Article
Unravelling the 2e$^-$ ORR Activity Induced by Distance Effect on Main-Group Metal InN$_4$ Surface Based on First Principles

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Abstract: The p-electron-dominated main-group metals (Sb, Se, In, etc.) have recently been reported to possess excellent oxygen reduction reaction (ORR) activity by means of heteroatom doping into graphene. However, on these main group metal surfaces, other approaches especially the distance effect to modulate catalytic activity are rarely involved. In this work, the origin of excellent 2e$^-$ ORR catalytic activity of graphene-supported InN$_4$ moiety by tuning the distance between metallic In atoms is thoroughly investigated by employing the first-principles calculations. Our DFT calculations show that the 2e$^-$ ORR catalytic activity strongly depends on the crystal orbital Hamilton population (COHP) between In and O atoms. This work is useful for the rational design of main group metal single atom electrocatalysts.

Keywords: distance effect; 2e$^-$ ORR; main group metal; metal-N doped graphene

1. Introduction
The oxygen reduction reaction (ORR) is an extremely important electrocatalytic process for energy storage and energy conversion [1]. So the ORR activities of many materials have been reported in the literature [2,3]. Among them, single atom catalysts (SACs) have been reported recently in frequent years, especially metal-N doped carbon nanomaterials [4–6]. Transition metal catalysts have an irreplaceable position in catalyst design due to their unique d orbital, and the d-band center model is widely used to understand and describe their ORR activity. Unlike transition metals, main-group metals have very wide sp-band and inactive d electrons that are considered to be of low activity in catalyst design [7]. However, main-group metal atoms anchored on nitrogen-modified graphene with non-delocalized sp-bands (such as Sb, Se, In) have been recently reported to exhibit promising 2e$^-$ ORR catalytic activity [8–11]. In previous studies, the modified graphene by transition metal atoms (Fe, Co, Ni, Cu, Mn, etc.) and adjacent non-metallic atoms (N, B, P, S, etc.) and the morphology of carbon materials had been reported to effectively modulate the ORR catalytic activity [12–18]. And the metal loading (distance between adjoining metal atoms) may play an important role in adjusting this [19–22]. However, the distance effect of main-group metal atoms supported on nitrogen-modified graphene has not been reported.

In this work, the p-electron-dominated 2e$^-$ ORR on the In and N co-doped graphene is systematically investigated by means of density functional theory (DFT) calculations. The distance between In atoms is controlled by adjusting the supercell size, which is a commonly used method for adjusting the distance (atomic ratio) in theoretical studies. We found that the InN$_4$ site of (4 × 4) graphene supercell has the optimal catalytic activity of 2e$^-$ ORR. The density of states (DOS) and crystal orbital Hamilton population (COHP) results well explain the correlation of the 2e$^-$ ORR catalytic activity with the distance between In atoms.
2. Results

2.1. Calculation Process

The distance of In atoms is controlled by the supercell size as shown in Figures 1a–c and S1 [22,23]. As is shown in Table S1, the doping energy of In atom ($E_{\text{doping}}$) are all smaller than $-3.40$ eV, implying the stable formation of In atom on graphene. $E_{\text{doping}}$ is defined as $E_{\text{doping}} = E_{\text{InN}_4} - E_{\text{NG}} - E_{\text{In}}$, where $E_{\text{InN}_4}$, $E_{\text{NG}}$, and $E_{\text{In}}$ are the energy of the InN$_4$, N-doped graphene (NG), and In atom [23]. In addition, we also investigated the In adsorption on graphene as shown in Table S2, which shows the unstable In adsorption compared to the formation of InN$_4$, indicating unfavorable diffusion of the In of InN$_4$ to the graphene surface. The In atom is suspended on the surface of the InN$_4$-doped graphene at a height of about 1.403, 1.410, and 1.404 Å in (3 × 3), (4 × 4), and (5 × 5) supercells, respectively, as shown in Figure 1d. Here we calculate the ORR process of 2e$^-$ and 4e$^-$ under acidic conditions (pH = 1). The specific reaction process can be represented by the following six step-by-step reactions:

\[
\begin{align*}
O_2 + * &\rightarrow *O_2 \\
*O_2 + H^+ + e^- &\rightarrow \text{HOO}^* \\
\text{HOO}^* + H^+ + e^- &\rightarrow O^* + H_2O \\
O^* + H^+ + e^- &\rightarrow \text{HO}^* \\
\text{HO}^* + H^+ + e^- &\rightarrow H_2O \\
\text{HOO}^* + H^+ + e^- &\rightarrow H_2O_2
\end{align*}
\]

in the above reaction formula, * is the surface of the catalyst material, and HOO*, O*, HO* are the three intermediates involved in catalysis. Reactions 1 to 5 are 4e$^-$ processes, and reactions 1, 2, and 6 are 2e$^-$ processes. Their reaction Gibbs free energies can be approximately calculated according to the following formula:

\[
\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{\text{pH}}
\]

\[
U_{\text{over}} = |U_0 - U_L| \tag{8}
\]

where $E$ is the theoretical internal energy of the DFT calculation, ZPE is the zero-point energy, and $\Delta S$ is the entropy change. $G_U = eU$, where $U$ is the electrode potential, $G_{\text{pH}} = k_B T \ln \times \text{pH}$, and in this work, pH = 1 is taken into account. The overpotential is calculated by Equation (8). $U_{\text{over}}$, $U_0$, and $U_L$ are the overpotential, standard electrode potential, and limit the potential of a catalytic reaction, respectively.
We found that the overall $p_z$ orbital energy levels of InN$_4$-4×, the $p_z$ orbital energy levels of InN$_4$-5×, and InN$_4$-6× are offset from the two-dimensional plane (from top to bottom are $3 \times 3$, $4 \times 4$, $5 \times 5$); (d) The distance that the In atoms on the surface of InN$_4$ are offset from the two-dimensional plane (from top to bottom are $3 \times 3$, $4 \times 4$, $5 \times 5$); (e) the ORR process that occurs on the InN$_4$ surface; (f) the distance between InN$_4$ adjacent metal In atoms in $4 \times 4$ unit cell. The unit of distance in the figure is Angstrom (Å) and gray-black, off-white, red, blue, and maroon are C atoms, H atoms, O atoms, N atoms, In atoms, respectively.

2.2. ORR Catalytic Activity

The potential energy profiles of $2e^-$ and $4e^-$ ORR by InN$_4$ sites are depicted in Figure 2c, and the results demonstrate that the $4e^-$ ORR process takes place much more difficult than $2e^-$ ORR. We also examined the various distances between In atoms for $2e^-$ and $4e^-$ ORR, and as shown in Figure 2a,b, and the $4e^-$ ORR is always suppressed by $2e^-$ ORR. There is a linear relationship between the OOH adsorption energy ($\Delta G_{\text{OOH}}$) and $U_{\overline{\text{ORR}}}$ ($U_{\overline{\text{ORR}}} = \Delta G_{\text{OOH}} - 4.24$) as shown in Figure 2a. Therefore, in this work, we mainly analyze the regulation of the $2e^-$ ORR activity on InN$_4$ sites by changing the distance between In atoms. Li’s group recently reported that InN$_4$ sites exhibit the excellent $2e^-$ ORR activity, in line with our findings [11]. While we also found that the InN$_4$ sites on the $(4 \times 4)$ graphene display the highest $2e^-$ ORR catalytic activity than the other candidates as shown in Figure 2a. On the InN$_4$ sites of $(3 \times 6)$ graphene, the overpotential of $2e^-$ ORR is 0.74 V, while drastically lowered to 0.15 V on the InN$_4$ sites of $(4 \times 4)$ graphene. Obviously, the distance between In atoms strongly influences the $2e^-$ ORR activity.

To explore the distance effect of In single atoms during $2e^-$ ORR, we conducted a thorough electronic structure analysis, including Bader charge [24], the density of states, and COHP. Unexpectedly, the Bader charge does not serve as a viable theoretical activity descriptor for distance effects on InN$_4$ surfaces as shown in Figure S2. Previously, the partial density of states (PDOS) of $d_{xy}$ and $d_{yz}$ of supported transition metal atoms is generally used to correlate their ORR or carbon dioxide reduction reaction (CO$_2$RR) activity [25,26]. In this work, the p orbitals of In atoms are examined. As shown in Figures S3 and S9, it’s clear from either the DOS or the band structure that the weight of $p_z$ is dominant in the p orbitals. While the catalytic activity (overpotential) of $2e^-$ ORR does not have a positive correlation with the center of their $p_z$ or $p_y$ orbital energy levels as shown in Figure S4a,b. We found that the overall $p_z$ level distribution is somehow related to the $2e^-$ ORR catalytic activity. Compared with InN$_4$-4×, the $p_z$ orbital energy levels of InN$_4$-5× and InN$_4$-6×...
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× 6 have a shift to the right, and InN$_4$-5 × 5 seems to shift a little to the right compared to InN$_4$-6 × 6. The reason is that the $p_z$ orbital is the host-orbital in the InN$_4$ system, and the higher the energy level of the $p_z$ orbital, the higher the energy level of the antibonding orbital when the adsorbing small molecules such as OOH, which enhances the adsorption energy. As shown in Figure 3b, the $p_z$ orbital energy levels of InN$_4$-3 × 5 and InN$_4$-3 × 4 are shifted to the Fermi level compared to InN$_4$-4 × 5, which reveals that InN$_4$-3 × 6 has extremely poor 2e$^-$ ORR activity. Moreover, when the OOH is adsorbed on the surface of the InN$_4$ site, the electrons of In atoms are transferred to the surroundings of O, H, and N atoms, especially the z direction, which is shown in Figures 3c and S5. Conclusively, the $p_z$ orbital energy level of the In atom can roughly describe the 2e$^-$ ORR catalytic activity trend of the InN$_4$ site.

![Figure 2](image)

**Figure 2.** The catalytic activity of ORR on InN$_4$ surfaces in different unit cells. (a) The linear relationship between 2e$^-$ ORR catalytic activity and OOH adsorption free energy; (b) The linear relationship between 4e$^-$ ORR catalytic activity and OH adsorption free energy; (c) The potential energy curve of ORR process on InN$_4$ (4 × 4) surface.

In addition, as noted from the energy band result diagram, the Conduction Band Minimum (CMB) and Valence Band Maximum (VBM) was intersecting in the 3 × 6 and 3 × 4 supercells, which facilitated the electron transport between adsorbed molecules and In atoms, making the OOH desorption more difficult and detrimental to the overall ORR process. In view of this, we analyze the bond strength between the In atom and the O atom of OOH. The COHP can describe the covalent bond strength between, and understand the distribution of bonding and antibonding orbital energy levels [27]. By calculating the COHP between the In single atom and O atom, we find the $p_z$ orbital is the main contributor to the In-O bond as shown in Figure 3d, which is consistent with the PDOS results. We found that ORR activity is related to the anti-bonding and bonding energy levels between In atoms and O of the OOH intermediate. The lower the antibonding or bonding energy level, the stronger the ORR catalytic activity, which is shown in Figures 4a–d and S6. It can be understood that InN$_4$-4 × 4 and InN$_4$-6 × 6 have more anti-bonding states around
the −4.0 eV energy level, and the anti-bonding energy level of InN\(_4\)-4 × 4 is lower. The bonding energy level of InN\(_4\)-5 × 6 is the lowest (about −0.5 eV), while the others are basically around 3.0 eV in this work. Obviously, the COHP can well explain the ORR activity of InN\(_4\) with different distances between the neighboring In atoms.

![Figure 3](image-url)

**Figure 3.** (a,b) The \(p_z\) orbital PDOS of InN\(_4\) is distributed in different unit cells. (a) several InN\(_4\) material with decent 2e\(^-\) ORR activity; (b) The PDOS distribution of the \(p_z\) orbital of less active InN\(_4\); (c) The difference charge distribution of the surface of InN\(_4\) (4 × 4) with adsorbing OOH. Yellow is the electron accumulation area and cyan is the electron deficient area; (d) The integral of the partial Crystal Orbital Hamilton Population (IpCOHP) proportion distribution between In atoms and O (OOH) atoms on the surface of InN\(_4\).

![Figure 4](image-url)

**Figure 4.** Cont.
we found that the integral of Crystal Orbital Hamilton Population (ICOHP) between the value of the ICOHP, while the anti-bonding energy level between the In atom and O atom quantitatively describe the strength of the chemical bond. The larger the ICOHP, the orbital of In atom and the s and p orbitals of O (OOH).

energy levels and the COHP between the In and the O atom cannot be used as theoretical covalent bond strength between the In and the O atom of OOH. However, the p-band at InN− energy level of the In atom from the DOS diagram could explain the order of ORR activity on the InN− intermediate is shifted to the Fermi level (about −2.0 eV) in InN4−5 × 6, which lowers the value of the ICOHP, while the anti-bonding energy level between the In atom and O atom in InN−4 × 4 is shifted below the Fermi level, and the overall −ICOHP is bigger. All in all, the more the bonding orbital energy level near −2.0 eV is shifted to the Fermi level, the smaller the −ICOHP between the 5 p orbital of the In atom and the O atom. If the antibonding orbital energy level is farther from the Fermi level, the bigger the −ICOHP. In this work, we propose a new descriptor for 2e− ORR activity on the InN4 sites.

3. Discussion and Conclusions

In this work, based on first-principles calculations, we first calculated the ORR activity on the InN4 surface with the different In-In atom distances. We found that the 2e− process is better than the 4e− process, and the distance between In atoms can significantly influence the 2e− ORR activity. The overpotential of the ORR on the surface of InN4 was 0.15–0.74 V by adjusting the distance of In-In in our DFT calculations. By calculating and analyzing the electronic structure, we found that the p electrons of In atom especially those in the p orbital play a very important role in the regulation of ORR catalytic activity. The p orbital energy level of the In atom from the DOS diagram could explain the order of ORR activity at InN4 sites. Moreover, we also found that the anti-bonding and the bonding energy level between In and the O atoms of OOH could explain their ORR activity by analyzing the covalent bond strength between the In and the O atom of OOH. However, the p-band energy levels and the COHP between the In and the O atom cannot be used as theoretical activity descriptors of ORR at InN4. After a series of attempts at the theoretical activity descriptors such as Bader charge, the metal atom load ratio of the In atom as well as the
distance of In-In, we propose that the ICOHP between the p electrons of the In atoms and the surface adsorbed OOH intermediate can be used as a theoretical activity descriptor for ORR activity at InN$_4$ sites. This work provides a theoretical understanding of the screening and designing of the main group metal catalysts in heterogeneous electro-catalytic reactions.

4. Materials and Methods

Calculations were performed under periodic boundary conditions employing Vienna Ab-initio Simulation Package (VASP). Projector-augmented wave (PAW) pseudopotentials and Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional of generalized gradient approximation (GGA) were used to describe the interaction between core electrons [29,30]. C (2s, 2p), H (1s), O (2s, 2p), N (2s, 2p), and In (5s, 4p) electrons are investigated as valence electrons in our DFT calculations. The vaspso implicit solvent model is introduced to describe solute-solvent interactions in density functional theory calculations [31–33]. And the DFT-D3 method with Becke-Johnson (BJ) damping is used to approximately describe the dispersion effect in the system [34]. In order to ignore the interlayer interactions, a vacuum layer of 15 Å was set up in the direction perpendicular to the 2D surface (z-directions). The cut-off energy was set to 400 eV and the convergence thresholds for the electronic structure and forces were set to $10^{-4}$ eV and 0.05 eV/Å, respectively. We have conducted convergence tests and found the energy difference of the 4 × 4 InN$_4$ within 0.09 eV by using different convergence thresholds as shown in Table S3. The geometric optimizations and DOS analysis were performed using a standard Monkhorst—Pack grid sampling at $3 \times 3 \times 1$ and $11 \times 11 \times 1$, respectively. After DFT calculations, the DOS and the free energy are calculated, based on the VASP toolkit (vaspkit) [35]. The COHP calculations and analysis are implemented in the Lobster program [36].

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27227720/s1, Figure S1 The doping structure of InN4 on the surface of two-dimensional graphene in different unit cells. (a) InN4-3 × 4; (b) InN4-3 × 5; (c) InN4-3 × 6; (d) InN4-4 × 5; (e) InN4-4 × 6; (f) InN4-5 × 6; (g) InN4-6 × 6. And gray-black, blue and maroon, are C atoms, N atoms and In atoms, respectively; Figure S2 The relationship between 2e− ORR catalytic activity and bader charge; Figure S3 The distribution of density of states (DOS) of InN4 in different supercells. (a) 3 × 3; (b) 3 × 4; (c) 3 × 5; (d) 3 × 6; (e) 4 × 4; (f) 4 × 5; (g) 4 × 6; (h) 5 × 5; (i) 5 × 6; (j) 6 × 6; Figure S4 The relationship between band center value and 2e− ORR overpotential. (a) pz orbit center; (b) py orbit center; (c) The center of the superposition of the pz orbital and the py orbital; Figure S5 The difference charge distribution of the surface of InN4 (4 × 4) with adsorbing OOH. Yellow is the electron accumulation area and cyan is the electron deficient area; Figure S6 The COHP distribution of In-O bonds in different unit cells of InN4. The left side is the antibonding component, and the right side is the bonding part (the abscissa is COHP). (a) InN4-3 × 3; (b) InN4-3 × 4; (c) InN4-3 × 5; (d) InN4-3 × 6; (e) InN4-4 × 4; (f) InN4-4 × 5; (g) InN4-4 × 6; (h) InN4-5 × 5; (i) InN4-5 × 6; (j) InN4-6 × 6; Figure S7 The relationship between the loading ratio of main group metal In atoms and the overpotential of 2e− ORR; Figure S8 The relationship between the loading ratio of main group metal In atoms and the overpotential of 2e− ORR. (a) The spacing of In atoms in the horizontal direction (d × ); (b) The spacing of In atoms in the vertical direction (dy); Figure S9 The band structure of InN4 and the weights of the pz orbitals in (4 × 4) 5 × 6 (c) 6 × 6 (d) 3 × 3 (e) 3 × 6 supercells. The density of the band points reflects the weight of the pz orbitals; Table S1 The doping energy of In atom in different supercells; Table S2 The adsorption energy of In atom on graphene in different supercells. Edoping is defined as Eadsorption = EIn-G − EIn – EG, where EIn-G, EIn and EG are the energy of the graphene with In atoms adsorbed on its surface (In-G), In atom and graphene, respectively; Table S3 The relative energy of InN4 calculated by using different convergence threshold.

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