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ORIGINAL ARTICLE

Certain doping concentrations caused half-metallic graphene

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Abstract The singly B and N doped graphene systems are carefully studied. The highly concentrated dopants cause a spin polarization effect in the systems. The spin polarization limits are affirmed in the singly B and N doped graphene systems through periodic hybrid density functional theory studies. The spin polarization effects must be considered indeed in the B and N doped graphene systems if the dopant concentration is above 3.1% and 1.4%, respectively. The system symmetry cooperating with the presence of the spin polarization brings half-metallic properties into the doping systems. The semiconducting channels in the half-metallic systems are in two different spin directions due to the different electron configurations of the B and N dopants in graphene.

1. Introduction

As one of the most popular topics at the moment, graphene attracts extensive studies for its unique electronic and mechanical properties [1–5]. It has the same electron configuration as the graphite. The sp^2 hybrid orbitals connect the carbon atoms with each other. The remaining non-hybrid 2p orbitals are perpendicular to the graphene and form a delocalized π-orbital together. The Dirac cone in the band structure of the graphene leads to a massless quasiparticle and a zero band gap in the ordinary state [2]. Hence, it exhibits the excellent electronic properties, such as the high conductivity [6,7], the quantum Hall effect in room temperature [8,9], and so on. Moreover, some external atoms, molecules or clusters can easily be adsorbed on the graphene [10–14] and carbon nanotubes [15–18], owing to the free electrons on the delocalized π-orbital. In some cases, the π-orbital could hybridize with the d-orbitals of its substrate atoms [19–22].

The unique zero band gap of the graphene could be a primary obstacle in the way of its practical applications. Thus, it's crucial for graphene to induce a band gap [23]. The gap can be opened in many ways. A narrow graphene ribbon can bring an energy gap at K and K' points in the Brillouin-zone owing to the lateral confinement of the charge carriers [24]. Castro's experiments and theoretical studies have proved that an applied electric field can adjust the band gap of the bilayer

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graphene system from zero to the mid-infrared energy region [25]. The strain within the single layer graphene investigated by Ni and his co-workers can bring a 300 meV band gap [26]. With the help of the external electric field, a tunable band gap for the dual-gate bilayer graphene can be opened in the range of 0–250 meV [27].

Recently, the graphene is suggested as a basic substance of the van der Waals heterostructure material by Geim and Grigorieva [28]. The atomic-scale "Lego" expands the application scope of the two-dimensional materials. Self-assembled graphene via multiple-step processes has been studied a lot for its novel structures and functionalities [29]. Wang and his co-workers employed the graphene as a conductive additive in the self-assembled TiO_2–graphene hybrid nanosystem to enhance the insertion/extraction of the Lithium ion in TiO_2 [30]. Xiao et al. have demonstrated a self-assembly method to construct the multilayered film containing the well-defined Quantum Dots/Graphene Nanosheets [31].

In practical cases, the graphene always contains kinds of defects, such as vacancies and impurities. Moreover, introducing the artificially defects is a way to open the band gap of graphene. It could also be a new pretreatment method for the self-assembled hybrid graphene systems. The defects within the graphene layers can interact with each other, so as to affect the assembly process. Therefore, the researches about the defect graphene systems are meaningful and indispensable. The boron (B), nitrogen (N), oxygen (O), sulfur (S), fluoride (F) and phosphorus (P) atoms are the common dopants in graphene, which have the similar van der Waals radius compared with the carbon (C) atom.

The heteroatoms can also change the other electrical properties of graphene. For example, graphene becomes p- or n-type semiconductor by doping with B- or N-atom, respectively [32–34]. Using arc discharge method, the B- and N-doped graphene can be directly synthesized with B_2H_6 and NH_3 or pyridine as the boron and nitrogen sources, respectively [35]. Wu et al. have studied the magnetic behaviors of graphene with adsorbed N-, O- and F-atoms [11]. In their work, a 0.84 μB magnetic moment has been detected in the graphene system with N adsorption, while the adsorbed O- and F-atoms cannot induce any magnetic moment. The geometries, electronic structures and magnetic properties of the light non-metallic atoms doped graphene have also been studied in their subsequent work [36]. They claimed that the dopants like N-, O-, B- and F-atoms could induce a band gap near the Dirac point. Furthermore, only F-atom can induce a 0.71 μB magnetic moment in graphene. Whereas, the graphene systems doped by the other three dopants present no magnetic nature. Zhou et al. [37] have introduced a general 3N rule to describe the size dependence of the electronic properties of the doped graphene. In short, a zero gap appears at Dirac point if the size of the primitive cell of the doped graphene is 3N times of the perfect graphene unit cell. Otherwise, there is a gap. Almost at the same time, Muhich et al. [38] revealed the nature of the non-spin polarized N and B dopant structures in graphene and explained the origins of their n- and p-type semiconduction, respectively. Zeng et al. [39] used B_2C graphene to modify the electron distribution in graphene. Thereby, the Li-atom can be localized on the graphene surface as potential hydrogen storage medium.

However, there are few researches talking about the spin polarization properties of the doped graphene systems. In this work, we want to discuss the spin polarization of the singly B and N doping in the graphene systems. The dopant concentrations are the key point of the appearing spin polarization in doped graphene. Therefore, different concentrations of the B- and N-dopants in graphene are studied carefully in order to find the spin polarization limits. This work is organized as follows: In Section 2, the simulation methods and models are introduced; In Section 3, the calculation results will be presented and discussed; In Section 4, a short conclusion will be given out.

2. Computational methods and details

The calculations, in this work, are carried out using the hybrid Becke-type three-parameter exchange functional [40] combined with the gradient-corrected Lee–Young–Parr correlation functional [41], namely B3LYP, which is fully implemented in the computer code CRYSTAL14 [42]. The basis sets are chosen at Triple-Zeta Valence with Polarization (TZVP) level for all related species (i.e., the B, N and C atoms), which are introduced by Peintinger and coworkers [43]. A 500 Å vacuum, which is automatically inserted into the 2D system by CRYSTAL14, ensures the spatial independence of the single layer graphene sheet. To investigate the spin polarization effects of the doped monolayer graphene, the size of the in-plane supercell increases from 2 × 2 to 8 × 8, gradually. Experimentally, an 8.9% N-doping on graphene has been synthesized by chemical vapor deposition [33]. Therefore, the doping sizes in this work are reasonable. A sketch for a 3 × 3 substituted graphene is illustrated in Fig. 1(a) as an example. To hold the in-plane homogeneity, the systems are two dimensional periodic. Denser substitution, e.g., 1 × 1 system, is not considered in this work because of its thermodynamic instability according to the research by Shi [44]. The sampling in the two-dimensional Brillouin zone of the supercell for the reciprocal space integrations is performed with the help of an 8 × 8 Pack–Monkhorst net. With the aid of such relatively sparse net, the Dirac cone can already be reflected in the band structure map for the pristine graphene using CRYSTAL14 (shown in Fig. S1 in the Supporting Information file). Moreover, some dense nets are also tested1, e.g., 16 × 16, 32 × 32, 64 × 64 and 128 × 128 Pack–Monkhorst nets for perfect monolayer graphene. The deviations among them are less than 0.8 meV. Thus, we believe that the 8 × 8 Pack–Monkhorst net is good enough to provide reliable results with relatively low time consumption in our research. Both of the spin and non-spin polarized cases are taken into account, in order to identify the stable electronic structures of the doped graphene systems. The thresholds N (i.e., the calculation of integrals with an accuracy of 10^{-N}) for the Coulomb overlap, Coulomb penetration, exchange overlap, the first- and second-exchange pseudo-overlaps are set to 7, 7, 7, 7 and 14.

The pristine structures of the graphite and monolayer graphene are full optimized. It is well known, that a proper dispersion correction is necessary for the description of the interlayer structure in graphite. The pure DFT functionals cannot provide the expected long range r^{-6} type of the London dispersion interaction. Although the focus of the present work is only on the graphene systems, the B3LYP-D2 method is still employed to retain the calculation consistency with the starting point, i.e., the graphite. The dispersion correction parameters for

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