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Divacancy-assisted transition metal adsorption on the BN graphene and its interaction with hydrogen molecules: a theoretical study

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ABSTRACT

We have performed first-principles calculations to study the chemical functionalization of the BN graphene with divacancy (DV) defect by 12 different transition metal (TM) atoms, including Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pt, and Au. The results indicate that the DV defect can assist the adsorption of TM atoms on BN graphene. Moreover, some impurity bands are induced within the band gap of DV-BN graphene, leading to the modification of its electronic properties in various ways. Interestingly, Ti- and Co-adsorbed DV-BN graphenes are found to possess ferromagnetic characteristic, while antiferromagnetic state is preferred for V-, Mn-, and Fe-functionalized DV-BN graphenes, and the paramagnetic state is the ground state for Sc-, Cr-, Ni-, Cu, Zn-, Pt-, and Au-decorated DV-BN graphenes. Finally, aiming at evaluating the potential of these functionalized BN graphenes in hydrogen storage, we study their interaction with H_2 molecules. It is found that the dispersed Sc, V, and Cr on DV-BN graphene are able to adsorb up to three H_2 molecules as strongly as 0.25–0.58 eV/H_2, suggesting that the three nanomaterials may be suitable candidates for hydrogen storage.

1. Introduction

Since its discovery in 2004 [1] graphene, a single layer of sp^2-bonded carbon atoms tightly packed into a two-dimensional honeycomb structure, has attracted a lot of attention due to its unique properties and wide potential application [2–13]. In particular, the interaction of graphenes with transition metal (TM) atoms has become a hot topic. This is because TM forms the largest block of the Period Table and offers the widest variety of magnetic, optical, catalytic, and other functional properties. The rich chemistry of TM when combined with the exciting properties of graphene, may lead to the generation of new families of functional materials. In fact, metal–graphene heterostructures have opened new highly promising avenues for applications in catalysis, hydrogen storage, and electronic devices [14–17]. Therefore, it can be expected that considerable studies have reported TM adsorption on graphene [18–39]. For example, using density functional theory calculations, Chan et al. investigated the adsorption of 12 different metal adatoms on graphene [18]. Mao et al. and Cao et al. have independently showed that adsorption of Fe and Co adatoms makes graphene half-metallic material, while adsorption of Ni makes it semiconducting nature [19,20]. The wide application prospects of TM/graphene nanocomposites have inspired us to further investigate and understand the bonding between graphene and TM.

On the other hand, the impressive progress in graphene research has motivated scientists to explore other 2D atomic based materials. Among them, the boron nitride (BN) graphene has become a hotly pursued system and many studies have reported its synthesis [40–53]. Although BN graphene has similar geometry as graphene, it may have more important advantages over graphene [54,55]. For example, (1) unlike graphene, BN graphene is stable under high temperature up to 1000 K, and (2) BN graphene is more resistant to oxidation than graphene. These properties make BN graphene exhibit amazing prospects of fabricating nanodevices to operate in harsh environment. However, the wide-band-gap of pristine BN graphene has hindered its application in electronic devices. To overcome this obstacle, various approaches have also been proposed to modulate the electronic properties of BN graphene [56–70], such as C adatom adsorption [57], defect introduction [57–61], fluorination [62,63] or hydrogenation [64], noncovalent functionalization with organic molecules [65], and charge doping [66].

In light of the important advantages of BN graphene as compared with those of graphene and the effectiveness of the functionalization of graphene with TM atoms to modify its magnetic and

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electronic properties, we feel that it is highly desirable to study the interactions of BN sheets and TM atoms. Knowledge of such properties should be useful finding potential applications of BN sheets as functional nanodevices. In this work, the adsorptions of 12 different TM atoms (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pt, and Au) on BN sheet with BN-divacancy (DV) have been systematically studied using density functional theory (DFT) calculations. It should be pointed out that, compared to previous reports on TM adsorption on BN graphene [71–73], we mainly focus the interaction of TM atoms with DV-BN graphene, which is inevitably formed during the electron beam thinning process and may be the most commonly observed defects in BN nanostructures. In particular, the following questions are mainly addressed: (1) can the introduction of DV defect enhance the adsorption strength of TM atoms on BN sheet? If can, do these TM atoms form cluster, or be dispersed on BN sheet? (2) How does the attachment of TM atoms affect the electronic and magnetic properties of BN sheet? (3) Which TM/DV-BN graphenes are suitable for hydrogen storage?

2. Computational models and methods

In this work, first-principles calculations, implemented in DMOL^3 package [74], were performed to study the adsorptions of 12 different TM atoms ((TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pt, and Au) on this kind of defective BN sheet. All electrons calculations were employed with the double numerical plus polarization basis sets (DNP). The exchange correlation energy was described by the Perdew–Burke–Ernzerhof [75] within the generalized-gradient approximation. For the 5d TM atoms, including Pt and Au, scalar relativistic effect (DSPP) was considered when dealing with their core electrons. Spin–unrestricted DFT calculations were carried out in a periodically 5×5 supercell consisting of 48 atoms. Sheets were separated by a vacuum space of 15 Å to avoid any interaction between successive sheets. The Brillouin zone of the supercell was sampled by $3 \times 3 \times 1$ k points within the Monkhorst–Pack scheme [76]. Our test calculations show that the results are not significantly altered upon increasing the k points. Self-consistent field (SCF) calculations were performed with a convergence criterion of 10^{-6} au on the total energy.

The binding energy (E_b) of an individual TM atom on the DV-BN sheet was defined as: $E_b = [E_{total}(\text{DV-BN sheet}) + E_{total}(\text{TM})] - E_{total}(\text{TM/DV-BN sheet})$, where E_{total} denotes the total energy of the optimized system in the bracket. $E_b > 0$ corresponds to a stable optimized configuration and indicates bonding.

3. Results and discussion

3.1. BN graphene with BN divacancy

First, we study the structure and property of BN graphene with BN divacancy (DV) by removing a pair of neighboring B, N atoms from perfect BN sheet. After full optimization, a rectangular structure is formed in the BN sheet (Fig. 1), which is completely different from that of BN nanotube (a 585 structure is obtained) [77,78]. Meanwhile, the B—B, N—N, and B—N bond lengths of DV-BN graphene are 1.98, 2.21, and 3.07 Å, respectively, in good agreement with Zhou's result [73]. This fact indicates that the chosen models and methods in this work are reliable. The calculated formation energy of DV-BN sheet, which is defined as: $E_{form} = E_{binding}[\text{defective BN sheet}] - E_{binding}[\text{perfect BN sheet}]$, is 23.06 eV. Here, the $E_{binding}[\text{defective BN sheet}]$ and $E_{binding}[\text{perfect BN sheet}]$ are the binding energy of defective and perfect BN sheets, respectively. Moreover, the formation energies of BN sheet with monovacancy of B and N are 16.38 and 12.83 eV, respectively. Obviously, the formation energy of DV-BN graphene (23.06 eV) is obviously less than the sum of the formation energies of BN sheet with B and N monovacancies (29.21 eV). Thus, DV-BN graphene is more stable than those with monovacancies of B and N distributed separately. In Fig. 2a and b, we present the band structures of perfect and defective BN graphenes. It is found that the calculated band gap of perfect BN sheet is 4.71 eV, which is significantly larger than that of DV-BN graphene (0.76 eV). This is as expected, because two defect states (labeled as "α" and "β") are induced within the band gap of pristine BN graphene after the incorporation of DV defect. The defect state (α) lies at 1.10 eV below the conduction-band edge (CBE), while the one (β) is above the valance-band edge (VBE) by 0.76 eV. The electron density isosurfaces of the top valence bands and bottom conduction bands of DV-BN graphene (Fig. 2c and d) clarify the origin of the two new levels: the α state originates mainly from the B atoms at the DV defect site, while the two N atoms around defect site dominate the β state.

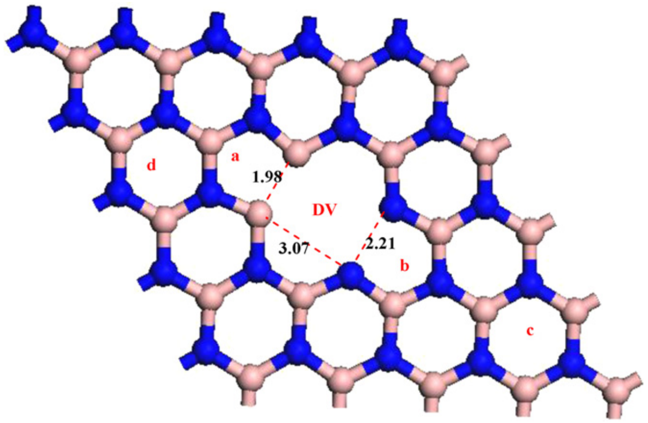

Fig. 1. The optimized structures of BN graphene with divacancy defect (the unit of the bond length is Å). The letters are the sites of TM atoms adsorbed on this kind of BN graphene. The blue balls represent the N atoms, and the gray balls represent the B atoms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3.2. Stability of TM atom on DV-BN graphene

In this section, we mainly elucidate the stability of all studied TM atoms on DV-BN graphenes. For perfect BN graphene, we find that its interaction with the TM atom is considerably weak, with binding energies ranging from 0.05 (Cu) to 1.12 eV (Pt), which are smaller than the cohesive energies of bulk TM [79]. Thus, these TM adatoms would "hover" above the perfect BN graphene and are easily mobile at room temperature to form TM cluster.

Upon TM atoms on DV-BN graphene, three kinds of adsorption sites are considered, including: (1) the DV defect site , (2) the sites near DV defect, such as a and b sites in Fig. 1, and (3) the sites further away from DV defect, such as c and d sites. After the full structural relaxation for each initial configuration, TM adsorption on the DV site is found to be the most stable. All TM atoms would be drawn back to the DV site when they are initially placed on a or b site. For the furthest site (c and d sites), the adatoms would be adsorbed on the stable sites (B or T) just as on the perfect BN sheet. Table 1 lists the structural parameters, binding energies, magnetic moments, and charge transfer from TM atom to defective BN sheet of the most stable configuration of TM atoms on DV-BN graphene (labeled as TM/DV-BN graphene).

As shown in Fig. 3, TM atoms occupy a "cross" configuration on the unreconstructed divacancy defect, characterized as forming two TM-B and two TM-N bonds. These adsorbed TM atoms are displaced out of the BN graphene plane to different degrees.