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Impermeability of boron nitride defect-sensitive monolayer with atomic-oxygen-healing ability

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ABSTRACT

Hexagonal boron nitride (h-BN) is a new type of anti-corrosion coating. However, a large number of studies have shown that defects can significantly reduce the barrier property of h-BN. So how to repair the defect of h-BN is a problem to be solved. In this study, we used the density functional theory of the first principle to calculate the barrier properties of perfect h-BN and the h-BN with various vacancies. The study showed that monolayer h-BN has impermeability to all gas molecules, and vacancies can greatly reduce the barrier ability of h-BN to oxygen molecules. Fortunately, atomic oxygen can block the vacancy site of h-BN by chemical adsorption, thereby reducing the impact of vacancies on h-BN. Compared to the situation before the vacancy repaired, the barrier ability of h-BN to oxygen molecules was greatly increased after being repaired. In addition, the electron cloud density at vacancies after the repair (with) atomic oxygen was also greatly increased. Therefore, atomic oxygen can repair vacancies of h-BN and enhance the barrier ability of the defective h-BN. The research in this paper is of some significance. It is helpful to repair h-BN and evaluate corrosion resistance of h-BN in oxygen-rich or atomic-oxygen-rich environment.

1. Introduction

Around the world, corrosion of metal materials can cause incalculable economic loss every year. Therefore, how to reduce or even avoid corrosion of materials has become one of the most urgent problems. Currently, organic coating is the most widely used method (for) corrosion protection (of) metallic materials [1]. Organic coatings, however, have a few disadvantages, such as thickness up to several tens of microns [2–4]; greater impact on optical property of covered material [5,6]; some of corrosion inhibitors added to organic coatings are toxic to the human body and also harmful to the environment [7]. Using inorganic two-dimensional monolayer materials can effectively solve these problems. There were many studies using graphene as anti-corrosion coating [8–12]. However, some studies had found that due to the poor dielectric properties of graphene, the electrochemical reaction occurs on the surface of the metal material, which will aggravate corrosion of the material in long-term [13].

h-BN is a kind of layered material, in which atoms within a layer are combined by covalent bonds, and atomic layers are mainly bound by van der Waals (vdW) force [14–16]. h-BN is a layered material similar to graphene [17–19], it has ultra-thin thickness [20], excellent heat conductivity [21,22], ultra-high impermeability [21,23–25], high thermodynamic stability, and easy formation of atomic layers on metal surfaces [26–28]. The main difference between h-BN and graphene is that h-BN has good dielectric property and wide band gap [29]. This property of h-BN avoids electrochemical reactions on the surface of the material and prevents accelerating corrosion like graphene [20]. Therefore, h-BN can be used as a great new generation of anti-corrosion coating.

There are many studies used h-BN as anti-corrosion coating. Ren. et al. showed that monolayer or multilayer h-BN growing on copper foil directly can effectively prevent copper foil from being oxidized at room temperature and 200 °C [30]. Zhang et al. reported that the large-area continuous h-BN film transferred to the copper surface can effectively reduce corrosion of copper in Na_2SO_4 solution [31]. Khan et al. directly grew one or more layers of boron nitride nanofilms (BNNFs) on the copper surface and found that 1–2 layers of high quality BNNFs can protect copper corrosion better than multilayer low-quality BNNFs [32]. It is worth noting that most of the related studies had emphasized that corrosion starts from the position of defects, and the defect weakens the h-BN barrier capability. Remarkably, studies by Simonov et al. showed that atomic oxygen preferentially adsorbs to the vacancy

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of h-BN [33]. However, there is no study that adsorption of atomic oxygen does repair the h-BN and enhance the impermeability of h-BN.

In this study, we used the density functional theory of the first principle to calculate the barrier properties of the perfect monolayer h-BN and the monolayer with various vacancies. First, the impermeability of perfect h-BN for all gas was calculated and verified. Next, it was proved that atomic oxygen is indeed chemically adsorbed at vacanciesby the calculation of the local density of states and the analysis of the population. We also calculated the change of barrier abilities before and after the repair of single atom vacancy and diatomic (B-N) vacancy by atomic oxygen. Finally, the change of pore electron density before and after the vacancy repair with atomic oxygen was calculated.

2. Computational Details

The results are obtained by performing first principles, density functional theory calculations using CASTEP package [34–40]. The distance between h-BN monolayer and an oxygen molecule varied from 2.78 Å to 0 Å. We used Generalized Gradient Approximation [41] PBE including spin-polarized. In calculating the pore electron density isosurface, 6 × 6 supercells were built so that ten atomic vacancies of the monolayer h-BN in the periodic structure had no influence each other. In other calculations in this paper, 4 × 4 supercells were used. A vacuum layer with a thickness of 12 Å was added between each monolayer h-BN to ensure that the layers did not interfere each other. There were 68 atoms in the supercells of 6 × 6, while 34 atoms in the supercells of 4 × 4.

In the calculation of the pore electron density isosurface, the cut-off kinetic energy of the wave function was 400 eV, and the grid of the k-point was 10 × 10 × 1. In addition, The cut-off kinetic energy was 500 eV and grid of the k-point was 21 × 21 × 1 in other calculations. The convergence threshold on total energy was 10^{-6} eV/atom. The structure optimization was also carried out before the calculation of the local density of states and the analysis of population. In structural optimization, maximum force in the convergence threshold was 0.01 eV/Å and maximum stress was 0.02 GPa.

3. Results and discussions

3.1. Barrier behavior of perfect monolayer h-BN

First, the impermeability of perfect monolayer h-BN was investigated. The barrier ability of perfect monolayer h-BN can also be compared with the barrier property of monolayer h-BN with vacancies (there will be illustrate in Section 3.2 later). The model used in this study (is) shown in Fig. 1a, in which oxygen molecule was prependicular to the h-BN, and the initial distance between oxygen molecule and h-BN was 2.78 Å (Fig. 1b). Then the oxygen molecule was gradually approached the monolayer h-BN until it was inserted into the h-BN. The insertion position of the oxygen molecule was "hollow" site (hexagonal center of h-BN lattice) [20]. In this process, total energy was calculated everytime when the coordinate of the oxygen molecule was changed. The total energy trajectory of this process is shown in Fig. 1c. The solid red line and the solid black line respectively represent the total energy that considering or not considering vdW force in calculation. It can be seen from the calculation results that the energy barrier calculated with and without vdW force is equal. Entirely, the total energy calculated without vdW force is 1.6 eV higher than that the total energy with vdW force. The results show that impermeability of perfect h-BN is independent of vdW interaction. In addition, it can be seen that the energy consumed by an oxygen molecule passing through the perfect monolayer h-BN is 34.2 eV. This energy barrier is three orders of magnitude higher than the kinetic energy of oxygen molecules at room temperature (about 39 meV). Therefore, perfect monolayer h-BN has excellent impermeability for oxygen at room temperature.

The impermeability of monolayer h-BN is far more than this. Because there are many molecules which dynamic diameter are smaller than oxygen molecule, so even if oxygen cannot pass through, other gases may can. He atom is the gas molecule with the smallest molecular dynamic diameter. If we can verify the impermeability of perfect monolayer h-BN for He atom, it can be said that h-BN has impermeability to all gases. The results are shown in Fig. 1d. The graph is a diagram of the potential barrier, and we define that the potential energy of the He atom at the lowest energy (at infinite distance) is zero. As with the previous results, the energy barrier is equal when vdW force was considered or not be considered. So the graph only shows the calculation results of which vdW force was considered. The calculated results show that a He atom through the monolayer h-BN consumes 10.7 eV of energy, much higher than the kinetic energy of the He atom at room temperature (about 39 meV). Therefore, in the case of h-BN with the unbroken lattice structure, perfect monolayer h-BN is impermeable to any gas. Like graphene, h-BN is also a kind of excellent barrier material.

3.2. Repair effect of atomic oxygen on monolayer h-BN mono-atomic vacancy

In order to study the influence of vacancies on barrier properties of monolayer h-BN, the potential energy changed with the distance between oxygen molecule and the V_N (Fig. 2a) was obtained. The oxygen molecule passed through the center of the V_N (the position of the original N atom). The black line represents the potential energy of the whole process without considering vdW force, and the red line represents the potential energy that includes vdW force. There are two potential wells in both curves, that is to say, there are two absorption sites above the V_N of monolayer h-BN whether or not to include vdW force. From the difference between the two curves in the graph, it can be seen that the V_N has a vdW attractive force to the oxygen molecule. Because of this vdW force, the potential energy of the oxygen molecule increases when the oxygen molecule is far away, and the two adsorption sites move to the V_N. Near the V_N, the vdW force reduces the energy barrier of the oxygen molecule passing through the monolayer h-BN, and reduces the barrier effect of monolayer h-BN to oxygen molecules. We speculate that this vdW force exists because of the overlapping dangling bonds of three boron atoms at the V_N, and this conjecture needs further study and discussion. From the potential energy curves considering vdW force, it can be seen as the oxygen molecules closing to the h-BN, potential energy of the system reduces at first, then reaches the first adsorption site (0.87 Å away from the V_N). When oxygen molecules continues closing the V_N , it will encounter an energy barrier(about 0.16 eV), and then reaches the second adsorption site (0.17 Å away from the V_N). The results show that the energy barrier for an oxygen molecule to pass through monolayer h-BN with V_N is about 1.74 eV. Although oxygen molecules are still unable to pass through the monolayer h-BN at room temperature, the barrier of monolayer h-BN to oxygen molecules is significantly reduced by the vacancy.

To verify the chemisorption of atomic oxygen on h-BN, the local state density diagram and population analysis were performed. Before that, the structure was optimized, the cut-off kinetic energy was set to 400 eV and the k-point was set to 15 × 15 × 1, and the structure after optimization is shown in Fig. 2b. Oxygen atom adsorbs among three boron atoms at the V_N. The oxygen atom is closer to two of the three boron atoms and farther from the other one. In the figure, the oxygen atom has a distance of 1.455 Å from the B1 (B2) atom and a distance of 1.608 Å from the B3 atom. It is noteworthy that the adsorbed atomic oxygen and monolayer h-BN are in a plane, while the B3 atom is deviated from the plane. The structural optimization results show that atomic oxygen is likely to form chemical bonds with B1 and B2.

The local density of states (LDOS) of B1, B2 and O atoms was calculated (Fig. 2c) to understand whether the atomic oxygen have chemisorption at the V_N. The results show that the LDOS of B1 and B2 are exactly the same, so the LDOS of the two atoms is represented by the