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Full Length Article

Transition metal (Pd, Pt, Ag, Au) decorated InN monolayer and their adsorption properties towards NO_2: Density functional theory study

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ABSTRACT

We performed the adsorption of NO_2 on transition metal (TM) doped InN monolayer by using density functional theory (DFT). Firstly, adsorption of four kinds of TM atom (Pd, Pt, Ag, Au) on pristine InN monolayer was explored including four different adsorption sites (T_{In}, T_N, B_{In-N} and H). Then, for NO_2 adsorption, by calculating adsorption energy, adsorption distance, charge transfer, magnetic moment and density of states, the chemical interactions between NO_2 and TM doped InN monolayer (TM-InN) were discussed. We have gotten the following results: (1) Pd, Pt, Ag, Au atoms are all likely to be adsorbed on T_N site with exothermal process; (2) Pt and Au gain electrons while Pd and Ag lost electrons and Ag and Au can introduce magnetic moment to InN monolayer; (3) NO_2 can be chemi-adsorbed on TM atom modified InN monolayer due to the considerable adsorption energy and charge transfer; (4) NO_2 molecule orbitals experience significant changes after adsorption. This study can provide prospects and possible application value for TM-InN to be a potential material to adsorb and detect NO_2.

1. Introduction

Ultrathin 2D materials have experienced much attentions and explorations these years because of their high specific surface area, excellent electronic properties, optical properties and energy storage characteristic which lead to potentially applications in battery, supercapacitor, gas sensing, biosensing, catalysis, optical devices etc. [1–4]. Unlike graphene which has difficulty in band gap adjustment, III–V compounds exhibit significant band gap, high stability and extraordinary electron mobility, and has reached 1 THz frequency response of InGaAs-based high-electron-mobility transistors (HEMTS) [5]. Among the III–V compound family, InN has a narrowest band gap of about 0.7 eV [6,7]. The much lower bandgap compared to AlN (from about 2.9 eV to 6.2 eV [8–11]) and high electron density lead it to be a well candidate in electro-optical devices. Different nanostructure of InN has been synthesized experimentally including InN nanotube [12], nanowire [12–14], monolayer InN quantum wells [15–18] etc. And also, First-principle study was adopted to explore the properties of InN monolayer, such as the geometric structure and its stability [19], electronic band structure [20], electronic and optical properties [7,21], adsorption properties to small gas molecule [22] and heterojunction with other 2D material [23]. High specific surface area and well electronic properties make it have potential application value in gas adsorption and gas sensing realm.

NO_2 is widely acknowledged as a kind of toxic gas and major air pollutant in the environment which is harmful to human health and growth of other species. The InN monolayer shows no apparent chemical interactions to NO_2 with adsorption energy lower than 1.0 eV. Based on this, it is necessary to take methods to promote the chemical interactions between InN monolayer and NO_2 molecule. Decorating transitional metal (TM) particles on surface can be an effective way. For many researches, TM atom especially noble metal particles on the surface of materials such as graphene, metal oxide or two-dimensional transition metal dichalcogenides (TMDCs) can provide more active sites in order to promote the gas sensing and catalytic performance. Typically, graphene or MoS_2 monolayer embedded with TM metal nanostructure especially noble metal (Pd, Pt, Ag, Au) shows clearly better performance in sensing, catalytic and optical properties than pristine materials [24–30]. However, the affections of doping TM metal on InN monolayer to its adsorption properties has hardly been discussed. To evaluate the adsorption or gas sensing properties affected by introducing TM atom, we perform the first-principle calculation on the adsorption of NO_2 on Pd, Pt, Ag, Au doped InN monolayer to make it have more development in field of gas sensor.

In this work, we take a theoretical study of noble metal atom (Pd, Pt, Ag, Au) doping on InN monolayer and their adsorption properties to

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NO_2 based on density functional study. Firstly, the adsorption sites and geometric structure of TM metal doped InN monolayer were discussed in order to obtain the most energetically favorable adsorption structure. For modified InN monolayer, the electronic structure, charge transfer between metal atom and InN monolayer as well as the spin effect were explored. As to NO_2 adsorbed on metal doped InN monolayer, our calculations include the comparison between different initial adsorption direction, the most energetically favorable adsorption structure, charge and magnetism transfer with spin polarization. To more specifically discuss the chemical interactions between gas molecule and doped InN monolayer, total density of states (TDOS) as well as partial density of states (PDOS) was analyzed before and after adsorption. Our results can shed light on the perspective of modified InN monolayer applied as adsorbent or gas sensing material.

2. Computational methods

We adopted all density functional theory calculation in this work through $Dmol^3$ package [31,32]. Linear combination of atomic orbitals (LCAO) method based on $Dmol^3$ code was employed which uses tight-binding model to handle the periodic structure [8]. We selected Perdew-Burke-Ernzerhof function (PBE) with generalized gradient approximation (GGA) to approximately treat the exchange and correlation of electrons [33]. The basis set was chosen as double numerical plus polarization (DNP). In view of the relativistic effect of heavy elements, we adopted DFT semi-core pseudopotential (DSSP) which uses norm-conserving pseudopotentials to treat the core electrons. In consideration of Van der Waals interaction including long range force, DFT-D2 was applied in all calculations in this study [34]. A convergence criterion of 1.0×10^{-5} Ha for energy tolerance, 0.002 Ha/Å for maximum force and 0.005 Å for displacement with 0.005 Ha smearing energy was performed in geometric optimization and a more accurate energy tolerance of 1.0×10^{-6} Ha for energy tolerance was used in electronic structure calculations. The global orbital cutoff radius was set as 5.0 Å with a Monkhorst-Pack grid k-point sample of $5 \times 5 \times 1$ in geometric optimization and $10 \times 10 \times 1$ of electronic structure [35]. All the calculations were spin-unrestricted to evaluate the magnetic moment of the structures.

Before building the super-cell model, we first examine the structure of pristine InN monolayer. From other researches of tight-binding calculations, GaN, AlN and InN monolayer have similar structure as graphene [36]. The lattice parameter we calculated was of 3.62 Å with 2.09 Å bond length of In-N which are very consistent with other experimental and theoretical studied (from 3.54 Å to 3.63 Å) [21,22,37,38]. The InN monolayer model was built using a 4×4 supercell with 16 In and 16 N atoms. The vacuum slab was set as 15 Å thickness to avoid the interaction between different monolayers. In order to consider the optimal position of one TM atom on InN monolayer, we set four different initial adsorption positions of each TM atom, that is the top site of In (T_{In}), the top site of N (T_N), the bridge site between In and N ($B_{In\text{-}N}$) and the hollow site (H). The lowest energy structures of one kind of TM atom embedded InN monolayer were then selected to adsorb NO_2 molecule.

The adsorption energy of one TM atom adsorbed on InN monolayer was defined as follow:

$$E_{ads} = E_{InN\ -\ TM} - E_{InN\ monolayer} - E_{TM\ atom} \quad (1)$$

where $E_{TM\ atom}$ and $E_{InN\ monolayer}$ represent the total energy of one isolated TM atom (Pd, Pt, Ag, Au in this work) and optimized pristine InN monolayer respectively and $E_{InN\text{-}TM}$ represents the total energy of one TM atom doped InN monolayer.

For NO_2 adsorption, we define the adsorption energy of one gas molecule adsorbed on modified InN monolayer as follow:

$$E_{ads} = E_{InN\ -\ TM/NO_2} - E_{InN\ -\ TM} - E_{isolated\ NO_2} \quad (2)$$

where $E_{isolated\ NO2}$ and $E_{InN\text{-}TM}$ represent the total energy of isolated NO_2 molecule and optimized TM doped InN monolayer and $E_{InN\text{-}TM/NO2}$ represents the total energy of ultimate adsorption structure. The equation denotes that when $E_{ads} < 0$, the adsorption process is exothermic and vice versa. To evaluate the charge transfer between TM and pristine InN monolayer or between NO_2 and modified InN monolayer, the Hirshfeld (HI) method was performed [39]. For TM atom adsorbed on InN monolayer, the charge transfer value $Q_t < 0$ means that electrons transfer from InN monolayer to TM atom and TM atom becomes negatively charged and $Q_t > 0$ denotes that the TM atom losses electrons. The definition of Q_t is applied equally to NO_2 adsorption.

The initial adsorption structure of NO_2 on TM-InN was chosen as three directions, NO_2 vertical with N atom below, NO_2 vertical with N atom upward, NO_2 parallel to InN monolayer. The initial adsorption distances between TM atom and N atom in NO_2 were set as 3.0 Å and then all atoms experience fully structural relaxing. To fully understand the interactions between NO_2 and TM-InN, the most energetically favorable adsorption structures were selected to discuss the charge transfer, magnetic moment and density of states.

3. Results and discussions

3.1. Pd, Pt, Ag and Au atom adsorbed on InN monolayer

Before proceeding NO_2 adsorption, we first obtain all the possible configurations of TM atom adsorbed on InN monolayer as described in Fig. 1 and Table 1. According to the comparison between the adsorption energies and structures of each type of atom on InN monolayer, it can be found that all the four kinds of TM atom are inclined to locate in the T_N site. And one thing to note is that, for most initial structures, after fully geometric optimization, TM atom experiences great displacement from initial position to T_N site. For Pd, Pt, Ag and Au, the adsorption energies are 2.47 eV, 3.53 eV, 1.09 eV, 1.52 eV with adsorption distance of approximate 2.06 Å, 2.01 Å, 2.27 Å, 2.46 Å respectively. Pt-InN has the largest adsorption energy and shortest adsorption distance which indicates that Pt has stronger binding with InN monolayer compared with other atoms. After introducing TM atom, the bond lengths of In_1-N, In_2-N, In_3-N all increase with different degree, from 2.09 Å to 2.18 Å for Pd, 2.21 Å for Pt, 2.16 Å for Ag and 2.17 Å for Au respectively. As to charge transfer, Pd and Ag act as electron donor and are positively charged after adsorption but Pt and Au receive electrons from InN monolayer. For pristine InN monolayer, In atom is positively charged with $+0.42$ |e| while N has -0.42 |e| negative charge but after TM atom adsorption, N releases electrons to adjacent In atoms causing the charge reduction of N and its all adjacent In atoms. The Ag-InN and Au-InN has 1.00 μ_B magnetic moment due to the odd number of electrons of the whole system. For Au-InN, the magnetic moment concentrates mainly upon Au and N right below it but for Ag-InN, the magnetic moment transfers more to other atoms in InN monolayer because Ag and N atom only process half of the magnetic moment of the whole structure.

To obtain insight into the magnetic moment as well as electron distribution, the spin-unrestricted density of states (DOS) containing total density of states (TDOS) and partial density of states (PDOS) were calculated including the pristine InN monolayer and the most energetically stable structure of each TM atom, shown in Fig. 2. The TDOS curves of Pd-InN and Pt-InN show very good symmetry between spin-up and spin-down due to the zero-magnetic moment of the structure but obvious asymmetry appears in TDOS of Ag-InN and Au-InN especially near Fermi-level. To better understand this phenomenon and the chemical interactions between TM atom and InN monolayer, we analyze the TDOS before and after adsorption as well as PDOS of each atom's electron orbital. After Pd adsorbed on InN monolayer, several new states appear, states near -12.4 eV belong to N 2s orbitals, states near -3 eV orbitals mainly refer to Pd 5s, 4d and N 2p orbitals, states near -1 eV belong to Pd 4d orbitals, states on the right side of Fermi level mainly refer to Pd 5p orbitals. It has been found that strong