



# Geometric, electronic, magnetic and catalytic properties of carbon deposited on metal embedded graphene



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## ABSTRACT

Based on the first-principles of density-functional theory (DFT), the effects of deposited C atoms on the geometric stability, electronic structure and magnetic property of metal embedded graphene (M-graphene, M = Pt, Ni and Al) systems are investigated. The metal dopants are stable enough at defective graphene due to the strong interaction between metal atoms and neighboring dangling bonds of carbon atoms. Besides, the deposited C atoms at active sites of M-graphene exhibit the different stability and the calculated diffusion barrier of C deposition is connected to the adsorption energy difference. The chemisorption of C atoms can effectively regulate the electronic structures and magnetic properties of M-graphene systems. Compared with the Pt- and Al-graphene, the interaction of C atom and O<sub>2</sub> molecule on Ni-graphene has the relatively smaller energy barrier, while these energy barriers are not small enough to occur at room temperature. This result gives a reference for the further study on exploring new way to avoid the carbon deposition.

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## 1. Introduction

The search for clean and renewable energy sources represents one of the most vital challenges facing us today [1]. Among the utilizable fuels, the abundant supply and low-cost of methane (CH<sub>4</sub>) has been viewed as the effective fuels [2–4]. Solid oxide fuel cells (SOFCs) are highly attractive for next generation energy systems, which enable the direct electrochemical conversion of hydrocarbons by internal stream reforming of methane [5,6]. Despite the Ni-based anode materials exhibit high catalytic activity for methane reforming [7], however, carbon deposition partially occurs in areas of large scale cells and the formation of carbon coking would block the active site, ultimately reduce the performance and energy conversion efficiency [8–10]. At the anode, the productions of H<sub>2</sub>, carbon and other carbonaceous species are the dominating steps in the dissociated CH<sub>4</sub> reactions [11]. Carbon deposition on catalyst mainly occur through the methane dissociation under certain concentrations [6], where oxygen atoms are

supplied to the anodes in the case of large scale cells [12], and the carbonaceous deposits from CH<sub>4</sub> are gasified by CO<sub>2</sub>. It is expected to explore an anode catalyst with good performances on both high stability and carbon-tolerance.

As a now form of carbon allotrope, graphene is a functional material to support metal atoms due to its outstanding electrical, mechanical and thermal properties [13–18]. Graphene-based devices have been considered as promising candidates for applications in chemical sensors, spintronics, catalysts, and so on [19–25]. Due to the weak interaction between the adsorbates and pristine graphene (pristine-graphene), the graphene sheet fails to detect some gas molecules [26]. The modified metal atoms have been proved an effective approach to regulate the surface morphology and the chemical activity of graphene substrate [27]. Recently, supported subnanometer-sized metal particles and even single-atom transition metals (TMs) on graphene substrates exhibit high catalytic activity and selectivity [28–30]. However, the deposited metal atoms easily diffuse and form clusters on pristine-graphene substrates [31,32]. In order to solve this problem, the boundaries, dopants, and vacancies in graphene [33–35] or graphene nanoribbon [36,37] supported TMs atoms have been proposed to modulate the electronic properties and the catalytic activities, which play vital roles in improving the dispersion of single-atom catalyst [38].

Generally, a perfect catalyst as anode material need have three characters: (a) a high catalytic activity for the fuel reactions, (b) an

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ability to prevent formation of carbon deposition, and (c) a high catalytic property to convert carbonaceous species [39]. Sometimes it is difficult to evaluate the specific factors of catalytic reaction with experiment, such as the surface phases of carbon deposition on catalysts, the transferred electrons and the strong (or weak) interaction between reactive gases and supported substrate. In this regard, the theoretical computations based on density functional theory (DFT) can tell us much about the reaction mechanism and evaluate the catalytic reactivity of metal atoms [39]. Gasification of the carbon deposits by CH<sub>4</sub> reforming is a vital reaction process and has significant effect on the conversion of CO<sub>2</sub> [40]. DFT-calculation investigated the direct C and O combination to CO pathway on the metal surfaces [9,41], which provides some important insight into pathway but leaving other possible reaction processes unexamined. For example, there is a lack of investigating the configuration of deposited C atoms on metal embedded graphene (M-graphene), and the conversion processes from deposited C to carbon dioxide (CO<sub>2</sub>).

Recently, the experimental [42,43] and theoretical [44–47] results confirmed that the metal impurities (Pt, Ni, Al) in graphene have been successfully doped in the single-atom form and exhibit highly active catalyst for CO oxidation, yet few reports provide systematic information about sensing performances for deposited C atoms and formation processes of CO<sub>2</sub> molecule on M-graphene surfaces. In this work, the stable geometries, electronic structures and magnetic properties of deposited C atoms on the M-graphene surfaces are comparably analyzed. Under the gaseous environments, we firstly present a systematic study on the sequential oxidation reactions from the deposited C atom to the CO<sub>2</sub> molecule. To the best of our knowledge, there is few theoretical studies about the conversion mechanism of C oxidation on the M-graphene substrates until now, which would provide a reference for inhibiting carbon deposition and boost the efficiency of fuel cells.

## 2. Computational model and methods

Spin polarized (SP) and non-spin polarized (NSP) DFT calculations are performed by the Vienna *ab initio* simulation package (VASP) [48,49] with the projector augmented wave (PAW) pseudo-potentials [50]. Both the van der Waals (vdW) correction [51,52] and the Perdew, Burke, and Ernzerhof (PBE) [53] to describe the effects of dispersion interactions between the embedded metal (or deposited C atom) and graphene substrates. The C *2s2p*, Pt *5d6s*, Ni *3d4s*, Al *3s3p* and O *2s2p* states are treated as valence electrons. The Kohn-Sham orbitals are expanded in terms of plane waves basis sets with a well-converged cutoff energy 450 eV and the convergence criterion for the electronic self-consistent iteration is set to 10<sup>-5</sup> eV. The graphene sheet is modeled using a hexagonal supercell containing 32 carbon atoms with a *p* (4 × 4) lateral replication in the *x-y* plane and a vacuum layer of 20 Å along the *z* direction placed between the slabs, which leads to negligible interactions between the systems and their mirror images. The calculated lattice constant of graphene sheet is 2.47 Å, which quite approximates to the experimental value of 2.46 Å [54]. Calculations of the total energies of a single metal atom, O atom, gaseous CO<sub>2</sub> and O<sub>2</sub> molecule are performed using periodic cell of 15 × 15 × 15 Å<sup>3</sup>. The Brillouin zone integration is sampled using a 3 × 3 × 1  $\Gamma$ -centered Monkhorst-Pack (MP) grid and a  $\Gamma$ -centered MP grid of 15 × 15 × 1 is used for the final density of states (DOS) calculations.

Bader charge analysis is used to evaluate the atomic charges and electron transfer in the reactions [55]. The climbing image nudged elastic band method (CI-NEB) is employed to investigate the saddle points and minimum energy paths (MEPs) for the dissociation or diffusion of reaction gases [56]. The geometric optimiza-

tion and the search for the transition state (TS) are tested by means of frequency calculations. Six images were inserted into the initial state (IS), TS and final states (FS) along the MEPs, and the spring force between adjacent images is set to 5.0 eV Å<sup>-1</sup>. Images are optimized until the forces on each atom are less than 0.02 eV Å<sup>-1</sup>. The energy barrier is calculated using the IS as a reference.

The adsorption energy ( $E_{ads}$ ) is calculated using the expression:

$$E_{ads} = E_A + E_B - E_{AB} \quad (1)$$

where  $E_A$ ,  $E_B$  and  $E_{AB}$  are the total energies of the optimized adsorbates ( $A$ : C, O<sub>2</sub> and CO<sub>2</sub>), the clean M-graphene substrates ( $B$ : M = Pt, Ni and Al), and the adsorbate–substrate systems, respectively.

## 3. Results and discussion

### 3.1. Geometric stability and adsorption energy

A suitable support is important for the supported metal catalyst in the chemical reaction [57]. For the pri-graphene, the adsorbed metal atoms (Pt, Ni and Al) have small adsorption energies (1.55, 1.62 and 1.03 eV) and diffuse barriers (0.19, 0.21 and 0.49 eV), indicating that these metal adatom prefer to move and aggregate to form large clusters. So the pri-graphene is not an ideal support for the dispersion of metal atoms to develop stable catalysts. To conquer this problem, the metal atom is embedded at defective graphene with a single vacancy (SV), where the metal adatom is placed at the top site of the SV site, and the calculated adsorption energies are 7.23, 6.98 and 5.65 eV for Pt, Ni and Al dopants, respectively. Bader charge analysis shows that the metal dopants provide more electrons (Pt 0.50 *e*, Ni 0.65 *e* and Al 1.30 *e*) to SV-graphene substrates than those on the pri-graphene, illustrating that these are strong covalent bonds between metal dopants and neighboring dangling bonds of carbon atoms. This result confirms that the M-graphene sheets would be stable enough to be utilized in catalytic reaction.

Generally, the adsorbate at most likely favored sites of substrate has the largest adsorption energy [31]. Based on the optimized structure of M-graphene sheets, the stable configurations of C adatom at possible adsorption sites are sought, each structure is fully relaxed and the corresponding adsorption energies, transferred electrons and structural parameters are summarized in Table 1. For the Pt-graphene substrate, the deposited C atom at the top (T) site of Pt atom has the larger  $E_{ads}$  (3.78 eV) than that on the neighboring Pt–C bond (3.56 eV), and the distance between adsorbed C atom and Pt-graphene is 1.85 Å, as shown in Fig. 1(a). In comparison, the deposited C atom at the bridge (B) site of Ni–C (and Al–C) bond (4.03 and 4.36 eV) is more stable those at the T site of Ni (and Al) atom (3.22 and 2.37 eV), as shown in Fig. 1(b) and (c). The deposited C atom on the Pt-graphene has relatively smaller adsorption energy than that on the Ni- and Al-graphene sheets. It is found that the adsorbed C atoms have high stability on M-graphene due to their large adsorption energies (>3.0 eV), belonging to chemisorption. Hence, the deposited C atom prefers to anchor at the M-graphene surfaces and then it readily forms the C deposition.

On the other hand, we further check the effect of vdW correction on the stability of metal doping and deposited C atom on M-graphene substrates, as shown in Table S1. Compared with the GGA-PBE results, it is found that the energy values increase quite a lot with the vdW correction. For the M-graphene systems, the  $E_{ads}$  of metal atoms is changed from 7.41 eV to 9.36 eV for Al, Ni and Pt dopants, respectively. Besides, the vdW correction method also increases the adsorption energies of C atoms on M-graphene surfaces, yet it dose not effect the most stable adsorption configurations and the trend in stability of C depositions. Further-

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