Simultaneously Enhancing Catalytic Performance and Increasing Density of Bifunctional CuN₃ Active Sites in Dopant-Free 2D C₃N₃Cu for Oxygen Reduction/Evolution Reactions

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ABSTRACT: Atomically dispersed M–N–C has been considered an effective catalyst for various electrochemical reactions such as oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), which faces the challenge of increasing metal load while simultaneously maintaining catalytic performance. Herein, we put forward a strategy for boosting catalytic performances of a single Cu atom coordinated with three N atoms (CuN₃) for both ORR and OER by increasing the density of connected CuN₃ moieties. Our calculations first show that a single CuN₃ moiety exhibiting no catalytic performance for ORR and OER can be activated by increasing the density of metal centers, which weakens the binding affinity to *OH due to the lowered d-band center of the metal atoms. These findings stimulate the further theoretical design of a two-dimensional compound of C₃N₃Cu with a high concentration of homogeneously distributed CuN₃ moieties serving as bifunctional active sites, which demonstrates efficient catalytic performance for both ORR and OER as reflected by the overpotentials of 0.71 and 0.43 V, respectively. This work opens a new avenue for designing effective single-atom catalysts with potential applications as energy storage and conversion devices possessing high density of metal centers independent of the doping strategy and defect engineering, which deserves experimental investigation in the future.

1. INTRODUCTION

Severe energy and environmental problems have prompted research efforts into developing electrochemical energy storage and conversion devices.¹ ⁴ Rechargeable aqueous metal–air batteries,⁶ represented by rechargeable Zn–air batteries,⁶ ⁷ possess the advantages of high theoretical energy density, low cost originating from the high-abundance anode material, and inherent safety using aqueous electrolytes.⁸ ¹⁰ Generally, a conventional rechargeable aqueous metal–air battery is made up of a metal foil anode and a cathode using oxygen as the cathode active material. In the air cathode, the vital catalytic processes of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are involved during the discharge and charge processes, respectively.¹¹ ¹³ However, the kinetics of the cathodic oxygen redox reaction is sluggish, which restricts the conversion efficiency between O₂ and H₂O.¹⁴ So far, precious metals, their alloys, and their oxides are the main commercial catalysts, but the large-scale application of noble-metal-based catalysts is seriously restricted by their scarcity, stability and cost.¹⁵ In particular, their catalytic performance is closely related to the types of noble metals, and the corresponding oxygen catalytic activities of different metals are quite disparate.¹⁶ For example, RuO₂/IrO₂ shows excellent OER activity; unfortunately, its catalytic ORR activity is not ideal. Pt-based catalysts are considered to be the best ORR catalysts, but their OER performance is low.¹⁷ In this case, the reasonable construction of a low-cost and highly efficient bifunctional catalyst is the research hotspot of secondary metal–air batteries.¹⁸

Single-atom catalysts (SACs) containing atomically dispersed metal centers immobilized on heteroatom-doped substrates have recently sparked tremendous interest due to their high material utilization efficiency and enhanced catalytic performances.¹⁹ ²¹ Among them, the most reported SACs are limited to transition-metal atoms (Fe, Co, Ni, Cu, etc.) supported by heteroatom N-doped carbonaceous materials, which can be applied to the catalysis of a wide range of electrochemical reactions of ORR,²² ²⁸ nitrogen reduction reaction (NRR),²⁹ ³⁴ carbon dioxide reduction reaction (CO₂RR),³⁵ ⁴¹ hydrogen reduction reaction (HER),⁴² ⁴⁴

Received: March 16, 2022
Accepted: May 17, 2022
Published: June 2, 2022
XANES, Yang et al. identify that the catalytic performance of MN₄ containing non-noble metals can be further enhanced by rationally tailoring the local structures of central metal atoms by introducing functional groups,²⁵ the second metal center,²⁶ and other heteroatoms beyond N.⁴⁵,⁴⁹ However, the low density of single-atomic sites is still one of the big challenges for SACs because high load and the aggregation of metal atoms have to be balanced. Recently, a metal load of up to 12.1 wt % is achieved based on a general cascade anchoring strategy for fabricating MN₄ (M = Fe, Mn, Co, Ni, Cu, Mo, Pt, etc.) toward ORR.²⁶ However, an ultrahigh load of metal atoms cannot be obtained without weakening the ORR performance. For example, when the distance between two neighboring Fe atoms is lower than 0.70 nm, the strengthened interaction between two adjacent FeN₃ moieties will worsen the catalytic performance for ORR.²⁷ This indicates as well that designing high-performance FeN₄ for ORR with a high concentration of active sites will be highly restricted based on the conventional heteroatom doping strategy.

The appearance of the MN₃ moiety cannot be excluded based on both the complex preparation concept⁴⁶ and dynamic evolution of the active sites during the reactions,⁵¹ which have recently attracted significant research efforts. Using operando XANES, Yang et al. identified that it is CuN₃ instead of CuN₄ that is responsible for ORR under working conditions, although ex situ characterizations show that MN₄ remains before and after the reaction.⁵¹ FeN₃ possesses mediocre catalytic performance toward ORR compared to FeN₄,²⁵ which could be enhanced when FeN₄ was deposited over Pd particles embedded in N-doped carbons.⁶⁰ Although enhanced ORR performance could be realized by increasing the concentration of the FeN₃ moiety, it requires preadsorption of functional groups onto the metal atoms adjacent to the active sites.²⁵ Such a complex strategy of introducing functional groups and/or interfaces for achieving MN₃ active sites toward ORR highlights the urgency of identifying new rationality for designing high-performance SACs, which can balance the high density of active sites and facile strategy of fabricating catalysts. In this regard, two-dimensional (2D) materials containing high concentrations of homogeneously distributed metal centers will be potential candidate catalysts.⁵³,⁵⁴ Therefore, a novel designing rationality is highly required, which is in turn dependent on the knowledge of appropriate arrangements of MN₃ leading to competitive catalytic performance.

Herein, we propose a novel strategy of designing bifunctional catalysts for ORR and OER, which contains a high density of MN₃ serving as active sites without involving additional strategies to tailor the local environment of metal atoms. Using density functional theory (DFT) calculations, we report the first demonstration of the density effect of CuN₃ on the catalytic performances for ORR and OER. Our calculations demonstrated that the systems containing three connected CuN₃ moieties could give rise to significantly decreased overpotentials of 0.91 and 0.48 V for ORR and OER, respectively, compared to those larger than 1.23 V with single CuN₃. These findings triggered the theoretical design of the 2D crystalline phase of C₃N₃Cu containing an even higher concentration of CuN₉, which was then predicted to be a bifunctional catalyst for ORR and OER with lowered overpotentials of 0.71 and 0.43 V, respectively. The catalytic performances of C₃N₃Ni and C₃N₃Zn for ORR and OER were also explored. Of the two, C₃N₃Ni possesses good OER activity, while it shows no catalytic performance for ORR. In contrast, the performances of C₃N₃Zn for both ORR and OER are low.

2. COMPUTATIONAL DETAILS

Geometry optimizations and total energy calculations were performed based on DFT⁵⁵ implemented in the Vienna ab initio simulation package (VASP).⁵⁶,⁵⁷ To describe the nucleus–electron interactions, the projector augmented wave (PAW)⁵⁸,⁵⁹ potentials were adopted. The analysis of the exchange–correlation energy was carried out by the Perdew–Burke–Ernzerhof (PBE)⁶⁰,⁶¹ functional within the generalized gradient approximation (GGA).⁶²,⁶³ The van der Waals interactions were described by the DFT-D3⁶⁴ approach. The plane wave basis set⁶⁵ with a cutoff energy of 520 eV was utilized throughout this work to expand the wave functions of valence electrons. To avoid interaction of periodic images along the z-direction, a vacuum layer region was set, which was larger than 15 Å. A 6 × 6 × 1 supercell of graphene was built to model these SACs with various concentrations of the CuN₃ moiety. For the structural optimization, self-consistent-field (SCF) calculations, and non-SCF calculations (NSCF), the corresponding Γ-centered k-mesh grids⁶⁵ for sampling the Brillouin zone were set to be 2 × 2 × 1, 3 × 3 × 1, and 6 × 6 × 1, respectively. For C₃N₃M (M = Cu, Zn, and Ni), a 6 × 6 × 1 k-mesh grid was used to optimize the original geometry, and a 9 × 9 × 1 k-mesh grid was set for electronic structure computations. We set up a series of 2 × 2 × 1 supercells of pristine C₃N₃M (containing 56 atoms) for exploring the adsorption properties of reaction intermediates of ORR and OER. A k-mesh grid of 2 × 2 × 1 was used for geometry optimization, while meshes of 3 × 3 × 1 and 6 × 6 × 1 were used for SCF calculation and NSCF calculation, respectively. All of the structure configurations were optimized until the energy and the force on each atom were less than 1 × 10⁻⁵ eV and 0.02 eV/Å, respectively. Additionally, the bonding behaviors were analyzed based on the electron localization function (ELF).⁶⁶ The phonon spectra were calculated using the Phonopy code.⁶⁷ The thermodynamic stabilities of a C₃N₃Cu monolayer and a C₃N₃Cu nanoflake were evaluated by ab initio molecular dynamics (AIMD) simulations in an NVT ensemble at 300 K. Note that the AIMD simulations for a C₃N₃Cu monolayer were carried out using a 3 × 3 × 1 supercell, which contains 126 atoms. While regarding the C₃N₃Cu nanoflake with 96 atoms, a simulation box with a = b = 32.00 Å, c = 21.29 Å, and α = β = γ = 90° was set up, giving rise to a vacuum layer region in x, y, and z directions of about 15, 15, and 20 Å, respectively. For the C₃N₃Cu monolayer and C₃N₃Cu nanoflake, the durations of AIMD simulations are greater than 3 ps, the time step is 3 fs, and the SMASS is set to be 2. The k-mesh grids used for both systems were set to be 1 × 1 × 1. More computational details on cohesive energies, adsorption energies, charge density difference, and Gibbs free energies⁶⁸ for electrochemical reactions and surface models are given in the Supporting Information.
3. RESULTS AND DISCUSSION

3.1. Effect of Concentrations of CuN3 Moiety on Performances of ORR and OER. We initially set up three models of SACs by introducing different numbers of CuN3 moiety in the simulation box to describe the systems containing various concentrations of active sites. As shown in Figure 1a−c, 1-CuN3, 2-CuN3, and 3-CuN3 refer to the model of SACs containing one, two, and three CuN3 moieties, respectively. Note that the reason why we utilized such arrangements of CuN3 moieties in 2-CuN3 and 3-CuN3 is claimed at the end of this section. The average bond lengths of Cu−N are 1.71, 1.89, and 1.89 Å in these three systems. Bader charge analysis shows that Cu losses 0.69, 0.69, and 0.71 |e| to its neighboring N atoms in 1-CuN3, 2-CuN3, and 3-CuN3, respectively. Calculated projected density of states (PDOSs) demonstrate that the increased density of CuN3 leads to enhanced electron conductivity as verified by the decreased band gaps following the order 1-CuN3 > 3-CuN3 > 2-CuN3.

Moreover, deep analysis of PDOS demonstrates that 3dxy and 3dx2−y2 contribute mainly to those occupied states near the Fermi level in 1-CuN3, while the highest occupied orbitals become 3dyz and 3dx2−y2 when it turns to the cases of 2-CuN3 and 3-CuN3 (see Figure S1). Although these properties of bond length, charge transfer, and band gap exhibit no positive correlation with the concentration of CuN3 moieties, their significant distinctions between 1-CuN3 and 3-CuN3 still might be a hint toward tuned catalytic performances.

We next systematically investigated the effect of CuN3 density on the activity toward ORR and OER based on the calculated free energies of reaction intermediates of *OOH, *OH, and *O involved in both reactions based on the equations listed in the Supporting Information. As is well known, neither too strong nor too weak interaction strength between the substrates and adsorbates is required for achieving an efficient catalytic performance of catalysts. Ideally, the free energy change for each reaction step should be 1.23 eV (when U = 0). In reality, however, the free energy steps are not distanced equally so that the reactions will be determined by the rate-determining step (RDS). As shown in Figure 1g−l, on the basis of these free energies, one can clearly see the distinct RDSs of (*OH + e− → OH−) and (*OH + OH− → *O + H2O (l) + e−) for ORR and OER, respectively, which were considered for obtaining the overpotentials of both reactions. Fully relaxed reaction intermediates adsorbed on the substrates are illustrated in Figures S2−S4. Using eq S9, we achieved the overpotentials (ηORR) of 2.30, 1.11, and 0.91 V for ORR catalyzed by 1-CuN3, 2-CuN3, and 3-CuN3, respectively. It demonstrates clearly that a single CuN3 moiety is not active for ORR, while upon increasing the number of CuN3 moieties from 1 to 3, the overpotential of ORR is gradually decreased. With order of 3-CuN3 < 2-CuN3 < 1-CuN3, the free energy change of RDS for three systems can provide us with insights into understanding the enhanced ORR performance. As shown in Figure 1g−i, when increasing the number of CuN3 there is a shift of the free energy change of RDS to a smaller value, leading to the lowest overpotential for 3-CuN3. Therefore, the enhanced ORR performance in 3-CuN3 could be attributed to the weakened interaction between reaction intermediates and substrates, especially between *OH and CuN3 moieties. The underlying mechanism will be discussed later.
DFT calculations also demonstrate the critical role of the high density of the CuN₃ moiety in boosting OER activity. As described in the Supporting Information, the OER proceeds by also involving the adsorption of three reaction intermediates of *OH, *O, and *OOH. On the basis of free energy profiles of OER shown in Figure 1j−l, we obtained the corresponding overpotentials of OER (ηΟΕＲ), which were 1.52, 0.52, and 0.48 V for 1-CuN₃, 2-CuN₃, and 3-CuN₃, respectively. This implies that with an increase in the density of the CuN₃ moiety, the OER performance will decrease the free energy change of the second step of OER (*OH + OH⁻ → *O + H₂O(l) + e⁻), which is determined mainly by the binding strength of *OH and substrates. Therefore, similar to the case of ORR, we believed that the enhanced OER performance can also be attributed to the weakened interaction of *OH and substrates.

Overall, 3-CuN₃ can serve as the best bifunctional catalyst for ORR and OER, outperforming the other two systems as reflected by the overpotentials of ηΟΡΡ = 0.91 V and ηΟΕＲ = 0.48 V, respectively. Note that the OER performance of 3-CuN₃ is even comparable to that of RuO₂. Additional calculations for exploring the trapping capabilities for O₂ and H₂O were also carried out, which show that 1-CuN₃, 2-CuN₃, and 3-CuN₃ possess strong binding strength to these two molecules as reflected by the adsorption energies and configurations (see Figure S5).

We theoretically designed a 2D C₃N₃Cu, as shown in Figure 2a, which contains not only the structural features of CuN₃ connecting to each other but also possesses homogeneously distributed metal atom sites. It was found to be dynamically stable as verified by the phonon dispersion curves along high symmetry directions in the Brillouin zone, as shown in Figure 2b. Fully relaxed C₃N₃Cu crystallizes in space groups of P3 with lattice vectors of a = b = 6.51 Å. Also, more structural details are given in Table S1. Close examination of the fully relaxed geometries of C₃N₃Cu structures shows that the 2D compound is composed of small hexagon patches of sp² carbons surrounded by six connected CuN₃ moieties. The
average Cu−N bond length is around 1.87 Å, which is slightly shorter than 1.90 Å in 3-CuN₃, as shown in Figure 1c. ELF can be utilized to map the localization of electrons in the neighborhood space. As shown in Figure S8, the ELF maps imply that in C₃N₃Cu the interaction of N−C and C−C is characterized as covalent bonds (ELF > 0.5), while that of Cu−N is characterized as ionic bonds (ELF < 0.5).

As shown in Figure 2c, C₃N₃Cu should be thermodynamically stable at room temperature as demonstrated by regular oscillations of instant temperature and kinetic energy near the equilibrium values and negligible structure distortion. Further, the stability of the C₃N₃Cu nanoflake was also evaluated by AIMD simulations, which indicate that nanoscale C₃N₃Cu should be stable at room temperature (see Figure S9). Note that in the C₃N₃Cu monolayer, there exists a N−N bond, as shown in Figure 2a, which has been confirmed to be stable in the graphene lattice by both experimental⁷⁰ and theoretical⁷¹,⁷² means. Aiming to further verify the stability of the N−N bond, we calculated the free energy diagram of N₂ formation by decomposition of the graphene in two different ways, which are illustrated in Figures S10 and S11. The free energy change values for the migration of the N dimer from the carbon lattice into the vacuum are around 4.62 and 1.00 eV, respectively, indicating that the N−N bond in the graphene lattice is significantly stable.

In addition, we also calculated the cohesive energies of C₃N₃Cu of −5.58 eV/atom, which is lower than those for Cu₂Si (−3.46 eV/atom),⁷³ FeB₆ (from −5.56 to −5.79 eV/atom),⁷⁴ and Be₂C (−4.86 eV/atom),⁷⁵ which demonstrates its thermodynamic stability as well. The band structures and density of states were also calculated, which possess a zero band gap, indicating their high conductivities, as shown in Figure 2d. More interestingly, C₃N₃Cu has a Dirac point located exactly at the Fermi level, which is similar to that of graphene.

ORR and OER processes in acidic solutions initialize with adsorption of O₂ and H₂O, and therefore, we next explored the trapping capabilities of C₃N₃Cu, which can be evaluated by the adsorption energies and other adsorption-induced changes of structural and electronic properties as well as charge transfer (see Figure 3). The fully relaxed geometry of O₂ on the substrate is shown in Figure 3, which has an adsorption energy of −0.93 eV. As shown in Figure 3a, upon the deposition of O₂, 0.43 lel charge is transferred from C₃N₃Cu to an adsorbed O₂ molecule, which activates the O−O bond due to the occupation of the antibonding state of the O₂ molecule. This enhanced activation could be also reflected by the adsorption-induced O−O bond length change (dₒₒ−O) of 0.06 Å as well as the magnetism of the O₂ molecule from 2 μₒ to 1.39 μₒ of the gas phase to 1.39 μₒ of the adsorbed phase. In addition, as shown in Figure 3c, upon deposition of the O₂ molecule, C₃N₃Cu becomes spin-polarized with spin density localized mainly in the vicinity of both adsorbed O₂ and CuN₃ moieties. Regarding H₂O adsorption, one can also see the chemisorption of H₂O with a bond length of 2.13 Å between Cu and O and an adsorption energy of −0.57 eV. In contrast to the case of O₂ adsorption, inverse charge transfer from the adsorbed H₂O to the substrates was observed but with a smaller amount of charge of 0.06 lel. Overall, the chemisorption of O₂ and H₂O is strong enough for C₃N₃Cu to catalyze both ORR and OER.

Figure 3. Charge redistribution induced by the adsorption of (a) H₂O and (b) O₂ on C₃N₃Cu, where the arrow refers to the direction of charge transfer and cyan and yellow denote charge depletion and accumulation, respectively. (c) Spin density distribution and local magnetism moments (μₒ) of O, Cu, and N atoms and (d) PDOS of O₂-adsorbed C₃N₃Cu. In the maps of spin density distribution, the yellow and cyan surfaces describe the densities of spin-up and spin-down states, respectively.

We next explored the catalytic performance of C₃N₃Cu for ORR and OER by calculating Gibbs free energies of all of the related oxygen-containing reaction intermediates adsorbed on the active sites (see Figure 4a−c). As expected, the active sites are still Cu atoms bonded with three N atoms, which exhibit an enhanced catalytic performance for ORR and OER as reflected by overpotentials of 0.71 and 0.43 V, respectively. These findings indicate again that increasing the density of CuN₃ will enhance simultaneously the catalytic performance for both ORR and OER. In particular, η_{OER} = 0.43 V is almost equal to that of 0.42 V for calculated RuO₂ catalysts.⁷⁶ Although the ORR performance of C₃N₃Cu (η_{ORR} = 0.71 V) is not as good as Pt/C with η_{ORR} = 0.45 V,⁷⁷ it is still comparable to some SACs reported previously, such as AgN₃/C (η_{ORR} = 0.75 V)²⁸

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ACS Omega http://pubs.acs.org/journal/acsomf Article 19798

ACS Omega 2022, 7, 19794−19803
and adsorbates. A lowered specie can be attributed to the weakened interaction of substrates involved in the RDS. Accordingly, it is easy to speculate that increasing the CuN₃ concentration weakens the interaction strength of substrates and accordingly a decrease in the free energy change of RDS, which resulted in lowered overpotentials, indicating enhanced catalytic performance. The nice correlation between ΔG*OH and ICOHP is shown in Figure 5f.

To unravel the underlying mechanism of the weakened binding affinity of substrates to *OH, it is straightforward to measure the intensity of Cu–O upon the adsorption of OH. To this end, we next performed crystal orbital Hamilton population (COHP) analysis⁷⁹ and then integrated values of COHP (ICOHP) below the Fermi level, which enabled us to quantitatively investigate the bond strength of Cu–*OH. A smaller value of ICOHP implies stronger binding strength and vice versa. We depicted in Figure 5b–e the COHP as well as the PDOS of the systems with *OH on 1-CuN₃, 2-CuN₃, 3-CuN₃, and C₃N₃Cu with the values of ICOHP of −2.58, −2.53, −2.44, and −2.38, respectively. This demonstrates that with an increase in the concentration of CuN₃ the ICOHP of Cu and *OH is increased, implying weakened interaction of the Cu site and *OH and accordingly a decrease in the free energy change of RDS, which resulted in lowered overpotentials, indicating enhanced catalytic performance. The nice correlation between ΔG*OH and ICOHP is shown in Figure 5f.

Inspired by the results of C₃N₃Cu, we next predicted 2D materials of CₙN₃M (M = Ni and Zn) and explored their catalytic performances as well. Interestingly, these two compounds are also thermodynamically and dynamically consistent with the trend of the density of the CuN₃ moiety in these systems. The unambiguous structure-property correlation inspired us to dig deeper into the mechanism of the weakened binding strength between *OH and substrates. (a) Linear relationship between the d-band center and ΔG*OH over 1-CuN₃, 2-CuN₃, 3-CuN₃, and C₃N₃Cu, respectively. (b–e) PDOS and the negative values of crystal orbital Hamilton populations (COHPs) of *OH on substrates with different densities of CuN₃. (f) Linear relationship between ICOHP and ΔG*OH over 1-CuN₃, 2-CuN₃, 3-CuN₃, and C₃N₃Cu, respectively.

Figure 5. Mechanism of the weakened binding strength between *OH and substrates. (a) Linear relationship between the d-band center and ΔG*OH over 1-CuN₃, 2-CuN₃, 3-CuN₃, and C₃N₃Cu, respectively. (b–e) PDOS and the negative values of crystal orbital Hamilton populations (COHPs) of *OH on substrates with different densities of CuN₃. (f) Linear relationship between ICOHP and ΔG*OH over 1-CuN₃, 2-CuN₃, 3-CuN₃, and C₃N₃Cu, respectively.
adsorbed O2 molecules. This leads to the adsorption energies of 0.77 and 0.11 Å for M = Ni and Zn, respectively. Similarly, H2O can also be chemically adsorbed on C3N3Ni and C3N3Zn with adsorption energies of −1.57 to −1.48 eV, respectively. The chemical bonds of O2 and substrates are also reflected by the charge transfers of 0.54 and 0.63 e from the substrates to adsorbed O2 molecules. This leads to the ΔdO−O values of 0.07 and 0.11 Å for M = Ni and Zn, respectively. Similarly, H2O can also be chemically adsorbed on C3N3Ni and C3N3Zn with adsorption energies of −0.71 and −0.81 eV, respectively, which involves the charge transfer from H2O to the substrates by 0.07 and 0.06 e for C3N3Ni and C3N3Zn, respectively. Regarding the catalytic performance, the calculated overpotentials are \( \eta_{\text{ORR}}^{\text{M}} = 1.29 \text{ V}/\eta_{\text{OER}} = 0.57 \text{ V for C3N3Ni and C3N3Zn, respectively. It shows that C3N3Ni can work as an efficient catalyst toward OER, which is illustrated in Figure S14.}

The relationship between the free energies of reaction intermediates (when \( U = 0 \)) was examined as well, aiming to explore the possible descriptor of activity. As shown in Figure 6a,b, one can see the fitted lines of \( \Delta G_{\text{OH}} \) vs \( \Delta G_{\text{O2}} \) and \( \Delta G_{\text{OH}} \) vs \( \Delta G_{\text{OOH}} \) with the linear relationships of \( \Delta G_{\text{O2}} = 0.77 \times \Delta G_{\text{OH}} + 1.74 \) and \( \Delta G_{\text{OOH}} = 0.95 \times \Delta G_{\text{OH}} + 3.28 \), respectively. These linear relationships reflect the similar feature of chemical bonds formed between reaction intermediates (\( \text{*OH, *OH2, and *O} \)) and substrates, which characterizes as a single Cu−*O bond. The RDS for ORR is the desorption of *OH to \( \text{OH}^− \), while the RDS for OER is the formation of *O from *OH. Accordingly, we prepared the activity volcano plots by considering the relationship of overpotentials vs \( \Delta G_{\text{OH}} \) for both ORR and OER, as shown in Figure S6c,d. The volcano plots indicate that the catalytic performances for ORR and OER of these systems containing MN3 moieties share a unique descriptor of \( \Delta G_{\text{OH}} \). Combined with Figure 6c,d, when \( \Delta G_{\text{OH}} \) is less than 0.80 eV, both overpotentials for the ORR and OER are in the left leg of the volcano plot, demonstrating that the performance of both reactions could be enhanced with weaker *OH adsorption intensity. The verification of this assumption requires additional calculations about the catalytic performances of C3N3M with M representing other metals.

4. CONCLUSIONS

The critical effect of the density of active sites on the electrocatalytic activity of CuN3 moiety toward both ORR and OER has been determined based on extensive DFT calculations. Our calculations demonstrate that the catalytic performance of CuN3 moiety can be gradually enhanced when increasing the concentration of it. We found that three connected CuN3 moieties become active for both ORR and OER as verified by the corresponding overpotentials of 0.91 and 0.48 V, respectively, much better than the performance of the single CuN3 moiety giving rise to overpotentials larger than 1.23 V. Given the fact that the conventional way of designing SACs is usually highly dependent on the doping strategy facing the challenge of precise control of high concentration and homogeneous distribution of active sites, the findings of enhanced ORR performance induced by high-density CuN3 inspired us to predict a 2D crystalline phase of C3N3Cu serving as a bifunctional catalyst for both ORR and OER exhibiting overpotentials of 0.71 and 0.43 V, respectively, which possesses superior electron conductivity and dynamical and thermodynamically stability. Furthermore, the enhanced catalytic performance is found to be attributed to the weakened
interactivity of OH* and substrates confirmed by the ICOHP calculations, characterizing the bonding strength. In addition, C3N3M with M = Ni and Zn has also been explored for their potential applications as catalysts for ORR and/or OER, where only C3N3Ni exhibits OER performance. The identification of bifunctional catalysts of C3N3Cu for ORR and OER containing high concentration and homogeneous distribution of CuN3 moiety without involving doping strategy and functional groups will guide the rational design of high-efficiency and low-cost electrocatalysts for other electrochemical reactions.

■ ASSOCIATED CONTENT

► Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01562.

Computational details, structural configurations of reaction intermediates of ORR and OER, AIMD simulations, and electronic properties of C3N3Ni and C3N3Zn (PDF)

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J.T. and Z.Z. contribute equally to this work who performed the calculations and wrote the initial manuscript. Z.Y. and Y.L. proposed the idea and provided the supervision. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

■ ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. U1801255, 51972350). The calculations were carried out using supercomputer “Tianhe-2” at NSCC Guangzhou.

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