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Density functional theory calculations for the oxygen dissociation on nitrogen and transition metal doped graphenes

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ABSTRACT

Oxygen adsorption and dissociation on a pristine graphene, nitrogen doped graphene (N-graphene), and transition metal doped graphene (M-graphene) are studied with density functional theory calculations coupled with nudged elastic band (NEB) method. Four 3*d* transition metals (Fe, Co, Ni, and Cu) are selected as the doping atoms. The O binding energies on the Co-graphene and Ni-graphene have intermediate strength. The O_2 dissociation barriers for these two types of doped graphenes are also lower than that on the pristine graphene and N-graphene. The Co and Ni doped graphenes are predicted to be promising ORR catalysts.

1. Introduction

The oxygen reduction reaction (ORR) is a fundamental reaction in many applications such as polymer electrolyte fuel cell (PEFC), Li/O_2 batteries and purification of exhausted gases [1–3]. Since the kinetics of an ORR process is very slow, an efficient ORR catalyst is needed to speed up the process. At the current stage, platinum (Pt)-based materials are the most efficient catalysts. The shortcoming for the Pt-based materials is that they are too expensive and have limited supply for large scale commercial use. Recently, carbon materials especially graphene-based materials have been widely studied as the promising catalysts to replace the noble metals or to reduce the usage of them [4–7,11,12]. Experimental and theoretical studies have shown that nitrogen doped graphene is a good catalyst [4,8,9]. The nitrogen doping atom changes the local electronic structure of graphene and increases the catalytic activity [5,7]. Transition metals with active 3*d* electrons (Fe, Co, Ni, and Cu) can also interact with graphene sheets and change their physical and chemical properties. [10,11,13,14]. However it is still not clear if transition metal doped graphene (M-graphene) is a good ORR catalyst.

Oxygen adatom binding energy on catalyst surface is important for the ORR activity. The ORR activity as a function of O binding energy on various metal surfaces shows a volcano curve and Pt is close to the peak of the volcano curve [15,16]. If a metal is near the peak of the volcano, the oxygen adatom adsorption energy should be neither too strong nor too weak. A strong adsorption energy of an oxygen adatom on metal surface corresponds to easy O–O bond breaking, but a high barrier for the cleavage of O_{ad}-catalyst for subsequent reactions. A weak adsorption energy usually means that it is hard to break the O–O bond of O_2 molecule to initiate catalytic reactions. A good catalytic activity requires intermediate oxygen bonding to the active site facilitating both O–O bond breaking and subsequent reactions of O atoms. Pt has shallow d-band electronic structure below the Fermi level and the corresponding intermediate bonding to reactants. Au has deeper d-band below Fermi level leading to weak oxygen adatom binding energy, but common transition metals have shallow d-band around Fermi level leading to strong oxygen adatom binding energy. To develop highly active catalysts, one can combine elements with strong and weak oxygen binding energies to achieve an intermediate bonding strength. There are three possible combinations of strongly and weakly binding elements to form intermediate binding site: alloy of common transition metal and nobler metal than Pt (e.g. PdAu alloy) [17]; common transition metal oxides (e.g. MnO_2) [18]; and common transition metal-carbon structure. In these structures, strongly binding species (TM metals) and weakly binding species (Au, oxygen, or carbon) are combined to form active sites with intermediate binding strength.

Graphene is a two-dimensional material. Because of their unique stable monolayer structures, graphene-based assemblies attract a growing interest as potential noble metal free ORR catalysts. Although pure graphene has shown some catalytic properties in several experimental studies [19], the adsorption of oxygen on graphene is still too weak and our calculated oxygen dissociation barrier is as high as 2.78 eV. Some research efforts have been done to adjust the graphene catalyst toward the peak of the volcano

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curve by doping method or creating defects on the graphene. For example, N-doped graphene has shown better performance in experiments [8,9]. Common transition metals like Fe, Co, Ni, and Cu are all on the strong adsorption side of the volcano plot for ORR catalyst [16], since they can easily form stable metal oxides with oxygen on the surface. Interesting catalytic properties may appear when they are doped into graphene due to the interaction between metal and carbon leading to intermediate activity. The adsorption and dissociation of an oxygen molecule on metal doped graphene (M-graphene) is studied in this work with first principles calculations coupled with nudged elastic band (NEB) method.

To get a better comparison and understanding of the M-graphene properties, we also investigated the oxygen adsorption and dissociation on a pristine graphene and nitrogen doped graphene (N-graphene). Our calculations show that the catalytic sites of N-graphene are carbons adjacent to the nitrogen atom, which are more active than that of pristine graphene, but the affinity toward O adsorption of carbon atoms is still weak compared with Pt materials, indicating a limited catalytic activity. M-graphene provides a more active metal site which can facilitate the dissociation of oxygen molecules, and the M–O binding energy is also moderate for the further removal of $O_{(ad)}$ due to the metal-carbon interaction. The single vacancies inside the graphene can not only anchor the metal atoms, but also reduce the affinity for the oxygen adsorption on the substituted metal atoms. As the M–O binding energy is tuned to a proper level, M-graphenes can match the Pt-based catalysts better and they are expected to exhibit superior performance as none noble metal ORR catalysts.

2. Computational methods

Density functional theory (DFT) calculations coupled with the nudged elastic band (NEB) method are carried out to study the adsorption and dissociation of an oxygen molecule on a pure or doped graphene. The system energy calculations are performed by using the Vienna *ab initio* simulation package (VASP) code [20–23]. The projector augmented wave (PAW) method [24,25] is used to describe the ionic potential and the Perdew-Burke-Ernzerhof (PBE) functional [26,27] is used to describe the exchange correlation interactions. The plane-wave kinetic energy cutoff is 400 eV. A $6 \times 6 \times 1$ Monkhorst-Pack $k-$point mesh is used for the Brillouin zone sampling in all the calculations. For structure relaxation, the energy convergence criteria for electronic relaxation is 1×10^{-6} eV, and the ionic relaxation is performed until all forces are smaller than 0.005 eV/Å. The conjugate gradient method is used to minimize the Hellmann–Feynman forces in the ionic relaxations.

The adsorption energy of an oxygen molecule and an oxygen adatom on graphene can be written as:

$$E_a = E_{gra+O_2} - E_{gra} - E(O_2), \quad (1)$$

$$E(O_{ad}) = E_{gra+O} - E_{gra} - E(O_2)/2. \quad (2)$$

Here, $E_{gra+...}$, E_{gra}, and $E(O_2)$ refer to the total energies of a graphene with an adsorbed oxygen molecule or atom, a bare graphene, and an oxygen molecule, respectively. The graphene substrate is allowed to relax during oxygen adsorption and dissociation.

The minimum energy paths and the energy barriers for oxygen dissociation are obtained by the climb image nudged elastic band (NEB) method [28–30]. Eight intermediate images are used to sample the reaction path between the initial adsorption state and the final dissociated state. The spring constant of the NEB calculations is 5.0 eV/Å^2 and the NEB force convergence criteria is 0.05 eV/Å.

3. Results and discussion

3.1. Graphene models

An orthorhombic supercell with the box size 8.55 Å × 7.40 Å × 16 Å is used to simulate the oxygen adsorption and dissociation processes (see Figure 1(a)). In this super cell, there are 24 C atoms in rectangle shape graphene supercell. The vacuum layer is 16 Å, which is big enough to reduce the interaction between neighboring graphene layers. The calculated C–C bond length inside a pristine graphene is 1.425 Å, agreeing well with the reported experimental value, 1.42 Å [33]. For the doping effect calculations, one carbon atom in a graphene is replaced by a nitrogen atom (see Figure 1(b)), or a transition metal atom (Fe, Co, Ni, or Cu see Figure 1(c)). We can find the nitrogen atom fills the vacancy well forming a planar N-graphene, while the metal doping atom is above the surface of the graphene substrate. That is because the N–C bond length is almost the same with the pristine C–C bond, but the metal–carbon bonds are much longer. It is calculated to be 1.76 Å for the Fe–C and Co–C bonds, 1.80 Å, 1.87 Å for the Ni–C and Cu–C bonds, respectively.

3.2. O_2 adsorption and dissociation on graphene

The O_2 adsorption and dissociation on a pristine graphene is studied first. Three possible initial physisorption configurations are chosen to optimize (see Figure 2). In Figure 2(a), the O–O bond is parallel to a C–C bond of the graphene. For the second case, there is an arbitrary angle between the O–O bond and the nearest neighbor C–C bond (see Figure 2(b)). In the third configuration, the oxygen molecule is above the center of the hexagonal ring (Figure 2(c)). DFT calculations show that in each case the adsorption energy is very small (see Table 1) and and the distance between the adsorbed oxygen molecule and the graphene sheet is larger than 2.6 Å, which indicate the chemical inertness of a pure graphene. Subsequently, three possible dissociation paths are examined.

The adsorption energies of an oxygen molecule on the graphene, the dissociation energy barriers and reaction energies for the dissociation processes are listed in the Table 1. Because of the inert chemical property of a pure graphene, the oxygen adsorption on graphene is very weak. Meanwhile, the reaction energies of the three dissociation processes are all positive (see Table 1), i.e., endothermic chemical reactions. Furthermore, our calculated binding energy of an oxygen atom on the pure graphene is 0.92 eV with Eqn. 2, compared to −1.26 eV on Pt(111) surface [31]. This result shows that pure graphene is on the weak adsorption side of the volcano plot for ORR catalyst [16], far away from the Pt peak. This binding energy is consistent with the activation barriers E_b for

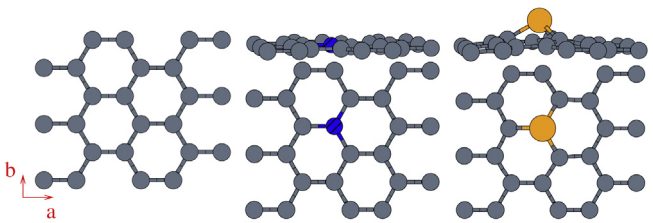

Figure 1. (a) structure of a pure graphene; (b) top and side view of a N-graphene, the blue ball with shadow is nitrogen atom; (c) top and side view of a M-graphene, M = Fe, Co, Ni, Cu, the big yellow ball is metal atom. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)