31G** basis set^[35]

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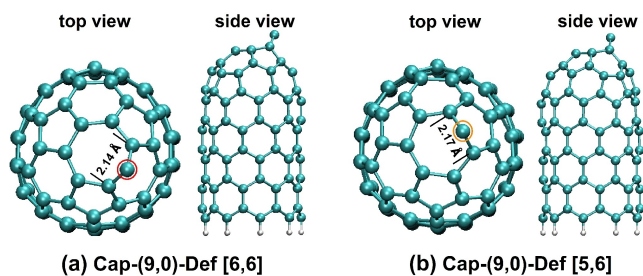


Figure 1. The geometric structures for Cap-(9, 0)-Def [6, 6] and Cap-(9, 0)-Def [5, 6] CNTs.

Results and Discussion

After optimization, the C adatom on the Cap-(9, 0)-Def [6, 6] structure destroys the [6, 6] bond and bonds with two adjacent C atoms, forming two heptagons (Figure 1a). So C adatom enlarges the distance between these two atoms by 0.74 Å (from 1.40 to 2.14 Å). Similarly, for Cap-(9, 0)-Def [5, 6], the C adatom also destroys the [5, 6] bond and bonds with adjacent C atoms to form a heptagon and a hexagon (Figure 1b), which also

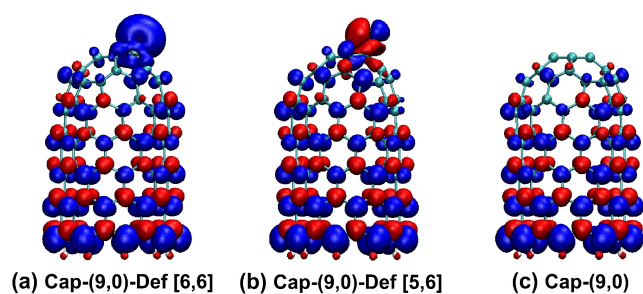


Figure 2. Net spin density diagram. The blue and red area indicate spin up and spin down. The isosurface value is 0.002.

enlarges the distance between these two atoms by 0.77 Å (from 1.40 to 2.17 Å). For the Cap-(9, 0)-Def [6, 6] CNT, its ground state is sextet, while the ground state of Cap-(9, 0)-Def [5, 6] CNT is quartet. And the total energy for Cap-(9, 0)-Def [6, 6] is lower than that for Cap-(9, 0)-Def [5, 6] about 0.19 eV, so the former structure is more stable. To illustrate in detail, the relative energies are listed in the Table S1 and S2 in the Supporting Information.

Figure 2 reflects the net spin distribution of ground states of Cap-(9, 0)-Def [6, 6] and Cap-(9, 0)-Def [5, 6] CNTs. From this figure, we can clearly see the source of the spin density. The spin density of open end is mainly derived from the p_z electrons of the carbon atoms at the zigzag edge, which is consistent with previous reports.^[8,16] And our previous study on cap-(9, 0)/(10, 0) CNTs indicated that the spin density of carbon atoms at the cap is 0, as shown in Figure 2c. And the ground state of perfect C_{60} is the closed-shell singlet state, without any net spin electron.^[36] For the two defect structures, there exist spin density at the cap end, and the net spin electrons are mainly originated from the C adatoms. And the number of net spin electrons distributed on the C adatoms of Cap-(9, 0)-Def [6, 6] and Cap-(9, 0)-Def [5, 6] are about 1.6 and -0.3 , respectively. For Cap-(9, 0)-Def [6, 6] CNT, the net spin orientation of the adatoms at cap end and the carbon atoms at zigzag edge are both spin up, showing spin ferromagnetic coupling phenomenon. While for Cap-(9, 0)-Def [5, 6] CNT, the net spin orientation of the adatom at the cap is spin down, and the spin orientation of the carbon atoms at zigzag edges is spin up, appearing spin antiferromagnetic coupling. This also shows that different types of adsorbed atoms can regulate the magnetic properties of cap-CNTs.

To further understand the mechanism of electronic states formation, we analyzed molecular orbitals (MOs), as shown in Figure 3. Since the ground state of the Cap-(9, 0)-Def [6, 6] CNT is sextet, that is, there are five unpaired electrons. The

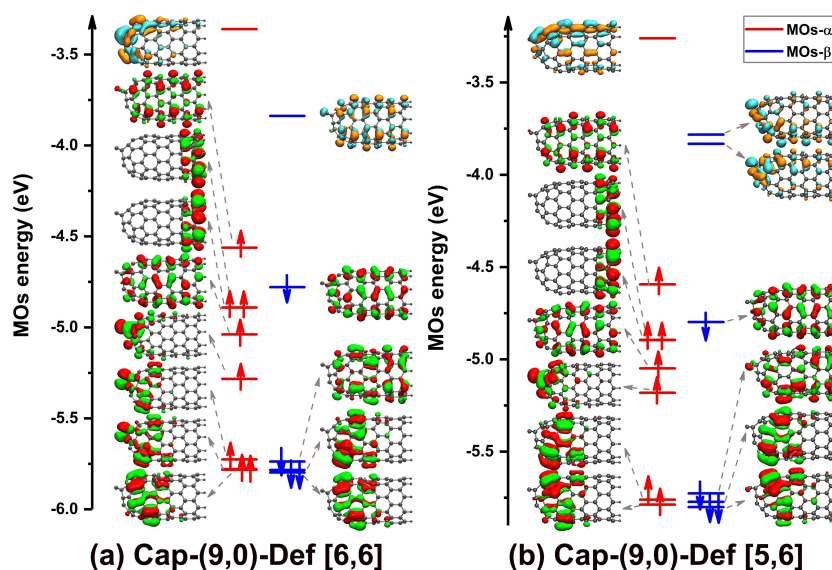


Figure 3. Frontier molecular orbitals (MOs) diagram. The MOs indicated by red and green are occupied MOs, while those indicated by orange and cyan are unoccupied MOs. Isovalue = 0.02.

corresponding five single-occupied MOs are the highest occupied molecular orbital minus one for the α -electrons (denoted as HOMO-1 α , HOMO-2 α , HOMO-4 α , HOMO-5 α and HOMO-6 α (Figure 3a). Among them, HOMO-1 α and HOMO-2 α are two degenerate MOs, and they are mainly contributed by carbon atoms at zigzag edges. While HOMO-4 α , HOMO-5 α and HOMO-6 α are mainly derived from the adatom at cap end. The ground state of the Cap-(9,0)-Def [5,6] CNT is quartet with three unpaired electrons, and these three single-occupied MOs are mainly contributed by carbon atoms at the zigzag edges and adatom at cap end (as Figure 3b), similar to Cap-(9,0)-Def [6,6]. Therefore, the spin density of Cap-(9,0)-Def [6,6] and Cap-(9,0)-Def [5,6] CNTs are mainly contributed by their single-occupied MOs.

The electron density diagram, as displayed in Figure 4, can clearly reflect the electron distribution of Cap-(9,0)-Def [6,6] and Cap-(9,0)-Def [5,6] systems. Figures 4a and 4c show the electron density of the hexagonal carbon atoms at the cap end. The color distribution as a direct indication of the bonding strength reveals that there are strong electron accumulations between C atoms. And the electron accumulation for Cap-(9,0)-Def [6,6] (Figure 4a) is stronger than Cap-(9,0)-Def [5,6] (Figure 4c). Figures 4b and 4d are the electron density diagrams between the C adatom and two adjacent C atoms. It can be seen that there are also strong electron accumulations between the adatom and two adjacent C atoms, and the electron accumulation for Cap-(9,0)-Def [5,6] CNT (Figure 4d) is slightly stronger than Cap-(9,0)-Def [6,6] CNT (Figure 4b). These results show that the C–C bond at hexagon for Cap-(9,0)-Def [6,6] is stronger than that for Cap-(9,0)-Def [5,6]. While the bond between the C adatom and two adjacent C atoms for Cap-(9,0)-

Def [5,6] structure is slightly stronger than that for the Cap-(9,0)-Def [6,6] structure. Thus, electron density indicates that different adsorbed positions show different electron accumulation.

Conclusion

In this work, two adatom defect structures of Cap-(9,0)-Def [6,6] and Cap-(9,0)-Def [5,6] were studied using first principles. The calculation results show that the adatom enlarges the geometric structure. The electronic properties further demonstrate that the adatom induces the generation of spin polarization, and the spin polarization phenomenon is different for different adsorption positions. That is, Cap-(9,0)-Def [6,6] exhibits spin ferromagnetic coupling, while Cap-(9,0)-Def [5,6] exhibits spin antiferromagnetic coupling phenomenon. MOs analysis shows that the single-electron occupied MOs are mainly contributed by the carbon atom at zigzag edge and the adatom at the cap. Furthermore, the electron density reveals that the adsorption position causes the difference in electron accumulation. The research will promote the regulation of spin polarization of carbon materials.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

Keywords: carbon systems · chemical adsorption · density functional theory · electronic states · spin polarization

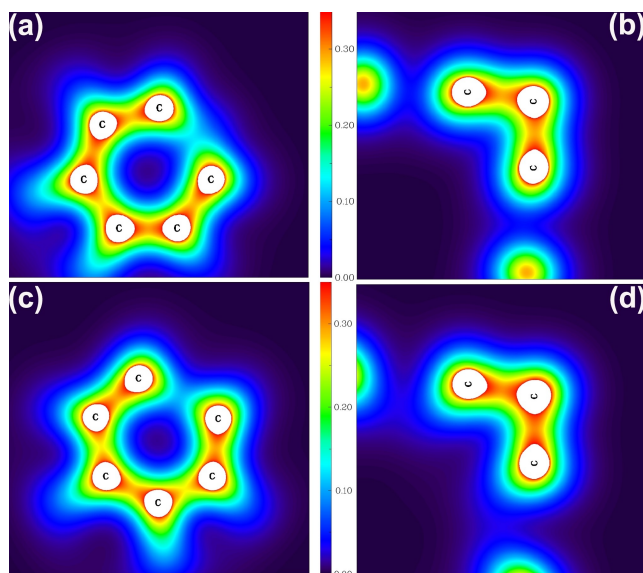


Figure 4. Electron density color filling diagram. Figures (a) and (b) are the electron density between the hexagonal carbon atoms at the cap end, and the electron density between the C adatom and adjacent atoms of the Cap-(9,0)-Def [6,6]. Figures (c) and (d) are the electron density for Cap-(9,0)-Def [5,6] between the hexagonal carbon atoms at the cap end, and between the C adatom and adjacent atoms. The white part in the figure means that the electron density in this area exceeds the upper limit 0.35.

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