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First-principles study of nitrobenzene adsorption on graphene

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ABSTRACT

Based on first-principles calculations, the properties of nitrobenzene adsorption on graphene have been investigated. The results show that nitrobenzene prefers to be parallel to the plane of graphene with nitro closer to graphene than phenyl. Due to molecular adsorption, there is a doping band near Fermi energy. The adsorbed molecules will become perpendicular to the plane of graphene under a electrostatic field, and the doping band varies conspicuously with respect to Fermi energy. In addition, a 5000 steps MD is performed at $T = 300$ K to test the stability of nitrobenzene molecules adsorbed erectly on graphene under electric field.

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1. Introduction

From the discovery of graphene[1,2] to now, tremendous scientific interests have been aroused for unusual electrical and mechanical properties of this two-dimensional (2D) honeycomb lattice of carbon atoms[3]. Many extraordinary properties, such as zero gap semiconducting electronic structure, massless Dirac quasiparticles, and anomalous quantum Hall effects[3,4], have been well known for several years. In practice, graphene can be cut into nanoribbons for practical applications, and further be modified on the brim by adatoms or molecules for the study and elucidation of its properties. Adsorbates on graphene have been used as dopants that vary the number of charge carriers[5–7], as a method of band-gap opening, and as a way to alter the electronic structure of graphene[8,9]. Both experimentally and theoretically, molecule dopings and the related chemical sensor properties of graphene have also been researched[10,11]. At the same time, some graphene oxides have been fabricated by many chemical methods[12]. In these new structures, a graphene sheet can contain functional groups on its network such as hydroxyl, epoxide, carboxylic and carbonyl groups, and these oxygen groups on 2D network can enhance its hydrophilic properties. Hahn et al have prepared some gold nanoparticles(AuNPs) and fabricated graphene oxide(GO) sheets decorated with AuNPs to further study their size-dependent electrical and catalytic properties, they find that the improved o-nitroaniline adsorption and electron transfer at the Au/GO interface leads to better catalytic activity[13]. In this paper, it is confirmed that graphene can be taken as a chemical sensor of nitrobenzene molecules. In addition to taking these phenomena into account, the formation of regular arrays of adsorbates, Kondo physics, the existence of local moments, and atomic collapse etc. have also explored by theoretical works[14,15]. Under an electrostatic field (EF), we also researched the formation of regular arrays of adsorbates and variation of electronic structure. It is concluded that not only the adsorbates tend to be regular arrays but also transport properties of the system change sharply upon variation of EF.

2. Theoretical model and calculation method

All calculations have been performed by VASP[16] code, which is based on first-principles density functional theory (DFT)[17,18]. The ultrasoft pseudopotentials (US-PP)[19] are adopted to describe the electron-ion interaction. Local density approximation (LDA) is used to express the exchange-correlation energy of interacting electrons. The non-spin-polarized performance is adopted because each elemental constituent for nitrobenzene adsorbate has closed valence shells. The supercell geometry with a vacuum layer larger than 18 Å is utilized. The cutoff energy was set to be 500 eV for plane wave basis, and the relaxation stopped until force acting on all atoms is less than 0.03 eV/Å. Molecules are placed on one side of the graphene surface for all geometries. Two kinds of supercell (3×3) and (5×5) graphene unit cells are used. The Brillouin zone was sampled by Γ-centered k-point mesh of $(12 \times 12 \times 1)$

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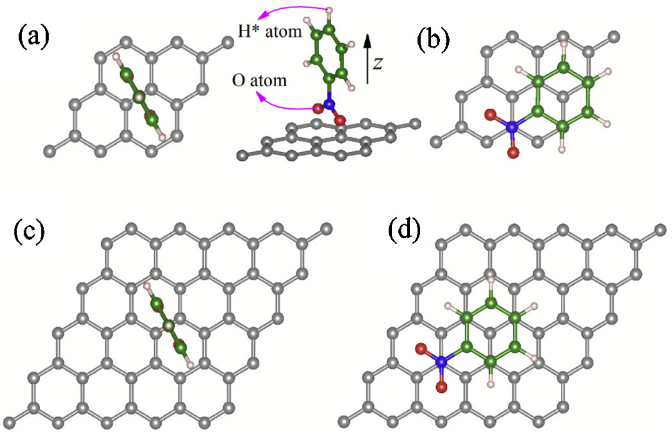

Fig. 1. Nitrobenzene erectly (a) and (c) or horizontally (b) and (d) adsorbed on (3 × 3) graphene (a) and (b) or (5 × 5) graphene (c) (d). H^* atom is the farthest atom of nitrobenzene molecule from graphene plane, and O atom is the closest atom of nitrobenzene molecule to graphene.

and (6 × 6 × 1) for (3 × 3) and (5 × 5) supercell, respectively. The Gaussian smearing with a width of 0.1 eV is utilized for the occupied electronic levels, and the EF is modeled by dipole correction in normal direction with 0.3 eV/Å and 0.6 eV/Å electric field force, respectively.

3. Results and discussion

First of all, four adsorption configurations are considered, where one nitrobenzene molecule is adsorbed vertically (perpendicular cases) or horizontally (parallel cases) on (3 × 3) and (5 × 5) graphene supercells, as shown in Fig. 1. After full relaxation, adsorbed molecules prefer to locate at atop sites of graphene with respective adsorption energies of 0.574 and 0.434 eV for (3 × 3) and (5 × 5) supercells [see Fig. 1(b) and (d)]. Here, the adsorption energy is calculated by the following expression

$$E_a = E_g + E_m - E_s, \qquad (1)$$

where E_g, E_m, and E_s are energies of pristine graphene, isolated nitrobenzene molecule, and adsorption system, respectively. If nitrobenzene molecule is placed on graphene erectly metastable state of systems can be obtained [see Fig. 1(a) and (c)]. Because of stronger interactions between nitro group and graphene, for all perpendicular cases, only the configurations in which phenyl ring is far away from graphene are taken into account.

In parallel cases, due to polar molecules arranging orderly within a plane, the main interaction between adsorbates is attractive Coulomb force, which leads to decrease of adsorption energy when coverage of adsorbed molecule is lowered. Similarly, in perpendicular cases, the interaction between adsorbates is mainly repulsive Coulomb force, explaining the increase of adsorption energy as increasing of nitrobenzene coverage [see Table 1]. For (3 × 3) supercells there is a lattice expansion in parallel case contrasting to a lattice shrink in perpendicular one. We believe that in parallel case the lattice expansion is mainly caused by strong van der waals interaction between adsorbate and graphene matrix. In all parallel cases there is a tilting angle between molecule plane and graphene surface because the nitro-graphene interaction is stronger than that of phenyl-graphene. In addition, the minimum nitrobenzene-graphene distance is smaller than 3.0 Å for all configurations.

To study the electronic structures of this kind of adsorption systems. Firstly, the relative dipole moment of single nitrobenzene molecule is calculated. Due to different electronegativity between phenyl and nitro, there is charge transference after the two functional groups combined to be one molecule. Based on analysis of the difference charge density, the quantity of transferred electrons from phenyl to nitro and dipole moment are calculated to be 0.188 e and 3.14 Debye, respectively [see Fig. 2(a)]. Then, the adsorption system of (3 × 3) supercell is taken as an example for the composite structure. In parallel case there is almost no charge transference between graphene and adsorbing molecules. However, in perpendicular case 0.033 electrons are transferred from graphene to adsorbate, as shown in Fig. 2(b). This is the reason why graphene lattice shrinks in perpendicular case [see Table 1].

Correspondingly, the change of systemic dipole moment induced by electron transfer is calculated to be only −0.10 Debye, having almost no effects on molecule polarity. Energy band and partial density of states (PDOS) for the (3 × 3) supercells are shown in Fig. 3(a) and (b). Near Fermi energy there is a doping band caused by the adsorption of nitrobenzene especially due to nitro group. Owing to strong physical adsorption, the doping state becomes more conspicuous in parallel case. In perpendicular case, due to 0.033 electrons transference from substrate to adsorbate, Fermi level and doping state lowers. In parallel case, because of no charge transfer between adsorbate and graphene, Fermi level remains unchanged, and the doping state is unoccupied.

Finally, adsorption features under the electrostatic field (EF) are researched. Along z-direction noted in Fig. 1(a), EF of 0.3 and 0.6 eV/Å is added, respectively. After relaxation, in perpendicular cases adsorption energy and lattice scale increase sharply with increasing of EF [see Table 1]. It is obvious that the interaction between molecular dipole moment and EF improves adsorption

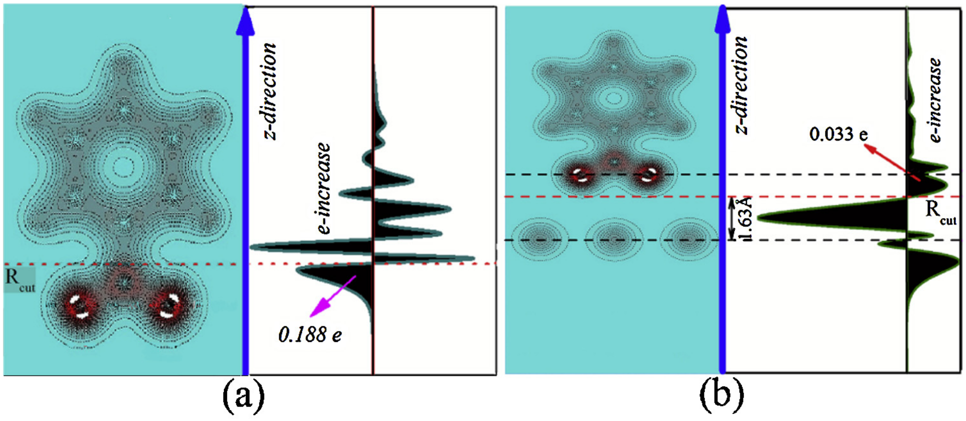

Fig. 2. Charge density and difference charge linear density (along z-direction) of single nitrobenzene molecule (a) and nitrobenzene molecule perpendicularly adsorbed on (3 × 3) graphene (b). Cutoff distance R_{cut} is marked in picture. Electron accumulated region is denoted by '*e-increase*'.

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