Unexpected monoatomic catalytic-host synergetic OER/ORR by graphitic carbon nitride: density functional theory†

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Although single metal atoms (SMAs) have been extensively investigated as unique active sites in single-atom catalysts, the possible active sites of the host catalysts have been unfortunately neglected in previous studies. In single-atom catalysts, the SMAs can promote the chemical and catalytic activities of host atoms, which may act as secondary active sites, resulting in a significant synergistic effect on the catalytic performance. Using density functional theory calculations, we studied the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) on two different types of active sites: single metal (M1) atoms and the neighboring host atoms of several M1/g-C3N4 samples. The contributions of M1 and host atoms towards the reduction of the OER/ORR overpotentials of Fe1, Co1, Ni1, Cu1 and Zn1/g-C3N4 bifunctional electrocatalysts with the OER/ORR overpotentials of 0.50–0.70 V were investigated. Finally, new M1/g-C3N4 catalysts with high OER/ORR performances could be estimated based on the d-band centre of the M1 atoms in the future.

Introduction

Ever since the application of single Pt atom loaded onto FeOx in CO oxidation has been reported by Zhang and co-workers in 2011, single-atom catalysts (SACs) have attracted significant attention.1,2 To date, various types of single metal atoms (SMAs), such as Pt, Pd, Au, Ir, Fe, Co, Ni and Cu atoms, have been anchored on different substrates, termed as metal/substrate, in experiments. Compared with heterogeneous catalysts of metal nanoparticles on substrates, SACs exhibit enhanced catalytic activity in the oxidation1,3–6 and reduction7–11 reactions due to the maximized atomic utilization, high catalytic selectivity, activity and stability. The dependence of the enhanced catalytic performance on the unique structures of SACs and the favorable interactions between the SMAs and the hosting catalysts have been well-verified through experiments and density functional theory (DFT) calculations.1,3,12–18 In recent years, the DFT calculations have been widely used to analyze the enhancement mechanism of known catalysts in atomic and electronic scales. Moreover, the design of new catalysts by predicting their structural, electronic and catalytic performances is a powerful tool.19,20

In situ observation of the active site, one of the most important factors of catalysts, by experimental techniques is extremely difficult. Generally, the SMAs of the SACs having high chemical activity are more readily bound to the reactants and intermediates than the host atom of substrates. Consequently, SMAs are recognized as unique active sites for all types of redox reactions: typical examples include the hydrogen evolution reaction of water by Mn1/N-doped carbon,21 the oxygen evolution reaction (OER) of water by the Ni1/B12 boron monolayer,14 the oxygen reduction reaction (ORR) of water by Fe1/or Co1/N-doped carbon,22,23 oxidation of CO by Au1/or Pt1/CeO2 and Pt1/FeOx or β-Al2O3,24–26 reduction of CO2 by Pd1/or Pt1/graphitic carbon nitride (g-C3N4) or Ir1/TiC,27,28 reduction of O2 by Pt1/TiC and TiN,29 ethanol synthesis catalyzed by Ni1/Mo6S8,30 hydrogen production from formic acid by Pt1/N-doped carbon,12 and selective hydrogenation of acetylene to ethylene by Pd1/Cu.31 The excellent catalytic activity of SMAs has been analyzed by DFT calculations. However, before the introduction of the SMAs, other possible active sites of host atoms were unfortunately neglected due to their poor catalytic activity. Note that the chemical and catalytic activities of host atoms can be improved since the SMAs can effectively adjust the electronic structures of the SACs. In this way, the host atoms can be regarded as secondary active sites and play a crucial role in some SACs; we have termed the common effect of M1 and host atoms as the synergistic effect of the SACs.

In this study, the electrochemical OER and ORR were studied at two active sites by the DFT calculations for several
SMAs supported on monolayer g-C3N4 (M1/g-C3N4, M = Fe, Co, Ni, Cu and Zn), where the two active sites are the M1 atoms (site 1) and the host atoms in the neighboring holes of M1 (site 2) (see Fig. 1). The inspiring synergistic effect of the SACs is confirmed by the stable and high catalytic activity of the site 2. The bifunctional electrocatalysts Fe1–Zn1/g-C3N4 with low overpotentials for the OER/ORR (0.50–0.70 V) have been predicted. Moreover, the segmented correlations between the OER/ORR performances and the d-band centre of the M1 atoms were obtained.

Computational methodologies

All calculations were performed by the DFT framework implemented with the DMol3 code.31 The exchange–correlation functional with the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) functional was utilized, and the all-electron treatment was considered.32,33 Double numerical atomic orbital plus polarization (DNP) was chosen as the basis set, the global orbital cut-off of 3.5 Å and a smearing of 0.005 Ha (1 Ha = 27.212 eV) were used to achieve precise electronic convergence, and the 5 × 5 × 1 k-point sampling set was tested to be sufficiently accurate. The lattice parameter in the z direction was fixed with the vacuum width of 15 Å, and the vacuum widths of the lattice parameters in the x and y directions were beyond 14 Å, which could adequately avoid the spurious interactions between repeating slabs. The lattice parameters in the xy plane and the atom coordinates are allowed to be fully relaxed. The convergence tolerances of force, energy and maximum displacement are 0.002 Ha Å−1, 1.0 × 10−5 Ha and 0.005 Å, respectively. The van der Waals interactions have been described using the empirical correction in the Grimme’s scheme D2.34 The complete LST/QST search protocol35 was used to calculate the transition states of all the intermediates from the site 2 to the site 1.

The bonding energy (ΔE_b) between the M1 atoms and g-C3N4 is described as follows:

\[ \Delta E_b = E(M_1/g-C_3N_4) - E(g-C_3N_4) - \mu_M(1) \]

where \( E(M_1/g-C_3N_4) \) and \( E(g-C_3N_4) \) are respectively the energies of the M1/g-C3N4 and g-C3N4 systems, and \( \mu_M \) denotes the chemical potential of the M atom in its bulk materials. The OER/ORR performances were evaluated by calculating the reaction free energy of each step:36

\[ \Delta G = \Delta E + \Delta E_{ZPE} - T \Delta S - eU \]

where \( \Delta E \) denotes the adsorption energy, and \( \Delta E_{ZPE} \) and \( \Delta S \) are the changes of zero-point energy and entropy, respectively; \( U \) is the potential measured against the normal hydrogen electrode (NHE) under standard conditions; \( e = 1 \) is the transferred.

Fig. 1  (a) Three different sites of M1 atoms on g-C3N4, (b) the bonding energies of M1 atoms on three different sites, (c) the schematic of the structure and (d) adsorption energies of H2O and O2 molecules at the sites 1 and 2 of M1/g-C3N4.
charge for one-electron reactions, and \( T = 300 \) K. For more computational details, refer to the ESI†.

To study the thermodynamic stability of the \( \text{M}_1/\text{g-C}_3\text{N}_4 \) specimens, \textit{ab initio} dynamics simulations were carried out for 10 ps at the intervals of 5 fs. The NVT ensemble, Massive GGM thermostat and a temperature of 300 K were considered when the monolayer models had the size of 2.78 nm × 2.78 nm in the \( xy \) plane.

**Results and discussion**

We considered three different bonding sites (sites I, II and III) of the \( \text{M}_1 \) atoms on the monolayer \( \text{g-C}_3\text{N}_4 \) (see Fig. 1a), and the stability of \( \text{M}_1/\text{g-C}_3\text{N}_4 \) was evaluated on account of the calculated bonding energy by eqn (1). The negative bonding energy values of the \( \text{Fe}_1-\text{Zn}_1/\text{g-C}_3\text{N}_4 \) specimens indicate that the \( \text{M}_1 \) atoms would be stably located in the monolayer \( \text{g-C}_3\text{N}_4 \). Moreover, the \( \text{Fe}_1-\text{Zn}_1 \) atoms prefer to locate at the site I due to its lowest bonding energy values among the abovementioned three sites (see Fig. 1b); this is consistent with the results reported in ref. 27. Therefore, only site I is considered in subsequent works. Moreover, the results of \textit{ab initio} dynamics simulation are shown in Fig. S1.† The total energies of the \( \text{M}_1/\text{g-C}_3\text{N}_4 \) specimens vary within \( ±0.03 \) eV in the last 5 ps, and the \( \text{Fe}_1, \text{Co}_1, \text{Ni}_1, \text{Cu}_1 \) and \( \text{Zn}_1 \) atoms are located at the site I during the whole dynamics simulation; this verifies the good thermodynamic stability of all the \( \text{M}_1/\text{g-C}_3\text{N}_4 \) specimens. Moreover, the Mulliken charges of \( \text{M}_1 \) and the neighbouring \( \text{N} \) atoms were calculated. As presented in Table S1,† there are evident electron transformations from the \( \text{M}_1 \) atoms to the neighbouring \( \text{N} \) atoms, indicating chemical bonding between the \( \text{M}_1 \) and the neighbouring \( \text{N} \) atoms. Furthermore, the electronic distributions and the chemical activity of most of the host atoms in the monolayer \( \text{g-C}_3\text{N}_4 \) were adjusted by embedding the \( \text{M}_1 \) atoms; this was indicated by the differences in the electron densities of the \( \text{M}_1/\text{g-C}_3\text{N}_4 \) specimens, as shown in Fig. S2a–e.†

Before the OER/ORR, the reactants (\( \text{H}_2\text{O} \) and \( \text{O}_2 \)) need to be adsorbed on two active sites; thus, we have determined the stability of the reactants on both active sites of \( \text{M}_1/\text{g-C}_3\text{N}_4 \), where one \( \text{M}_1 \) atom is anchored on one hole of the \( 2 \times 2 \) supercell \( \text{g-C}_3\text{N}_4 \) to obtain two different active sites (Fig. 1c). As shown in Fig. S3,† a water or oxygen molecule is linked with \( \text{M}_1/\text{g-C}_3\text{N}_4 \) by the O–M bond at the site 1 or by the H–N (or O–N) bond at the site 2. The adsorption energies of the individual water or oxygen molecules on the substrates were calculated by eqn (S1) and (S2)† and are shown in Fig. 1d. Although the adsorption energies of the water molecule at the site 1 (from \(-0.74 \) to \(-1.25 \)) are lower than those at the site 2 (from \(-0.65 \) to \(-1.04 \)), the negative adsorption energies ensure the stable and synchronous adsorption of water molecules at both active sites in a liquid environment. Moreover, the adsorption energies of the first (second) oxygen molecule at the site 1 are smaller (larger) than those of the first oxygen molecule at the site 2 for the corresponding specimens; this suggests that the oxygen molecule is first adsorbed at the site 1 and then at the site 2; thus, the site 2 is the second active site for \( \text{Fe}_1-\text{Zn}_1/\text{g-C}_3\text{N}_4 \). Although the reaction probability at the site 2 is smaller than that at the site 1, catalytic reactions can also occur at the site 2 and should not be ignored. The \( \text{Co}_1/\text{g-C}_3\text{N}_4 \) specimen is illustrated to certify the synergistic effect of the SACs during the OER/ORR, and the results can be compared with the available experimental results.†

To check the stability of the intermediates at the site 2, the transition states of all intermediates (\( \text{OH}, \text{O} \) and \( \text{OOH} \) groups) from the site 2 to the site 1 were calculated. As observed in Fig. 2a, the sizeable transition energy barriers can effectively hinder the migrations of the \( \text{OH}, \text{O} \) and \( \text{OOH} \) groups, and hence, the OER/ORR can takes place at the site 2 of \( \text{Co}_1/\text{g-C}_3\text{N}_4 \). To highlight the importance of the synergistic effect of \( \text{Co}_1 \) and host atoms in \( \text{Co}_1/\text{g-C}_3\text{N}_4 \), four \( \text{Co}_1 \) atom-supported \( 2 \times 2 \) supercell \( \text{g-C}_3\text{N}_4 \) (4\( \text{Co}_1/\text{g-C}_3\text{N}_4 \)) possessing only site 1 and pristine \( \text{g-C}_3\text{N}_4 \) possessing only site 2 were compared with \( \text{Co}_1/\text{g-C}_3\text{N}_4 \) possessing both the site 1 and 2. The atomic and electronic structures of the abovementioned three systems are presented in Fig. 3. For pristine \( \text{g-C}_3\text{N}_4 \) (Fig. 3b), the valence band maximum (VBM) (red regions) and conduction band minimum (CBM) (yellow regions) are located at the neighboring \( \text{N} \) and \( \text{C} \) atoms, respectively; this badly decreases the lifetime of the carriers. By embedding \( \text{Co}_1 \) atoms, the electronic distributions of the \( \text{g-C}_3\text{N}_4 \) monolayer were adjusted, as shown in Fig. 3d and f. The separated VBM and CBM contributed to increase the carrier lifetime of \( \text{Co}_1/\text{g-C}_3\text{N}_4 \) and 4\( \text{Co}_1/\text{g-C}_3\text{N}_4 \). Considering the significances of the adsorption energies of intermediates, the linear relationships between the adsorption energies of *O and *OH or *O and *OOH were obtained, as shown in Fig. 2b. The adsorption structures of the intermediates at both sites are shown in Fig. S4,† where the OHG group binding with the \( \text{Co}_1 \) atom at the site 1 is considered while calculating the OER/ORR at the site 2 since the determining step of the reaction is from *OOH to \( \text{O}_2(\text{g}) \) (see Fig. 2c). Compared with the case of \( \text{g-C}_3\text{N}_4 \), the chemical activity of the host atom at the site 2 of \( \text{Co}_1/\text{g-C}_3\text{N}_4 \) can be improved by the anchored \( \text{Co}_1 \) atom on account of the lower adsorption energy values. Similarly, the chemical activity of the \( \text{Co}_1 \) atoms in \( \text{Co}_1/\text{g-C}_3\text{N}_4 \) is weaker than that in \( 4\text{Co}_1/\text{g-C}_3\text{N}_4 \) due to the lower d band-centre value of the \( \text{Co}_1 \) atom in the \( \text{Co}_1/\text{g-C}_3\text{N}_4 \) specimen, as shown in Fig. 2e. Moreover, the adsorption energies of each intermediate at the site 1 are lower than that at the site 2; this may be caused by the higher chemical activity of the \( \text{Co}_1 \) atoms than that of the host atoms. All the abovementioned results indicate that the adjusted chemical activity of \( \text{Co}_1 \) and host atoms leads to various catalytic activities. To prove the point, the Gibbs free energy changes were calculated and are displayed in Fig. 2c and d based on the four one-electron reactions of the OER/ORR. The overpotentials of the OER/ORR (\( \eta_{\text{OER}}/\eta_{\text{ORR}} = 0.72/1.11 \) V at the site 1 of \( \text{Co}_1/\text{g-C}_3\text{N}_4 \)) are similar to those of \( \text{g-C}_3\text{N}_4 \) (1.07/1.03 V) and smaller than those of \( 4\text{Co}_1/\text{g-C}_3\text{N}_4 \) (1.28/1.33 V). Importantly, the lowest \( \eta_{\text{OER}}/\eta_{\text{ORR}} \) values (0.50/0.59 V) appear at the site 2 of \( \text{Co}_1/\text{g-C}_3\text{N}_4 \), which...
are close to the experimental results of Co1/g-C3N4 on a multi-walled carbon nanotube (0.33/0.40 V).\textsuperscript{4} Moreover, the proportional relationships between the $\eta_{\text{OER}}$ (or $\eta_{\text{ORR}}$) values and the d band-centre values of the Co1 atoms for the Co1/g-C3N4 and 4Co1/g-C3N4 specimens were obtained, as shown in Fig. 2f. In brief, the catalytic activity at the site 2 of Co1/g-C3N4 was enhanced by the anchored Co1 atom at the site 1; this indicated the excellent synergistic effect of the Co1 and host atoms.

The excellent synergistic effects also appeared on other M1/g-C3N4 specimens besides Co1/g-C3N4. For the Fe1–Zn1/g-C3N4 specimens, the separation of the VBM and the CBM at both active sites (Fig. S2f–j\textsuperscript{†}) contributed to the increase in the carrier lifetime. In addition, the large transition energies of the intermediates ensure the progression of the OER/ORR at the site 2 in all M1/g-C3N4 (Fig. S5a\textsuperscript{†}) although the adsorption energies at the site 1 are lower than those at the site 2 for the same specimen (Fig. S5b\textsuperscript{†}). The adsorption structures of the
Intermediates on $\text{M}_1$/$\text{g-C}_3\text{N}_4$ are similar to that on $\text{Co}_1$/$\text{g-C}_3\text{N}_4$ (Fig. S6 and S7†). To further verify the synergistic effect of the $\text{M}_1$ and host atoms, the Gibbs free energy changes at both active sites of $\text{M}_1$/$\text{g-C}_3\text{N}_4$ were calculated and are shown in Fig. S8 and S9,† where the bonding of OOH or OH with the $\text{M}_1$ atom was considered to calculate the adsorption energies of the intermediates at the site 2 on account of the determining steps of the reaction at the site 1. At the site 1, $\text{Co}_1$/$\text{Ni}_1$ and $\text{Cu}_1$/$\text{g-C}_3\text{N}_4$ have lower (or higher) overpotentials of the OER (or ORR) than $\text{g-C}_3\text{N}_4$. However, the overpotentials of the OER/ ORR at the site 2 of all $\text{M}_1$/$\text{g-C}_3\text{N}_4$ (in the range of 0.50–0.70 V) are smaller than those at the site 1 and also smaller than those of $\text{g-C}_3\text{N}_4$. Thus, well synergistic effects appear in the $\text{M}_1$/$\text{g-C}_3\text{N}_4$ specimens, which may be bifunctional electrocatalysts with excellent catalytic activities.

Considering the effects of the $\text{M}_1$ atomic concentrations,37,40 the $3 \times 3$ supercell samples were also examined. The schematic of the structure is displayed in Fig. S10,† and the Gibbs free energy changes of the OER/ ORR for the $2 \times 2$ and $3 \times 3$ supercells are compared, as shown in Fig. S11.† Compared with the $2 \times 2$ supercell samples, the $\eta^{\text{OER}/\text{ORR}}$ values at the site 1 (or site 2) of the $3 \times 3$ supercell samples are reduced by 0.03–0.12 V (or increased by 0.01–0.04 V); this may be caused by the transfer of more electrons between the $\text{M}_1$ atoms and the monolayer $\text{g-C}_3\text{N}_4$ in $3 \times 3$ supercell samples. Although the $\eta^{\text{OER}/\text{ORR}}$ values of all the samples are affected by the $\text{M}_1$ atomic concentration, the OER/ ORR overpotentials at the site 2 are still smaller than those at the site 1 for the corresponding samples, and thus, the synergistic effect still exists in the $3 \times 3$ supercell $\text{M}_1$/$\text{g-C}_3\text{N}_4$ samples.

To find out the correlations between the OER/ ORR performances and the electronic structure of $\text{M}_1$/$\text{g-C}_3\text{N}_4$, the d-band center ($\epsilon_d$) of the $\text{M}_1$ atoms at the site 1 and p-band center ($\epsilon_p$) of the C plus N atoms at the site 2 were calculated from their PDOS (Fig. S12†), which is related to the bonding strengths of the intermediates and catalytic activities of the specimens.42,43 Since the electronic structures of the C and N atoms at the site 2 are effectively adjusted by the $\text{M}_1$ atoms at the site 1, the proportional relationships between the $\epsilon_d$ values and the $\epsilon_p$ values are obtained, as shown in Fig. S12† and thus, the $\epsilon_d$ values are used to estimate the OER/ ORR performances at both activity sites of $\text{M}_1$/$\text{g-C}_3\text{N}_4$. For both active sites, the Gibbs free energies of all the intermediates decreased with the increasing $\epsilon_d$ values, as shown in Fig. 4a and b, where $\text{Cu}_1$ and $\text{Zn}_1$ atoms

Fig. 3 The atomic structures of (a) $\text{g-C}_3\text{N}_4$, (c) $\text{Co}_1$/$\text{g-C}_3\text{N}_4$, (e) $4\text{Co}_1$/$\text{g-C}_3\text{N}_4$ and the VBM (red regions)/CBM (yellow regions) of (b) $\text{g-C}_3\text{N}_4$, (d) $\text{Co}_1$/$\text{g-C}_3\text{N}_4$, (f) $4\text{Co}_1$/$\text{g-C}_3\text{N}_4$. Isosurface is taken at a value of 0.003 e per Bohr.3
with full d-orbits were not considered. The approximate linear relationships between the $\Delta G$ and $\varepsilon_d$ values indicate that the bonding strengths of the intermediates at the site 1 (or site 2) are directly (or indirectly) related to the electronic structures of the M$_1$ atoms; this strongly reveals the synergistic effects of the M$_1$ and host atoms.

The correlations between the $\varepsilon_d$ and OER/ORR potentials at both active sites are shown in Fig. 4c and d. For the OER at the site 1 (Fig. 4c), the potentials are reduced with a decrease in the $\varepsilon_d$ values from $-0.50$ to $-1.34$ eV; accordingly, the final step of the OER is the potential-determining step; as $-1.34 > \varepsilon_d > -1.60$ eV, the potentials are increased as the $\varepsilon_d$ values are reduced; accordingly, the second step of the OER is the potential-determining step. The inflection point of the $\varepsilon_d$ values is $-1.34$ eV for the OER, and hence, Co$_1$/g-C$_3$N$_4$ has lowest OER potential and highest catalytic activity when compared with Fe$_1$/g-C$_3$N$_4$ and Ni$_1$/g-C$_3$N$_4$. For the ORR at the site 1 (Fig. 4c), the potentials are reduced as the $\varepsilon_d$ values decrease in the range from $-0.50$ to $-1.60$ eV; accordingly, the first step of the ORR is the potential-determining step. Similar results are also found at the site 2 (Fig. 4d); this indicates that the $\varepsilon_d$ values have indirect effects on the catalytic performances at the site 2. The inflection point of the $\varepsilon_d$ values is $-0.96$ eV for the OER. Based on the correlations between $\varepsilon_d$ and OER/ORR potentials, the bi-directional OER/ORR overpotentials may reach the minimum value of 1.04/1.04 V when $\varepsilon_d$ reaches $-1.57$ eV at the site 1 (Fig. 4c) and 0.56/0.56 V when $\varepsilon_d$ reaches $-1.55$ eV at the site 2 (Fig. 4d). The $\varepsilon_d$ values of the M$_1$ atoms can be utilized to estimate the OER/ORR performances of M$_1$/g-C$_3$N$_4$ and would accelerate the design of new M$_1$/g-C$_3$N$_4$ catalysts in future.

**Conclusion**

We have studied the catalytic activities of several M$_1$/g-C$_3$N$_4$ specimens for the OER and ORR at two different active sites using the DFT calculations. Based on the stability of the reactants and intermediates on surface, the M$_1$ and host atoms can be considered as the primary and secondary active sites, respectively. Although the reaction probability on the host atoms is smaller than that on the M$_1$ atoms, the host atoms play a prominent role in reducing the OER and ORR overpotentials. The calculated OER/ORR overpotentials of Co$_1$/g-C$_3$N$_4$ are lower than those of g-C$_3$N$_4$ and 4Co$_1$/g-C$_3$N$_4$; this demonstrates the importance of the synergistic effects to improve the cata-
lytic activity of the SACs. Moreover, Fe$_2$-Zn$_2$/g-C$_3$N$_4$ with the OER/ORR overpotentials in the range of 0.50–0.70 V have been predicted to be excellent bifunctional electrocatalysts. Based on the d-band centre of the M$_1$ atoms, new M$_1$/g-C$_3$N$_4$ catalysts with high OER/ORR performances may be predicted in the future.

Conflicts of interest
There are no conflicts to declare.

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References


