Unveiling the HER and ORR activity origin of isolated Co sites supported on N-doped carbon

Aijian Huang and Zhiguo Wang*

School of Electronics Science and Engineering, University of Electronic Science and Technology of China, Chengdu, 610054, P.R. China.

Abstract. Electrocatalysis plays very important role in clean energy conversion. In which, developing high active and robust electrocatalysts for the hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) are highly crucial and challenging. Using density functional theory (DFT) calculations, the Gibbs free energy diagrams and electronic structure of N-graphene, Ir-N4 and Co-N4 are investigated in this work. The results show that Co-N4 have the appropriate H adsorption and lower ORR overpotentials, which gives expectation of high multifunctional electrocatalytic performance. This theoretical study provides vital insights into the enhanced electrocatalytic mechanism of Co sites supported on N-doped carbon.

1. Introduction

Electrochemical reactions, including hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) are significantly essential in energy-related applications and future renewable energy technologies. Rational developing the highly active and robust electrocatalysis are crucial and desirable. [1]. Among various promising alternatives, single-atom catalysts (SACs) with the isolated active sites have attracted tremendous interest, owing to its unique coordination geometry, strong metal–support interaction and maximum atomic efficiency [2]. The above characteristics also offer ideal configurations for exploring the origin of the activity. Though great efforts have been devoted, the electronic structure of SACs has remained elusive and the electrocatalytic activity origin of SACs are still not clear.

Recently, single-atom iridium catalysts [3] and single-atom cobalt on N-doped carbon [4] catalysts has been synthesized and exhibited excellent electrochemical ability for ORR. Meanwhile, single-atom catalysts also show good performance in application of HER [5]. Hence, gain deep insights into the electronic structure and catalytic mechanism of these catalysts are vitally important. In this work, we investigate the Gibbs free energy diagrams and electronic structure of pure N-doped graphene (N-graphene), isolated iridium on N-doped carbon (Ir-N4) and isolated cobalt on N-doped carbon (Co-N4). The results show that Co-N4 have the appropriate H adsorption and lower overpotentials for ORR. Meanwhile, unique electronic interactions between dopants of Co and N form near the Fermi level, ensuring fast charge transfer kinetics and guaranteeing excellent electrocatalytic performance.

2. Computational methods

All calculations here are performed by spin polarized density functional theory (DFT) methods using Vienna Ab initio Simulation Package (VASP) [6]. The Projector augmented wave (PAW) method is adopted to describe electron-ion interaction [7]. And Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within a generalized gradient approximation (GGA) is employed, while a 520 eV cut off energy for the plane-wave basis set is used for the valence electrons. The self-consistent filed (SCF) calculations are performed with an energy and force convergence of 10-5 eV and 0.02 eV Å-1, respectively. To avoid the interactions between two adjacent periodic images, the vacuum thickness was set to be 15 Å. All atomic configurations are analyzed using the VESTA code [8]. In order to model the Ir-N4 and Co-N4 monolayers, the 6×6 supercell consisting of 72 carbon atoms is used firstly as the substrate. Then, the Ir/Co atoms are anchored via displacing two neighboring carbon atoms, and four carbon atoms bond with metal atom are replaced by N atom, forming the Ir-N4 and Co-N4 catalyst model.

For HER, the integral adsorption energy is defined by:

$$\Delta E_H = E(\text{surface+H}) - E(\text{surface}) - \frac{1}{2}E(H_2) \qquad (1)$$

where the E(surface+H) and E(surface) are the total energy of metal surface with H atoms adsorption and without, respectively. E(H2) is the total energy of hydrogen molecule in the gaseous phase. The Gibbs free energy of H atoms (ΔG_H) is an important parameter for the descriptor of HER activity:
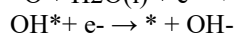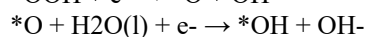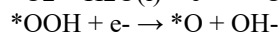
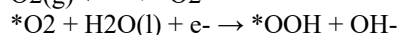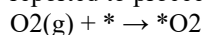$$\Delta G_H = \Delta E_H + \Delta ZPE - T\Delta S \qquad (2)$$

where ZPE is the zero-point vibrational energy using the harmonic approximation, T is the kelvin temperature, and

* Corresponding author: zgwang@uestc.edu.cn

S is the entropy. According to thermodynamics, large positive values of ΔGH indicate that the hydrogen atom is difficult to bind to the catalytic sites, whereas large negative values of ΔGH indicate that molecular hydrogen is difficult to be released from the catalytic sites [9].

The reaction steps considered for the electrochemical reduction of ORR under base condition are generally reported to proceed as follow:

$O_2(g) + * \rightarrow *O_2$

$*O_2 + H_2O(l) + e^- \rightarrow *OOH + OH^-$

$*OOH + e^- \rightarrow *O + OH^-$

$*O + H_2O(l) + e^- \rightarrow *OH + OH^-$

$OH* + e^- \rightarrow * + OH^-$

where * represents either the catalytic active sites of vacant surface, or intermediate species adsorbed on the active sites. By considering the zero-point energy (ZPE) and entropy corrections, the Gibbs free energy for OER can be calculated with the following equation [10]:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S \qquad (3)$$

where ΔE indicates the adsorption energy difference for each species adsorbed on the catalyst, ΔZPE and ΔS are the zone point energy and entropy difference between the adsorbed state and corresponding free-standing state, respectively.

3. Results and discussion.

We perform the density functional theory (DFT) calculation to understand the HER intrinsic activity of N-graphene, Ir-N4 and Co-N4. Various active sites are considered and we calculate their Gibbs free energy for H (ΔGH), which is widely accepted as the HER activity descriptor that has an optimal value of zero when the HER activity reaches the maximum [11]. For N-graphene (Figure 1a), H atoms thermodynamically preferred to adsorb on N sites owing to their lower ΔGH (-1.41 eV), the lower value of ΔGH also suggest the molecular hydrogen is difficult to be released on N-graphene and not active for hydrogen evolution. As shown in Figure 1b, the values of ΔGH on Ir-N4 increased to -0.37 eV getting much closer to optimum value (0 eV), which indicates that doping of Ir greatly assisted the HER performance. Remarkably, the ΔGH on Co-N4 is 0.15 eV (Figure 1c), which is better than N-graphene and Ir-N4. The catalytic activity is also related to the positions of i0 and ΔGH, the closer the position of these values to the peak, the better the catalyst is. As can be seen from Fig. 1d, the Co site on Co-N4 locate near the peak of the volcanic curve indicating Co-N4 is more catalytically active for HER.
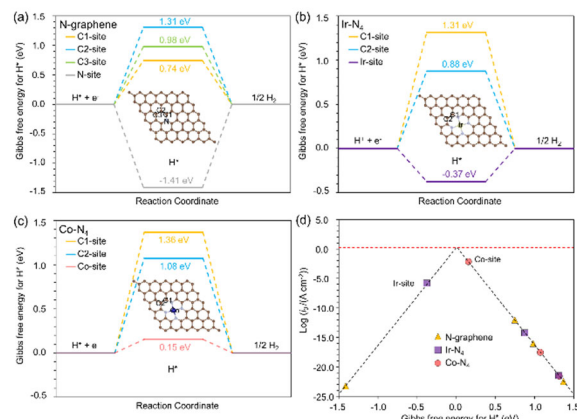

Figure 1. Gibbs free energy diagrams of hydrogen adsorption on different active sites of (a) N-graphene, (b) Ir-N4 and (c) Co-N4. (d) The calculated exchange current (log (i_0)) for hydrogen evolution over different configurations as a function of Gibbs free energy for H*.
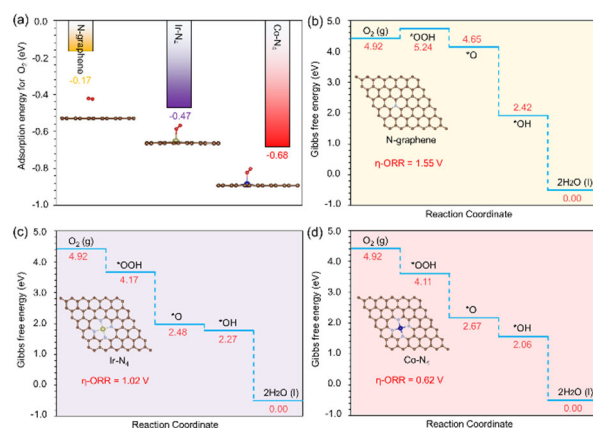
Figure 2. (a) The adsorption energies and corresponding configurations of O2 on N-graphene, Ir-N4 and Co-N4. The calculated Gibbs free energy evolution diagrams for through a 4e⁻ ORR pathway on different active sites of (b) N-graphene, (c) Ir-N4 and (d) Co-N4.

For oxygen reduction reaction (ORR), the metal active sites will adsorb oxygen molecules in the first step and the negative adsorption energies of O_2 reveal that the above structures can spontaneously activate O_2 molecules (Figure 2a). The $Co-N_4$ show lower O_2 adsorption than that of N-graphene and $Ir-N_4$, demonstrating the better activation ability of O_2 molecules. However, due to the weak adsorption of OOH species, the N-graphene site shows a high overpotential of 1.55 V (Figure 2b). After the introducing of Ir and Co, the overpotential on $Ir-N_4$ and $Co-N_4$ structures decline to 1.02 V, and 0.62 V, respectively (Figure 2c and 2d), suggesting that the doping of Ir and Co are beneficial to optimize the adsorption energies of ORR intermediates. Here, the $Co-N_4$ shows lowest overpotential, confirming its better ORR electrocatalytic performance.
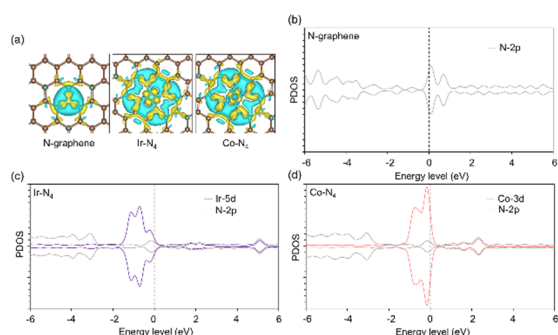
Figure 3. (a) Charge density differences of N-graphene, $Ir-N_4$ and $Co-N_4$ configurations. The isosurface levels are set to 0.003 e Å^{-3}, where charge depletion and accumulation were depicted by cyan and yellow, respectively. Projected density of state (PDOS) analysis of (b) N-graphene, (c) $Ir-N_4$ and (d) $Co-N_4$. The Fermi level is set to be zero and the spin-polarization is considered.

In order to gain deep insights into the catalytic mechanism and electronic structure. we further investigate the projected density of states (PDOS) and charge density of different catalyst configurations. Interestingly, the interaction between Co and N result in unique electronic structure for $Co-N_4$ (Figure 3a), more charge depletion region exists. And as can be observed from the PDOS (Figure 3b,3c and 3d), for $Co-N_4$, there are more hybridization effect between Co 3d and N 2p orbitals compared with that of pure N-graphene and $Ir-N_4$, which leads to more electron overlaps in the vicinity of Fermi level, demonstrating fast charge transfer kinetics and guaranteeing excellent electrocatalytic performance. Based on the above theoretical analysis, we give expectation of high HER and ORR electrocatalytic performance of $Co-N_4$.

4. Conclusion

In summary, DFT calculations have been carried out to investigate the Gibbs free energy diagrams and electronic structure of N-graphene, $Ir-N_4$ and $Co-N_4$. The results here show that $Co-N_4$ show appropriate H adsorption (0.15 eV) and lower ORR overpotentials (0.62 V) than that of N-graphene and $Ir-N_4$, which shows expectation of high multifunctional electrocatalytic performance. This theoretical study gives vital insights into the enhanced catalytic mechanism of $Co-N_4$ and also helps to institute the principles for designing high performance SACs.

References

1. Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Norskov, T. F. Jaramillo, Combining theory and experiment in electrocatalysis: Insights into materials design, Science 355 (2017)

2. S. K. Kaiser, Z. Chen, D. Faust Akl, S. Mitchell ,J. Perez-Ramirez, Single-Atom Catalysts across the Periodic Table, Chem Rev 120 (2020) 11703-809.

3. J. Z. Meiling Xiao+, Gaoran Li, Na Li, Shuang Li, Zachary Paul Cano, Lu Ma,, P. X. Peixin Cui, Gaopeng Jiang, Huile Jin, Shun Wang,* Tianpin Wu,* Jun Lu, Aiping Yu, ,a. Z. C. Dong Su, A Single-Atom Iridium Heterogeneous Catalyst in Oxygen Reduction Reaction, Angew. Chem. Int. Ed. (2019) 9640 –5.

4. X. Xie, C. He, B. Li, Y. He, D. A. Cullen, E. C. Wegener, A. J. Kropf, U. Martinez, Y. Cheng, M. H. Engelhard, M. E. Bowden, M. Song, T. Lemmon, X. S. Li, Z. Nie, J. Liu, D. J. Myers, P. Zelenay, G. Wang, G. Wu, V. Ramani ,Y. Shao, Performance enhancement and degradation mechanism identification of a single-atom Co–N–C catalyst for proton exchange membrane fuel cells, Nature Catalysis 3 (2020) 1044-54.

5. Y. Pan, S. Liu, K. Sun, X. Chen, B. Wang, K. Wu, X. Cao, W. C. Cheong, R. Shen, A. Han, Z. Chen, L. Zheng, J. Luo, Y. Lin, Y. Liu, D. Wang, Q. Peng, Q. Zhang, C. Chen ,Y. Li, A Bimetallic Zn/Fe Polyphthalocyanine-Derived Single-Atom Fe-N4 Catalytic Site:A Superior Trifunctional Catalyst for Overall Water Splitting and Zn-Air Batteries, Angew Chem Int Ed Engl 57 (2018) 8614-8.

6. G. Kresse, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, PHYSICAL REVIEW B 54 (1996) 11169e86.

7. G. K. J. Furthmu¨ller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, PHYSICAL REVIEW B 54 (1999) 11169-86.

8. K. Momma,F. Izumi, VESTA: a three-dimensional visualization system for electronic and structural analysis, Journal of Applied Crystallography 41 (2008) 653-8.

9. J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov ,U. Stimming,

Trends in the Exchange Current for Hydrogen Evolution, J Electrochem Soc 152 (2005)

10. M. Li, L. Zhang, Q. Xu, J. Niu ,Z. Xia, N-doped graphene as catalysts for oxygen reduction and oxygen evolution reactions: Theoretical considerations, Journal of Catalysis 314 (2014) 66-72.

11. J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov ,U. Stimming, Trends in the Exchange Current for Hydrogen Evolution, Journal of The Electrochemical Society 152 (2005) J23.