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Hydroxylation of metal-supported hexagonal boron nitride monolayer by oxygen induced water dissociation

Yufeng Guo and Wanlin Guo*

State Key Laboratory of Mechanics and Control of Mechanical Structures and MOE Key Laboratory for Intelligent Nano Materials and Devices, Institute of Nanoscience, Nanjing University of Aeronautics and Astronautics, Nanjing, 210016, China

ABSTRACT. Hydroxylated hexagonal boron nitride (h-BN) nanosheets exhibit application potential in nanocomposites and functional surface coating. Our first-principles calculations reveal possible hydroxylation of h-BN monolayer on Ni substrate by surface O adatom induced spontaneous dissociation of water molecule. Here one H atom is split from water molecule by bonding with the O adatom on the B atom and the resulted O-H radical then bonds with an adjacent B atom, which leads to two hydroxyl groups formed on the h-BN/Ni. Hydroxylation slightly influences the electronic properties of Ni-supported h-BN layer. Similar water dissociation and hydroxylation can occur on the surface of O functionalized h-BN/Cu depending on the O adsorption configuration. The metal substrates play an important catalytic role in enhancing chemical reactivity of O adatoms on h-BN with water molecules through transferring additional charges to them.

KEYWORD: hydroxylation, h-BN, metal substrate, water dissociation, oxygen, adsorption.

1. Introduction

Two-dimensional (2D) materials such as graphene, hexagonal boron nitride, and transition metal dichalcogenides and oxides comprised of one or a few atomic layers have attracted tremendous scientific interests and hold great promises of application in future functional devices. Due to high surface-to-volume ratio, surface functionalization is a feasible way to alter and tailor 2D materials' properties and behaviors^{1,2}, while the functionalizing process is also of broad interest in comprehending the chemistry of 2D materials. Hexagonal boron nitride (h-BN) is a graphene-like 2D material with the same honeycomb plane but alternating B and N atoms in the hexagonal lattice, possessing excellent mechanical properties³⁻⁵, high thermal conductivity^{6,7} and outstanding chemical stability⁸⁻¹¹. The h-BN nanosheet is a wide bandgap insulator¹², whereas surface hydrogenation, fluorination, decorating and doping significantly modulate the electronic and magnetic properties of h-BN nanosheets¹³⁻¹⁸. The ability to chemically functionalize h-BN has massively expanded its potential for electronics and spintronics applications. Moreover, hydroxylation of h-BN nanosheets has been recently realized by oxygen radical functionalization with subsequent hydrolytic defunctionalization¹⁹, air-plasma²⁰ and ultrasonic treatments²¹. Grafted hydroxyl groups can drastically change the surface chemistry of h-BN and the resulting hydroxyl functionalized BN nanosheets are expected to be employed as mechanical enhancement elements in polymer nanocomposites¹⁹ or superhydrophilic surface coating²⁰.

Water dissociation on metal oxide and the subsequent formation of hydroxyl groups on the surfaces are extensively studied and confirmed by experimental and theoretical works²²⁻²⁶, which can also be considered as a valuable route to conduct surface hydroxylation in a green manner with less pollution of the environment. In such hydroxylation process, surface oxygen sites play

a key role in the dissociation of water molecules. Recently, uniform and high-quality h-BN nanosheets have been successfully achieved on transition metal and Cu substrates²⁷⁻³⁰ by chemical vapor deposition methods. The metallic substrates are important catalysts for synthesizing the h-BN nanosheets, and could also affect their electronic properties and chemical reactivity³¹⁻³³. Meanwhile, the BN nanosheet and its supporting metal substrate can be considered as a heterogeneous structure. To impart more functionality to this kind of BN/metal structure is highly advantageous and attractive for the development of BN based devices. Atomic oxygen can stably adsorb on the free-standing³⁴ or metal supported h-BN nanosheets¹⁷. Further study on the interaction of water molecule with surface O adatoms will be helpful for a better understanding of surface chemistry of BN/metal heterogeneous system.

In this study, we have extensively investigated water dissociation on O functionalized h-BN monolayer on Ni substrate by first-principles calculations. A water molecule is split with one H atom bonding with the adsorbed O of h-BN where the O atom is on the top of B atom or on the bridge site of the B-N bond. Two hydroxyl groups (O-H) are finally formed on the B atoms. The water dissociation and hydroxylation process is spontaneous and exothermic because of high chemical activity of the O adatom induced by charge transfer from the Ni substrate and strong interaction between the BN layer and Ni. The formed hydroxyl groups slightly influence the electronic properties of h-BN on Ni substrate. Similar hydroxylation has also been observed for O functionalized h-BN monolayer on Cu, but its reaction activity is lower than that on Ni substrate.

2. Model and method

We chose a rhombus unit cell with lattice length of 0.992 nm where a 4×4 h-BN monolayer (32 atoms) is placed on a 4×4 Ni (111) substrate. The Ni (111) substrate (80 atoms) is composed of five layers and atoms in the bottom layer are fixed during structural relaxation. The lattice parameter of the h-BN in experiment results is 0.252 nm³⁵. To match with the Ni substrate, the lattice of the h-BN monolayer is compressed 1.6%. There is a 2.2 nm vacuum region perpendicular to the plane of h-BN/Ni. All our computations were performed within the framework of density-functional theory (DFT) as implemented in the VASP code by using the projector augmented wave method with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional³⁶⁻³⁸. The influence of van-der-Waals interactions is considered by choosing a modified version of vdW-DF, referred to as “optB86b-vdW,” in which the revPBE exchange functional of the original vdW-DF of Dion *et al.*, is replaced with the optB86b exchange functional to yield more accurate equilibrium interatomic distances and energies for a wide range of systems^{39, 40}. All considered systems were firstly relaxed by using a conjugate-gradient algorithm until the force on each atom was less than 0.1 eV/nm. After structural relaxation, more exact calculations about energy were conducted with an energy cutoff of 500 eV and special k points sampled on a $6 \times 6 \times 1$ Monkhorst-Pack mesh⁴¹. Our calculations showed that the band structure and energy gap of h-BN monolayer are slightly affected by the 1.6% compressive strain. As spin polarization effect slightly influences the electronic properties of h-BN monolayer on Ni substrate³³, our calculations were conducted in spin-unresolved situations. We created a large number of starting geometries by placing a water molecule in different nonequivalent positions on the O functionalized h-BN/Ni surface. The starting structures were optimized without any geometry constraints.

3. Results and discussion

For an h-BN monolayer on Ni substrate, our calculations show that the equilibrium interlayer distance between BN layer and Ni is 0.205 nm. There are two stable adsorption sites for an O atom on the h-BN/Ni. One is O bonding on the top of B atom and another is O bonding on the bridge site of B-N bond. In the first case, the length of B-O bond is 0.135 nm, and in the latter the lengths of B-O and N-O bonds are 0.148 and 0.154 nm, respectively. We calculate the binding energy E_b of O atom with the Ni-supported h-BN monolayer by $E_b = E_{tot} - E_o - E_{bn/ni}$, here E_{tot} is the total energy, $E_{bn/ni}$ is the energy of the h-BN/Ni system after interacting with O atom, and E_o is the energy of a single O atom calculated in a spin-resolved manner. The binding energies for O on the B atom and the B-N bond are -5.57 and -2.21 eV, respectively. The O atom on the top of the B atom is more stable than on the B-N bond. The values of binding energies are different from that presented in Reference 33 because we considered the van-der-Waals interactions both in the structural relaxation and total energy calculations, and selected the energy of the h-BN/Ni system after interacting with O atom as $E_{bn/ni}$. When we choose the energy of the noninteracting h-BN/Ni system as $E_{bn/ni}$ and the van-der-Waals interaction is not included, the binding energy for O on the B atom is -3.70 eV, which is consistent with Reference 33. Moreover, the equilibrium interlayer distance between h-BN layer and Ni decreases to 0.201 nm when the O atom bonds on the B atom, but increases to 0.288 nm when bonding on the B-N bond. The corresponding interlayer cohesive energies E_c ($E_c = E_{tot} - E_{bno} - E_{ni}$, E_{bno} is the energy of O functionalized h-BN monolayer and E_{ni} is the energy of Ni substrate) for the two cases are -0.56 and -0.14 eV per B-N pair, respectively. Surface oxygen functionalization could remarkably modify the interlayer distance and interaction between the h-BN monolayer and its supporting substrate. Recent experiments^{41, 42} have shown that under slight oxidation condition oxygen atoms and molecules can adsorb on the surface of h-BN nanosheets and form B-O bonds without

causing any dramatic morphology change of the BN nanosheets, so the bonding of oxygen on the B atom or B-N bond of the h-BN nanosheets presented in our theoretical model could be experimentally realizable.

For a water molecule at different starting structures on the O functionalized h-BN/Ni system, it is found that two hydroxyl groups finally form on two adjacent B atoms of the h-BN layers after fully structural relaxations. To better understanding this chemical reaction and its intermediates, we calculated and recorded the total energies at different reaction stages. The energy change ΔE relative to the starting state and corresponding initial, intermediate and final configurations are shown in Figure 1 and 2. For the case of O on the top of B atom (Figure 1), the water molecule is first split into H and O-H. Then the dissociated H atom bonds with the O adatom and the O-H radical bonds with another adjacent B atom. In another case (Figure 2), the approaching of water to the adsorbed O will weaken the N-O bond and facilitate the O atom moving to the B atom. After this intermediate state reached, the water molecule incorporating with the O adatom will split into two hydroxyl groups, which is the same as that shown in Figure 1b. The interlayer distance between the hydroxylated h-BN layer and underlying Ni substrate is 0.2 nm. To compare the reaction activity, we calculate the reaction energy E_r ($E_r = E_{2oh/bn/ni} - E_{bno/ni} - E_w$, here $E_{2oh/bn/ni}$ is the total energy after hydroxylation, $E_{bno/ni}$ is the energy of the O functionalized h-BN/Ni, and E_w is the energy of a water molecule) of -2.81 eV for the case that O on the top of B atom and -6.42 eV for that O on the B-N bond. The difference in reaction energies is due to the system of O on the top of B atom is more stable than that system of O on the B-N bond. As shown by Figure 1a and 2a, the water dissociation and surface hydroxylation in these two cases are all spontaneous and exothermic with total energy decreasing. The water molecule is energetically favorable to firstly react with the O site, and

there will be a high energy barrier for directly splitting of H₂O into O-H and H on the surface of h-BN/Ni. Therefore, the chemical reaction of water dissociation prefers to be conducted with the Eley-Rideal (ER) mechanism.

The effects of hydroxylation on the electronic properties of h-BN layer are presented by the local density of states (LDOS) of B, N and O atoms in Figure 3. For an h-BN monolayer on Ni, there is a small peak at the Fermi level for the N atom because of a weak doping from the Ni substrate. After two hydroxyl groups formed on the h-BN/Ni, the LDOS of the B and N atoms around the Fermi level are slightly changed as shown in Figure 3b. However, the LDOS of the B, N and O atoms of the hydroxylated h-BN layer significantly increase at the Fermi level when the Ni substrate is removed (Figure 3c). This means that surface hydroxylation slightly influences the electronic properties of Ni-supported h-BN layer and the Ni substrate is a determinant factor in preserving the insulating nature of h-BN layer.

Figure 4a shows the LDOS of the O adatoms of the Ni-supported h-BN layer bonding on the B atom and the B-N bond. There is a peak appearing near the Fermi level for O on the B atom. After the formation of a hydroxyl, the peak of the LDOS for this O atom disappears (Figure 3b). Similarly, the LDOS of the H atom in a water molecule also exhibits a small peak near the Fermi level (the inset in Figure 4a), and it disappears when bonding on the O site. The local states around the Fermi level are directly related to the chemical activity. To elucidate the role of Ni substrate in the dissociation of water molecule, we calculate the charge density difference $\Delta\rho = \rho_{tot} - \rho_{bno} - \rho_{ni}$, here ρ_{tot} is the total charge density of O functionalized h-BN/Ni, ρ_{bno} is the charge density of the O functionalized h-BN layer, and ρ_{ni} is the charge density of Ni substrate. Negative $\Delta\rho$ denotes charge depletion and positive for charge

accumulation. Contour plots of $\Delta\rho$ for O on the top of B atom and on the B-N bond are shown in Figure 4b. Obvious charge accumulation transferred from the Ni substrate is observed on the O site when the O atom only bonds with the B atom. Larger charge accumulation indicates higher activity to bond with the H atom of water molecule, so the Ni substrate significantly enhances the chemical reactivity of this O site. On the contrary, there is approximately no charge exchange between the Ni substrate and O functionalized BN layer because of large interlayer distance and only a very slight charge accumulation observed for O on the B-N bond. Furthermore, to better understand the interaction between water molecule and O adatom, we present in Figure 4c the charge densities of the bands of the O functionalized h-BN/Ni in the energy range of 0.2 eV higher than the Fermi level (unoccupied bands) and a single water molecule in the energy range of 1.0 eV lower than the Fermi level (occupied bands). The energy bands below or above the Fermi level are directly related to the capability of chemical reactivity. It can be seen from Figure 4c that the unoccupied bands distribute around the O sites, but more concentrated for the O on the top of B atom. For water molecule, some occupied bands distribute around the H atoms, which could play a role of electron donation. When a water molecule interacts with the O atom on the bridge site of B-N bond, some charges transfer to the O atom. The additional electrons firstly drive the O atom move to the B atom, the intermediate state shown in Figure 2b, and then the dissociation of water molecule occurs. A necessary condition for water dissociation is that there is a dissociated O site available for bonding with the dissociated H and another unoccupied B atom to bond with the O-H radical. No water dissociation occurs when all B atom are unoccupied.

In contrast to atomic O, oxygen molecules are more popular and easier to obtain. So we have also studied water dissociation on O₂ functionalized h-BN/Ni by using the same method.

According to the calculations of DFT technique based nudged elastic band method⁴⁴, it is shown in Figure 5a that the adsorption of an O₂ molecule on the h-BN/Ni is energetically favorable. The most favorable adsorption configuration is O₂ molecule bonding with two B atoms (the middle inset in Figure 5a), where the O-O bond of the O₂ molecule is stretched to 0.151 nm. The length of the corresponding B-O bond is 0.149 nm larger than that of single O on the top of B atom, and the binding energy E_b ($E_b = E_{tot} - E_{o_2} - E_{bn/ni}$, here E_{tot} is the total energy, $E_{bn/ni}$ is the energy of the noninteracting h-BN/Ni system, and E_{o_2} is the energy of an O₂ molecule) of the O₂ molecule with the h-BN/Ni is -2.12 eV per molecule. Water molecule can not dissociate on this O₂ functionalized h-BN/Ni. However, the adsorbed O₂ will dissociate and transform into vertical O-B adsorption configuration after overcoming an energy barrier of 0.83 eV (Figure 5a) where two O atoms bond on two nearest B atoms. Although the stability of such O-B adsorption is low (the reverse energy barrier is only 0.024 eV), we demonstrate by structural relaxation and total energy calculations that a water molecule spontaneously dissociates on the O site and two hydroxyl groups form on the h-BN surface, as shown in Figure 5b. Another rest O site will lead to other water molecule dissociation. These results demonstrate that it is feasible to directly utilize oxygen molecules and water under a proper condition to obtain hydroxylated h-BN on Ni substrate. It should be mentioned that water molecule cannot dissociate when the surface of the h-BN/Ni is fully occupied by the O₂ molecules as no B atom is available for bonding with the O-H radical.

Moreover, in order to understand the effects of substrate, we have studied water dissociation on O functionalized h-BN/Cu by using the same method. Here the lattice of the h-BN monolayer is stretched 1.3% to match with the Cu substrate. There are two stable O adsorption sites: one is vertically on the B atom and another is on the B-N bond. The O binding energies on the B atom

and B-N bond are -5.29 eV and -3.29 eV, respectively. Similar to the case of h-BN/Ni, the water molecule spontaneously splits on the O site and becomes two hydroxyl groups when O is on the top of B atom. The whole process for this reaction is exothermic with total energy decreasing. However, the O atom bonding on the B-N bond can not cause the dissociation of water molecule. According to the minimum energy pathway⁴⁴, it is shown in Figure 6 that there will be an energy barrier of 0.77 eV to transform into 2OH functionalized h-BN/Cu. To explain the difference in chemical reaction with water on Ni and Cu substrates, Figure 7 shows the charge density difference $\Delta\rho$ ($\Delta\rho = \rho_{tot} - \rho_{bno} - \rho_{cu}$) of the O functionalized h-BN/Cu. Obviously, the interlayer charge exchanges between the O adsorbed h-BN layer and Cu are weaker than that with Ni for both cases that O on the top of B atom and on the B-N bond. The corresponding equilibrium interlayer distances between the h-BN layer and Cu substrate after O adsorption are 0.28 and 0.32 nm, respectively. Due to larger interlayer distance and less charge transfer, the catalytic influence of Cu is weaker than that of Ni. Without the Ni or Cu substrate, the vertical O-B bond is not stable and no water dissociation is observed on the O functionalized h-BN layer. Therefore, the metal substrate plays a key catalysis role in oxygen induced water dissociation by providing additional electrons.

4. Conclusions

In summary, our DFT calculations reveal hydroxylation of h-BN layer on Ni substrate by dissociation of water molecule on the surface O adatom. One H atom of the water molecule bonds with the O adatom and the resulted O-H radical bonds with an adjacent B atom. This leads to two hydroxyl groups formed on the h-BN/Ni. Similar water dissociation and hydroxylation can occur on the O functionalized h-BN/Cu depending on the O adsorption configuration. The

metal substrates are essential catalysts for this hydroxylation process and enhance the chemical reactivity by transferring charges to the O sites. Our results highlight a possible way to achieve hydroxylated h-BN on metal substrates by using oxygen and water that are abundant and easily obtained in natural source.

AUTHOR INFORMATION

Corresponding Author

*yfguo@nuaa.edu.cn; Ph 86-25-84890513; Fax 86-25-84895827.

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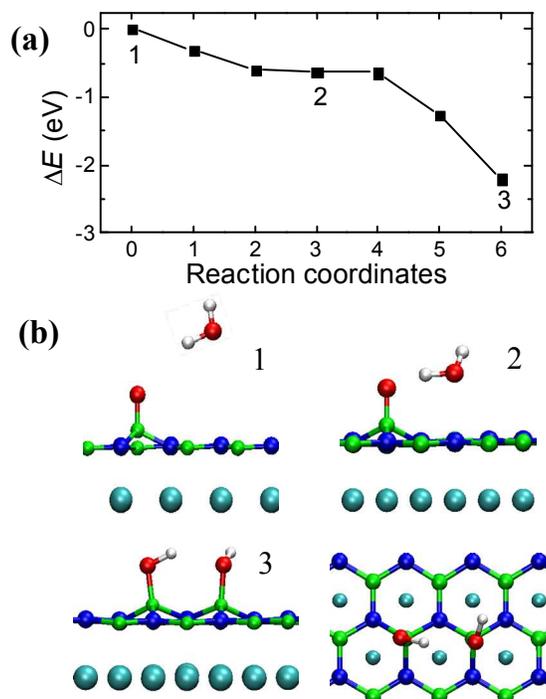


Fig. 1 Dissociation of a water molecule on O functionalized h-BN/Ni system for O on the top of B atom. (a) The energy change ΔE relative to the starting state at different reaction stages, and (b) the corresponding starting, intermediate and final stable configurations. The red, green, blue, white and cyan dots are oxygen, boron, nitrogen, hydrogen and nickel atoms, respectively.

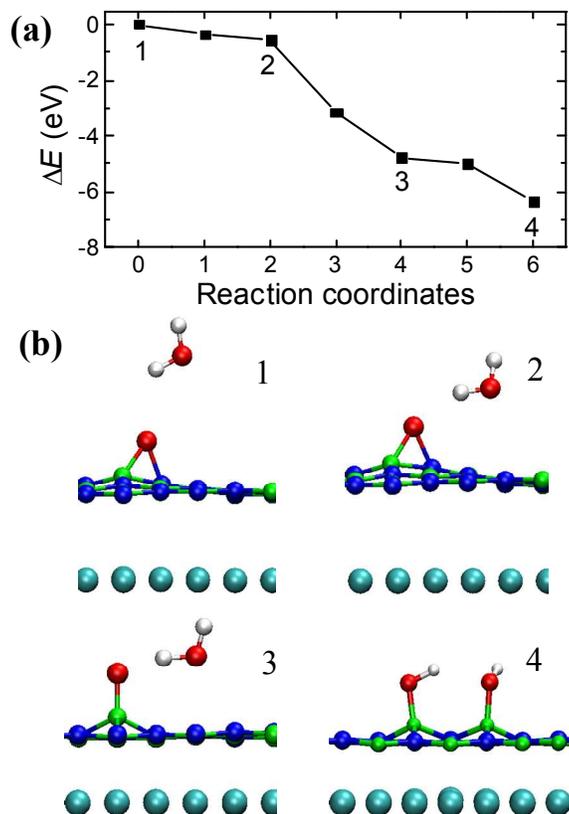


Fig. 2 Dissociation of a water molecule on O functionalized h-BN/Ni system for O on the bridge site of the B-N bond. (a) The energy change ΔE relative to the starting state at different reaction stages, and (b) the corresponding starting, intermediate and final stable configurations. The red, green, blue, white and cyan dots are oxygen, boron, nitrogen, hydrogen and nickel atoms, respectively.

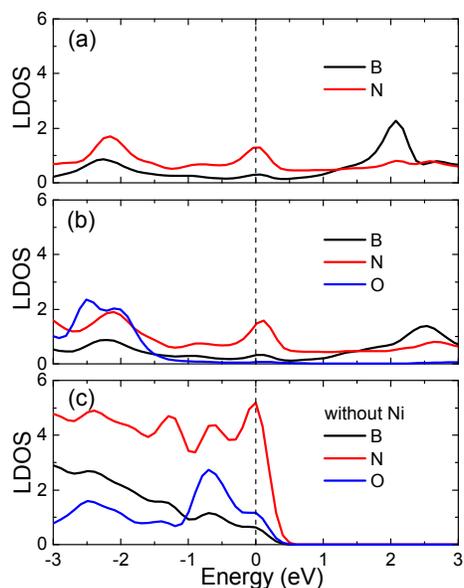


Fig. 3 The LDOS (in units of states/atom) of (a) the B and N atoms of an h-BN monolayer adsorbed on Ni substrate, (b) the B, N and O atoms of two hydroxyl groups functionalized h-BN/Ni and (c) the B, N and O atoms of the corresponding hydroxylated h-BN without Ni substrate. The Fermi level is set to zero.

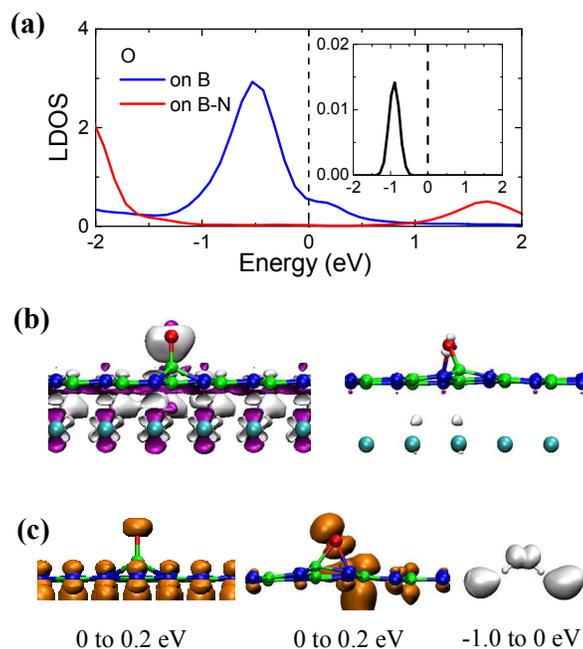


Fig. 4 (a) The LDOS (in units of states/atom) of the O atom bonding on the B atom and the B-N bond, and the inset shows the LDOS of the H atom of the water molecule. The Fermi level is set to zero. (b) Contour plots of the charge density difference $\Delta\rho$ [in unit of $0.02 e/(\text{\AA})^3$] of the O functionalized h-BN/Ni with O on the top of B atom and on the B-N bond. Here positive $\Delta\rho$ (white color) represents charge accumulation, and negative (purple color) charge depletion. (c) The corresponding isosurfaces of the charge densities of the bands [in unit of $0.005 e/(\text{\AA})^3$] of the O functionalized Ni/h-BN with O on the top of B atom and on the B-N bond, and a single water molecule. Here the dot denotation is the same as that in Figure 1. For clarity, the Ni substrates in (c) are not shown.

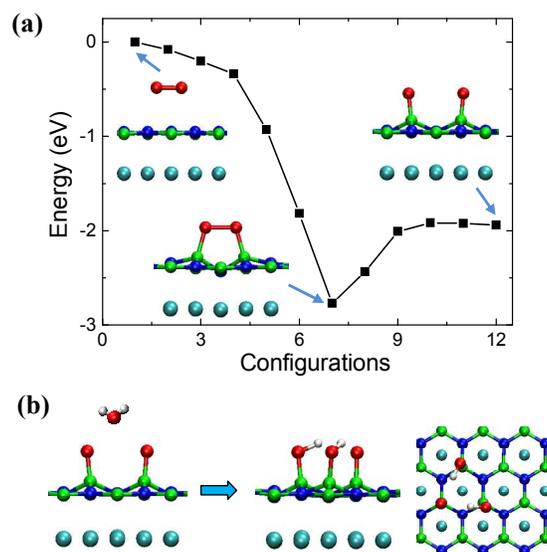


Fig. 5 (a) Minimum energy pathway of an O₂ molecule bonding with two B atoms of h-BN/Ni and dissociating into two separated O atoms. The insets show starting, most stable and dissociated O₂ structures. (b) A water molecule dissociation on 2O functionalized h-BN/Ni system.

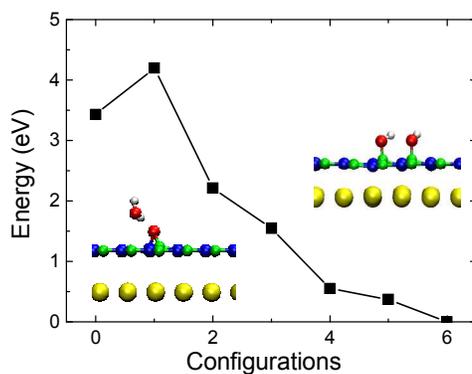


Fig. 6 Minimum energy pathway of a water molecule adsorbing on the O functionalized h-BN/Cu with O on the B-N bond and dissociating into two hydroxyl groups. The inset shows the initial (left) and final (right) structures. The red, green, blue, white, cyan and yellow dots are oxygen, boron, nitrogen, hydrogen, nickel and copper atoms, respectively.

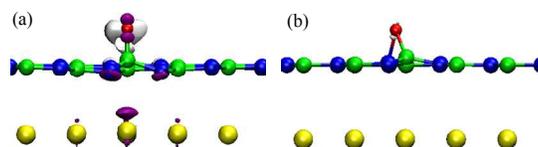


Figure 7. Contour plots of the charge density difference $\Delta\rho$ [in unit of $0.02 e/(\text{\AA})^3$] of the O functionalized h-BN/Cu with O (a) on the top of B atom and (b) on the B-N bond. Here positive $\Delta\rho$ (white color) represents charge accumulation, and negative (purple color) charge depletion. The dot denotation is the same as that in Figure 6.