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# Atomic-level modulation of electronic density of metal-organic frameworks-derived Co single-atom sites to enhance oxygen reduction performance

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Abstract: Tuning the electronic structure of single-atom active sites via engineering atomic configuration is an effective strategy to boost oxygen reduction reaction (ORR), but still remains challenging because of the lack of rational guidance and effective methods. Here, we demonstrate the correlation between atomic configuration induced electronic density of single-atom Co active sites and ORR performance by combining density functional theory (DFT) calculations and electrochemical analysis. Guided by DFT calculations, we design and synthesize a MOFs-derived Co singleatom catalyst with the optimal Co<sub>1</sub>-N<sub>3</sub>PS active moiety incorporated in hollow carbon polyhedron (Co1-N3PS/HC). As predicted, Co1-N<sub>3</sub>PS/HC exhibits outstanding alkaline ORR activity with a half-wave potential of 0.920 V and superior ORR kinetics with record-level kinetic current density and ultralow Tafel slope of 31 mV dec-1, exceeding the Pt/C and almost all non-precious ORR electrocatalysts. Even in more challenging acidic media, the ORR kinetics of Co1-N3PS/HC still surpasses that of Pt/C. This work offers an atomic-level insight into the relationship between electronic density of active site and catalytic property, promoting rational design of highly efficient catalysts.

#### Introduction

The commercial applications of energy conversion devices such as fuel cells and metal-air batteries are strongly dependent on highly efficient and cost-effective catalysts to drive electrochemical oxygen reduction reaction (ORR).<sup>[1]</sup> As a consequence, the exploration and development of efficient and durable non-precious metal catalysts as substitutes for the expensive and scarce Pt-based materials have attracted extensive research attention.<sup>[2]</sup> Metal-organic frameworks (MOFs) are a class of crystalline porous materials, featured with abundant porous structure, great designability and tunable functionality,<sup>[3]</sup> which have been considered as promising templates of metal-nitrogen-carbon (M-N-C) based ORR electrocatalysts.<sup>[4]</sup> Despite numerous efforts have been devoted

to engineer MOFs-derived M-N-C materials, their ORR catalytic performance are not good enough as the alternatives to Ptbased electrocatalysts.<sup>[5]</sup> One primary reason is the compositional and structural heterogeneity of M-N-C catalysts hinder the identification of exact active center and further enhancement on catalytic performance.<sup>[6]</sup>

Recently, single-atom catalysts (SACs) are emerging as a promising class of catalysts due to maximum atom-utilization efficiency and unique properties,<sup>[7]</sup> which have delivered excellent catalytic performance in a variety of important reactions.<sup>[8]</sup> Moreover, SACs exhibits great potential to serve as ideal platforms to identify and modulate the structure of active centers for enhanced catalytic performance.<sup>[9]</sup> Much progress has been made to reveal the intrinsic ORR activity of the active metal of SACs follows the order of Fe > Co > Cu > Mn > Ni.<sup>[10]</sup> However, the deleterious Fenton effect of Fe-based materials limits their practical applications.<sup>[11]</sup> Therefore, enhancing the ORR performance of Co-based SACs has regarded as an important target for the development of ORR electrocatalysts.

Currently, the active centers of the common M-N-C singleatom ORR electrocatalysts are the four-coordinated structure of M-N<sub>4</sub> moiety.<sup>[12]</sup> Some recent researches have demonstrated that the symmetrical planar structure results in the symmetric electronic distribution, which is not beneficial to the adsorption and activation of the ORR-relevant species, thereby leading to limited ORR kinetics and performance.[13] Owing to the difference on electronegativity of different coordination atoms (N, P, S etc.), modulating the types of coordination atoms of active metal centers is an effective and sensible strategy to break the symmetry of electronic density.<sup>[14]</sup> However, this strategy is rarely reported, due to the lack of reasonable guidance and effective methods to achieve the precise control over the types of coordination atoms at the atomic scale. Therefore, it is highly desirable to advance scientific understanding of atomic structure-property relationship and achieve atomic-level regulation of electronic structure of single-atom active sites for

enhanced ORR performance, but it still remains a grand challenge.

Here, we demonstrate the electronic density of single-atom Co active sites can be tailored through regulating atomic configuration by the modulation of the types of coordination atoms. Furthermore, the correlation between electronic density of active sites and ORR performance is revealed by density functional theory (DFT) calculations and electrochemical analysis. Directed by DFT calculations, we design the synthesis of MOFs-derived single-atom Co catalyst that comprises an optimal Co1-N3PS active moiety supported on hollow carbon polyhedron (Co1-N3PS/HC). The as-prepared Co1-N3PS/HC exhibits excellent alkaline ORR performance with outstanding half-wave potential (E1/2) of 0.920 V, which is 71 mV more positive than that of the commercial Pt/C. Moreover, the recordlevel kinetic current density  $(J_k)$  of 28.0 mA cm<sup>-2</sup> at 0.900 V and unexpectedly remarkable Tafel slope of 31 mV dec<sup>-1</sup> are accomplished over the Co1-N3PS/HC catalyst, far exceeding most known non-precious metal ORR catalysts. Furthermore, Co1-N3PS/HC also shows excellent ORR performance and stability in more challenging acidic media, whose E<sub>1/2</sub> of 0.790 V is closed to that of the Pt/C (0.798 V). The acidic ORR kinetics of Co<sub>1</sub>-N<sub>3</sub>PS/HC with a  $J_k$  of 25.8 mA cm<sup>-2</sup> at 0.775 V and a Tafel slope of 43 mV dec<sup>-1</sup> even outperform that of the Pt/C with a  $J_k$ of 10.0 mA cm<sup>-2</sup> at 0.775 V and a Tafel slope of 87 mV dec<sup>-1</sup>. Moreover, Co1-N3PS/HC based Zn-air battery demonstrates great battery performance and charge/discharge durability, suggesting the promising application in Zn-air battery. Experimental and DFT results reveal that the high reactivity and outstanding ORR kinetics are ascribed to unique electronic density of single-atom Co active sites.

#### **Results and Discussion**

To investigate the relationship between coordination structure induced electronic density and the four-electron ORR reaction energetics, seven different single-atom Co structural models of CoN<sub>4</sub>, CoN<sub>4</sub>@P<sub>2</sub>, CoN<sub>4</sub>@S<sub>2</sub>, CoN<sub>3</sub>P@P, CoN<sub>3</sub>S@S, CoN<sub>4</sub>@P<sub>2</sub>S<sub>2</sub>, CoN<sub>3</sub>PS@PS were firstly constructed and optimized by the density functional theory (DFT) simulations in Figure S1, in which one graphite N atom was introduced randomly on every model to balance the high elementary ratio of N in the real M-N-C based ORR electrocatalysts. For these models, the common accepted CoN<sub>4</sub> was initially chosen as the single-atom Co catalyst un-doped with heteroatoms. Then, two P or S atoms were introduced symmetrically into the two orthopositions of CoN<sub>4</sub> to form the CoN<sub>4</sub>@P<sub>2</sub> and CoN<sub>4</sub>@S<sub>2</sub> model, which represented the single-atom Co catalyst doped with nearrange P or S atom. After that, one of the atomic P or S in the model of  $CoN_4@P_2$  and  $CoN_4@S_2$  was transferred to coordinate with Co atom to form the new models of CoN<sub>3</sub>P@P and CoN<sub>3</sub>S@S, which represented the single-atom Co catalyst directly coordinated with P or S atom. Subsequently, via comparing the doping energy of P and S atom in CoN<sub>4</sub>@P<sub>2</sub> and CoN<sub>4</sub>@S<sub>2</sub> (Figure S2), it was found that the P atom was more stable than the S atom. Subsequently, on the basis of  $CoN_4@P_2$ , two S atoms were further introduced into the two ortho-positions of P atoms to form the CoN<sub>4</sub>@P<sub>2</sub>S<sub>2</sub> model (Figure S3), which represented the P and S atoms double doped single-atom Co catalyst, while the P and S atoms uncoordinated with Co atom. Furthermore, one of the two S atoms in CoN<sub>4</sub>@P<sub>2</sub>S<sub>2</sub> was transferred to coordinate with Co atom, while the other S atom was unchanged or changed to close to the transferred S atom to form different CoN<sub>3</sub>S@P<sub>2</sub>S (Figure S4); for comparison, other four models with different sites of P atoms were also constructed. Interestingly, it was found that, via structure optimizing, there were two CoN<sub>3</sub>S@P<sub>2</sub>S models that were distorted to form CoN<sub>3</sub>PS@PS, in which the Co atom coordinated with five atoms (3N, 1P and 1S), and the CoN<sub>3</sub>PS@PS-1 was the most stable structure.

Consequently, to study the effect of the introduced heteroatom (S and P) on the ORR activity, we calculated the associative ORR reaction mechanisms (Figure S5, the corresponding most stable intermediate structures of O2\*, OOH\*, O\* and OH\* are shown in Figures S6-S10) at the electrode potential of U = 1.23 V vs. reversible hydrogen electrode (RHE) on the seven models of CoN<sub>4</sub>, CoN<sub>4</sub>@P<sub>2</sub>, CoN<sub>4</sub>@S<sub>2</sub>, CoN<sub>3</sub>P@P,  $CoN_3S@S$ ,  $CoN_4@P_2S_2$  and  $CoN_3PS@PS$ , respectively. In view of the presence of positively charged heteroatoms such as P and S near the Co active site, the dissociative ORR reaction mechanisms (Figure S11, the corresponding most stable intermediate structures of  $O_2^*$ , 20\*,  $O_h^*$ +OH\*,  $O_h^*$  and  $OH_h^*$  are shown in Figures S12-S15, the suffixs of "h" represents the species is adsorbed on the top site of the heteroatom of P or S) were also calculated at U = 1.23 V on the six models with doped heteroatoms of P and/or S. For comparison, it has been clearly found that the first and third electrochemical steps of OOH\* formation ( $O_2^*$  +  $H^+$  +  $e^- \rightarrow OOH^*$ ) and  $OH_h^*$  formation ( $O_h^*$  +  $H^+$ +  $e^- \rightarrow OH_h^*$ ) for the associative and dissociative mechanisms are the rate determining steps on almost all these single-atom Co catalysts except for the dissociative mechanism of CoN<sub>3</sub>P@P, its rate determining step is the last electrochemical step of  $OH_h^*$  desorption ( $OH_h^* + H^+ + e^- \rightarrow H_2O + *$ ). By contrast, the CoN<sub>3</sub>PS@PS model has the lowest overpotential (η) of ORR both for the associative and dissociative mechanisms (Figure S5 and S11), and the former is much more favorable than the latter (0.58 V vs. 1.16 V). Besides, to get in-depth understanding, the barriers of  $O_2^*$  dissociation (Figure S16,  $O_2^* + * \rightarrow 20^*$ ) were calculated on the six models with doped heteroatoms of P and/or S. The calculation results show that, only on the three models of CoN<sub>4</sub>@P<sub>2</sub>, CoN<sub>4</sub>@P<sub>2</sub>S<sub>2</sub> and CoN<sub>3</sub>PS@PS-re, the O<sub>2</sub>\* might be able to be dissociated forming the Oh\* with a lower barrier (< 0.5 eV) at the room temperature, and all the three formed O atom are adsorbed on the top P atom uncoordinated with Co atom. Therefore, it can be reasonable concluded that although there may be some O<sub>h</sub>\* adsorbed on the top of P atom, the associative mechanism still is the major ORR reaction pathway on these single-atom Co catalysts, and the model of CoN<sub>3</sub>PS@PS has the highest ORR activity.

For the associative mechanism, there is a parabolic relationship (Figure 1a) for the overpotential ( $\eta$ ) of ORR as a function of the O<sub>2</sub>\* adsorption energy ( $\Delta G_{O2}$ ), in which the single-atom Co active center coordinated by 3N, P and S atoms has the highest ORR activity ( $\eta$  = 0.58 eV) and lowest  $\Delta G_{O2}$  (0.02

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eV), while the Co active center only coordinated by 4N atoms (CoN<sub>4</sub>) has the lowest ORR activity ( $\eta = 1.02 \text{ eV}$ ) and highest  $\Delta G_{O2}$  (-0.30 eV). For the other five models, the Co active center coordinated either by 4N atoms (CoN<sub>4</sub>@P<sub>2</sub>, CoN<sub>4</sub>@S<sub>2</sub> and CoN<sub>4</sub>@P<sub>2</sub>S<sub>2</sub>), or by 3N atoms and only one heteroatom (CoN<sub>3</sub>P@P and CoN<sub>3</sub>S@S), although the  $\Delta G_{O2}$  can be reduced (-0.27 ~ -0.06 eV), the overpotentials are still similar with the CoN<sub>4</sub>, indicating only the synergistic coordination of P and S atoms can promote the ORR activity of the single-atom Co active center.



**Figure 1.** DFT study for the ORR activity on different single-atom Co catalysts. (a) The linear relationship for ORR activity (i.e. the overpotential) as a function of the  $O_2^*$  adsorption energy ( $\Delta G_{O2}$ ) at U<sup>RHE</sup> = 1.23 V; in the inserted model structures, the Co, N, P and S atoms are in cyan, blue, pink and yellow, the carbon layer is given in the grey stick. (b) The inverse volcances of ORR overpotential for the Bader charge of active center Co atom, the negative value represents electron donation. (c) The charge density difference of Co atom in the seven catalyst models, the red and blue represents electron increase and decrease, respectively, the units for the color scale bar is a.u.<sup>-3</sup>. (d) The partial density of states (pDOS) of Co atom in the models, the d-band center is inserted with the red font and line.

With that, to evaluate the electronic control effects of all the seven models of single-atom Co catalysts, we analyzed the Bader charge (Figure 1b), charge density differences (Figure 1c and Figure S17) and partial density of states (pDOS, Figure 1d) of the active center Co atom, as well as the Bader charge of the other elements in these models (Table S1). The electronic property analysis reveals that almost all the charge of N atoms are negative (N<sup> $\delta$ -</sup>), while the charge of P and S atoms in these models are positive (P/S<sup> $\delta$ +</sup>) except for the S atom coordinated with Co atom in CoN<sub>3</sub>PS@PS, suggesting the N atoms in the single-atom Co catalysts are the electron acceptor, but the P and S atoms are the electron donor, which finally leads to the positive charge of metal center Co (Co<sup> $\delta$ +</sup>). Interestingly, Figure 1b shows that the overpotential of ORR has the inverse volcanic

relationship with the Bader charge of active center Co atom, the highest active model of CoN<sub>3</sub>PS@PS has the moderate charge of  $Co^{\delta^+}$ . In other words, the appropriate charge of  $Co^{\delta^+}$  in CoN<sub>3</sub>PS@PS model turned by synergistic coordination of P and S atoms can display the excellent ORR performance. In Figure 1c, the charge density differences of the active center Co atom show that there are obvious different charge distributions of these models. Compare with the perfectly symmetric electron structure of CoN<sub>4</sub>, some red area appears in the carbon layer of  $CoN_4@P_2$  and  $CoN_4@S_2$ , the blue area of the center  $CoN_4$ moiety in these two models become narrowed slightly, and meanwhile the charge of Co atom in CoN4@S2 is reduced slightly (0.811 vs. 0.862), indicating the electron can transfer from P and S atoms to the carbon layer and then to the Co atom. However, because of the symmetry of the two P and S atoms in CoN<sub>4</sub>@P<sub>2</sub> and CoN<sub>4</sub>@S<sub>2</sub>, the charge distributions are not broken in these two models. In CoN<sub>3</sub>P@P and CoN<sub>3</sub>S@S model, when one of heteroatom is transferred to coordinate with Co atom, the blue area of the center CoNx moiety becomes narrowed obviously, the charge of Co atom is further reduced (0.703 and 0.677), and meanwhile the symmetry of the charge distribution is broken. Moreover, the continued introducing of P and S leads to the asymmetrical charge distribution of  $CoN_4@P_2S_2$  and CoN<sub>3</sub>PS@PS. Relatively, because of the direct coordination between P, S and Co atom, the charge of Co atom in the model of CoN<sub>3</sub>PS@PS is decreased more than that in the CoN<sub>4</sub>@P<sub>2</sub>S<sub>2</sub> (0.768 vs. 0.838), and the charge distribution is more asymmetry. In Figure 1d, the pDOS analysis shows that the d-band center of Co atom can be reduced dramatically from 0.86 eV (CoN<sub>4</sub>) to -1.98 eV (CoN<sub>3</sub>PS@PS) by the synergistic coordination of P and S atoms, and the effect of the S atom is more obvious (-0.07 vs. 0.36 eV, and -0.64 vs. -0.23 eV). Thus, it is inferred that the introducing of heteroatom P and S for synergistic coordination can modulate the electronic structure of active center Co atom, evoke the distortion of electronic density, break the symmetry of Co-N<sub>4</sub> moiety, and reduce the d-band center of the active center Co atom. And then, the overpotential of ORR is reduced on the single-atom Co catalysts. In summary, a rational design strategy of single-atom Co catalysts for ORR is developed, which achieves the optimal electronic density distribution to enhance ORR activity and kinetics through modulating slightly the coordination and electronic structure surrounding the metal center Co-N<sub>4</sub> moiety by synergistic coordination of the heteroatom of P and S.

In light of the excellent ORR performance of CoN<sub>3</sub>PS@PS model through DFT studies, we developed a MOFs-derived twostep pyrolysis strategy to prepare a unique single-atom Co catalyst with an optimal Co-N<sub>3</sub>PS active configuration supported on hollow carbon polyhedron (Co<sub>1</sub>-N<sub>3</sub>PS/HC). The synthetic scheme of Co<sub>1</sub>-N<sub>3</sub>PS/HC catalyst is illustrated in Figure 2a.

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Figure 2. Synthesis and structural characterizations of Co<sub>1</sub>-N<sub>3</sub>PS/HC. (a) Scheme of the synthesis of Co<sub>1</sub>-N<sub>3</sub>PS/HC. (b) TEM and (c) HAADF-STEM images of Co<sub>1</sub>-N<sub>3</sub>PS/HC. (d) Enlarged HAADF-STEM image and the corresponding EDS mappings of Co<sub>1</sub>-N<sub>3</sub>PS/HC. (e) AC HAADF-STEM image and (f) enlarged intensity image of Co<sub>1</sub>-N<sub>3</sub>PS/HC. (g) Intensity profiles of Co<sub>1</sub>-N<sub>3</sub>PS/HC obtained in the dotted rectangle region 1# and 2# in (f).

The highly cross-linked poly(cyclotriphospazene-co-4,4'sulfonyldiphenol)(PZS) coated zeolitic imidazolate framework (ZIF-8) core-shell composites (ZIF-8@PZS) was firstly pyrolysed at 650 °C under an Ar atmosphere to form nitrogen, phosphorus and sulfur co-doped hollow carbon polyhedron (NPS-HC-650) sample (Figure S18). The formation procedure of hollow structure follows a Kirkendall effect.<sup>[15]</sup> The interdiffusion between the S<sup>2-</sup> ion from PZS shell and Zn<sup>2+</sup> ion from ZIF-8 core occurs during this process. Because the ionic radius of Zn2+ ion is smaller than that of S<sup>2-</sup> ion, the outward transport of Zn<sup>2+</sup> ion is faster compared with the inward transport of S2- ion. The continuous unequal interdiffusion leads to the appearance of Kirkendall voids and then generates hollow structure. Similar to the S species, the P species from PZS shell also diffuses into and uniformly disperses over the entire hollow NPS-HC-650 architecture (Figure S19). Subsequently, the cobalt precursor was added, which can absorb on hierarchical pore on the NPS-HC-650 (Co/NPS-HC-650). Followed by the pyrolysis of

Co/NPS-HC-650 at 950  $^{\circ}\text{C}$  under an Ar atmosphere, the final Co $_1\text{-}N_3\text{PS/HC}$  catalyst was obtained.

The transmission electron microscopy (TEM) image demonstrates that Co<sub>1</sub>-N<sub>3</sub>PS/HC displays a hollow polyhedral morphology with uniform size (Figure 2b). The high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) shows the shell thickness of Co1-N3PS/HC hollow structure is about 20 nm. And no obvious nanoparticles are observed (Figure 2c). Energy-dispersive spectroscopy (EDS) mappings of Co<sub>1</sub>-N<sub>3</sub>PS/HC reveal the presence of Co, C, N, P and S elements (Figure 2d and Figure S20). To investigate the dispersion state of Co species at the atomic scale, the aberration-corrected HAADF-STEM (AC HAADF-STEM) measurement was carried out. As shown in Figure 2e and 2f, several isolated bright dots associated with single Co atoms (marked by white circles) are clearly distinguished from heteroatoms-doped carbon matrix. The atomic dispersion of Co species in Co1-N3PS/HC is further confirmed by the analysis of intensity profiles (Figure 2g).

Powder X-ray diffraction (XRD) pattern of Co1-N3PS/HC exhibits only one broad peak at approximate 25° (2 theta) indexed to the (002) plane of the graphitic carbon, which is similar with that of NPS/HC that derived from Co-free PZS@ZIF-8 (Figure S21). And no typical peaks ascribed to crystalline Co species are observed, excluding the existence of Co-related nanoparticles. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the Co content in Co1-N3PS/HC as 0.39 wt%. In order to investigate the chemical state of C, N, P and S elements in Co1-N3PS/HC, X-ray photoelectron spectroscopy (XPS) analysis was performed. And the element atomic contents of the Co1-N3PS/HC are shown in the Figure S22. As shown in Figure S23, the C 1s spectrum can be fit well with four peaks at the binding energy of 284.8 eV, 288.1 eV, 285.8 eV and 284.6 eV, assigned to graphitic C=C, C-N, C-P and C-S, respectively. The N 1s spectrum in Figure S24 exhibits five peaks, which are indexed to pyridinic N (398.6 eV), pyrrolic N (400.2 eV), graphitic N (401.5 eV), oxidized N (403.8 eV) and Co-N (399.1 eV). The P 2p spectrum demonstrates the co-existence of four peaks at the binding energy of 132.7 eV, 133.9 eV, 129.5 eV and 130.4 eV, corresponding to P-C, P-O and 2p<sub>3/2</sub>, 2p<sub>1/2</sub> splitting of Co-P (Figure S25). The S 2p spectrum can be deconvoluted into five peaks at 164.0 eV, 165.3 eV, 168.3 eV, 161.9 eV and 163.1 eV, associated with the 2p<sub>3/2</sub>, 2p<sub>1/2</sub> splitting of the S 2p spin orbital (-C-S-C-), oxidized S and the  $2p_{3/2}$ ,  $2p_{1/2}$  splitting of Co-S, respectively (Figure S26).

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**Figure 3.** Atomic structural analysis of  $Co_1-N_3PS/HC$ . (a) Co K-edge FT-EXAFS spectra of  $Co_1-N_3PS/HC$  and reference samples. (b) Co K-edge WT-EXAFS contour plots of  $Co_1-N_3PS/HC$  and reference samples. (c) Co K-edge EXAFS fitting analysis of  $Co_1-N_3PS/HC$  in *R* space and (d) *k* space. (e) Comparison between the experimental FT-EXAFS spectra (purple line) and theoretically simulated FT-EXAFS spectra (red line) of  $Co_1-N_3PS/HC$  based on DFT model of the inset. (f) Co K-edge XANES spectra and (g) first derivative curves of  $Co_1-N_3PS/HC$  and reference samples. (h) Comparison between the experimental XANES spectra (purple line) and theoretically simulated T-EXAFS spectra (purple line) and theoretically simulated XANES spectra (red line) of  $Co_1-N_3PS/HC$  based on DFT model of the inset.

Synchrotron-radiation-based X-ray absorption fine structure (XAFS) measurements were conducted to confirm the local structure of Co<sub>1</sub>-N<sub>3</sub>PS/HC. As shown in Figure 3a, the Fourier transformed (FT) extended X-ray absorption fine structure (FT-EXAFS) of Co1-N3PS/HC exhibits one major peak at about 1.4 Å and one shoulder peak at about 1.8 Å. In comparison with the FT-EXAFS spectra of cobalt phthalocyanine (CoPc) and cobalt oxide (Co<sub>3</sub>O<sub>4</sub>), which are assigned to the backscattering between Co and light atoms (N, P, S etc.). The FT-EXAFS peak at 2.2 Å from Co foil is associated with Co-Co coordination. The absence of Co-Co scattering path in Co<sub>1</sub>-N<sub>3</sub>PS/HC demonstrates that Co species exist as the isolated single atoms. To further confirm the atomic dispersion of Co species in Co1-N<sub>3</sub>PS/HC, the wavelet transform (WT) analysis was performed, which can discriminate the backscattering atoms and offer the powerful resolution in both R and k spaces. As shown in Figure 3b, the WT contour plot of Co1-N3PS/HC exhibits one intensity

maximum at approximately 3.4 Å<sup>-1</sup>, which is close to the intensity maximum of CoPc and the first-shell intensity maximum of Co<sub>3</sub>O<sub>4</sub>, suggesting it can be attributed to the contribution from the backscattering between Co and light atoms. Additionally, compared with Co foil, the intensity maximum at approximately 6.8 Å<sup>-1</sup> ascribed to Co-Co coordination is not observed in Co<sub>1</sub>-N<sub>3</sub>PS/HC. The above results well confirm that Co species are atomically dispersed in Co<sub>1</sub>-N<sub>3</sub>PS/HC without the existence of metal-derived crystalline structures.

Quantitative least-squares EXAFS curve-fitting analysis was carried out to investigate the coordination configuration. The best-fitting result of Co<sub>1</sub>-N<sub>3</sub>PS/HC clearly demonstrates the major peak at 1.4 Å and one shoulder peak at 1.8 Å are attributed to superimposition of Co-N, Co-P and Co-S first-shell coordination (Figure 3c, 3d and Figure S27). The structural parameters were further extracted. The corresponding

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coordination numbers of N, P and S are estimated to be 3.1, 0.9 and 1.1 with the average bond lengths of 1.97 Å, 2.32 Å and 2.34 Å, respectively, which suggests a single-atom  $Co_1-N_3PS$ moiety. The first-shell EXAFS curve-fitting results of CoPc,  $Co_3O_4$  and Co foil are also shown in Figure S28-S30 and Table S2. The average bond lengths and coordination numbers of the synthesized  $Co_1-N_3PS/HC$  are close to those of the DFT model of  $CoN_3PS@PS$  (Table S3), indicating the optimal  $Co_1-N_3PS$ active moiety is prepared. To further confirm it, we performed theoretical simulation to reproduce the corresponding EXAFS spectra of the  $Co_1-N_3PS/HC$  catalyst based on the structural models of  $CoN_3PS@PS$  that optimized by DFT calculations. As shown in Figure 3e, the theoretically simulated EXAFS spectra are in good agreement with the experimental EXAFS spectra.

X-ray absorption near-edge structure (XANES) spectroscopy can reflect the electronic structure of center metal. Figure 3f displays the XANES curves of  $Co_1$ -N<sub>3</sub>PS/HC and reference

samples. The atomically dispersed Co species in Co1-N3PS/HC carry partially positive charges, which is determined by comparison of the first derivative XANES curves of Co1-N<sub>3</sub>PS/HC with reference samples (Figure 3g). Moreover. XANES spectroscopy possesses a much high sensitivity to the three-dimensional arrangement of atoms around center metal, which is a powerful tool to identify the atomic configuration. Therefore, we carried out XANES theoretical calculation and found that the XANES profile of Co1-N3PS/HC can be well reproduced by the structure of CoN<sub>3</sub>PS@PS moiety from the above DFT calculations (Figure 3h). The above XAFS analysis results as well as the element atomic content analysis by XPS and EDS mappings well confirm that the Co single-atom catalyst with the optimal Co1-N3PS moiety is synthesized, which has great potential to achieve highly efficient ORR performance, as predicted by the DFT calculations.



**Figure 4.** Electrocatalytic alkaline ORR performance of Co<sub>1</sub>-N<sub>3</sub>PS/HC. (a) ORR polarization curves of Co<sub>1</sub>-N<sub>3</sub>PS/HC and reference catalysts in 0.1 M KOH. (b) Comparison of  $J_k$  at 0.90 V and  $E_{1/2}$  of Co<sub>1</sub>-N<sub>3</sub>PS/HC and reference catalysts. (c) Tafel plots of Co<sub>1</sub>-N<sub>3</sub>PS/HC and reference catalysts. (d) Comparison of  $E_{onset}$  and  $E_{1/2}$  of Co<sub>1</sub>-N<sub>3</sub>PS/HC and the previously reported Co based catalysts and other non-precious metal catalysts in Table S4. (e) Electron transfer numbers (top) and H<sub>2</sub>O<sub>2</sub> yield of Co<sub>1</sub>-N<sub>3</sub>PS/HC. (f) Electrochemical double-layer capacitance (C<sub>dl</sub>) of Co<sub>1</sub>-N<sub>3</sub>PS/HC and reference catalysts. (g) Tolerance to methanol of Co<sub>1</sub>-N<sub>3</sub>PS/HC compared with 20% Pt/C at 0.70 V. Methanol is injected into the 0.1 M KOH solution at the time of 200 s. (h) ORR polarization curves of Co<sub>1</sub>-N<sub>3</sub>PS/HC before and after 10000 potential cycles. Inset is AC HAADF-STEM image of Co<sub>1</sub>-N<sub>3</sub>PS/HC after durability test.

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The rotating disk electrode (RDE) technique was employed to assess the ORR activity of Co1-N3PS/HC in O2-saturated 0.1 M KOH. As shown in Figure 4a, the linear sweep voltammetry (LSV) measurements demonstrate that Co1-N3PS/HC exhibits the most positive onset potential of 1.00 V. And Co1-N3PS/HC also shows excellent ORR activity in term of outstanding halfwave potential ( $E_{1/2}$ ) of 0.920 V, which is 71 mV more positive than that of the state-of-art commercial Pt/C ( $E_{1/2} = 0.849$  V). Moreover, Co1-N3PS/HC exhibits the record-value kinetic current density  $(J_k)$  of 28.0 mA cm<sup>-2</sup> at 0.90 V, which is 30 times higher than that of Pt/C (Figure 4b). As shown in Figure 4c, the ultralow Tafel value of 31 mV dec<sup>-1</sup> is observed over Co<sub>1</sub>-N<sub>3</sub>PS/HC. The record-value kinetic current density and unexpectedly outstanding Tafel value of Co1-N3PS/HC suggests that the ORR kinetics achieves a remarkable enhancement over Co1-N3PS/HC compared with the commercial Pt/C. Figure 4d and Table S4 show the comparison of alkaline ORR performance between Co1-N3PS/HC and previously reported non-precious ORR electrocatalysts, demonstrating Co<sub>1</sub>-N<sub>3</sub>PS/HC is one of the best alkaline ORR electrocatalysts in term of onset potential, halfwave potential, kinetic current density and Tafel value. Moreover, the ORR pathway of Co<sub>1</sub>-N<sub>3</sub>PS/HC was evaluated by the RDE measurements at various rotation rates (Figure S31a). As shown in Figure S31b, the corresponding Koutecky-Levich (K-L) plot is linear, suggesting Co1-N3PS/HC demonstrates the first-order reaction kinetics toward the concentration of dissolved oxvgen. Based on the K-L equation, the value of electron-transfer number (n) is calculated to be in the range from 3.93 to 3.99 over the potential range from 0.3 to 0.7 V. This result is close to the theoretical value of 4 for the four-electron ORR pathway. Furthermore, rotating ring disk electrode (RRDE) measurement was performed, which demonstrates H<sub>2</sub>O<sub>2</sub> yield of Co<sub>1</sub>-N<sub>3</sub>PS/HC maintains below 3.5 wt% over the potential range from 0.3 to 0.9 V with the corresponding high electron-transfer number of 3.93-3.98 (Figure 4e), indicating Co1-N3PS/HC catalyzes ORR via a highly efficient and four-electron process.

To investigate the effect of single Co atoms on ORR performance, the cobalt-free N, P, S co-doped hollow carbon polyhedron (NPS/HC) material was prepared and characterized (Figures S32-S34). The NPS/HC catalyst shows an obviously lower ORR activity with a negatively shifted  $E_{1/2}$  of 0.825 mV, and more sluggish ORR kinetics with extremely low kinetic current density of 0.287 mA cm<sup>-2</sup> at 0.90 V and large Tafel value of 70 mV dec-1. The above results reveal the crucial role of single Co atoms in enhancing ORR performance. To reveal the effect of synergistic P and S coordination of Co<sub>1</sub>-N<sub>3</sub>PS/HC on ORR performance, we synthesized the single Co atoms with Co<sub>1</sub>N<sub>4</sub> coordination active center supported on N, P, S co-doped hollow carbon polyhedron (Co1-N4/HC) catalyst (Figures S35-S38). The content of Co in the Co<sub>1</sub>-N<sub>4</sub>/HC catalyst is determined as 0.42 wt% by the ICP-OES measurement. The FT-EXAFS curve of  $Co_1-N_4/HC$  displays only one main peak at about 1.5 Å, which is similar with that of CoPc, indicating that the main peak is assigned to Co-N coordination. And no peaks associated with Co-P and Co-S coordinations as well as Co-Co coordination are detected, suggesting the Co species in Co1-N4/HC are atomically dispersed and coordinated by N species (Figure S39 and S40). Co1-N4/HC exhibits a half-wave potential of 0.876 mV, which is 44 mV more negative than that of Co1-N3PS/HC, indicating lower ORR activity of Co1-N4/HC. And, the kinetic current density of Co1-N3PS/HC at 0.90 V outperforms than that of  $Co_1-N_4/HC$  by a factor of 21. In comparison to  $Co_1-N_4/HC$ , the obviously higher kinetic current density and smaller Tafel value of Co1-N3PS/HC reveal that the better ORR kinetics is achieved over Co1-N3PS/HC. Raman spectra demonstrate that Co1-N<sub>3</sub>PS/HC has higher degree of graphitization compared with NPS-HC, which is beneficial to the electrical conductivity for enhanced electrochemical performance (Figure S41). Furthermore, Co1-N3PS/HC exhibits highest electrochemical double-layer capacitance (C<sub>dl</sub>) of 98 mF cm<sup>-2</sup> than that of NPS-HC (61 mF cm<sup>-2</sup>) and Co<sub>1</sub>-N<sub>4</sub>/HC (63 mF cm<sup>-2</sup>), indicating the existence of N, P, S synergistic coordinated Co atomic sites facilitates to increase the electrochemically active surface area (ESCA) (Figure 4f and Figures S42-S44). Moreover, we analyzed and compared the compositions of the Co<sub>1</sub>-N<sub>3</sub>PS/HC, Co<sub>1</sub>-N<sub>4</sub>/HC and NPS-HC catalysts by combining ICP-OES, XPS and EDS map sum spectra (Tables S5-S7), suggesting the element contents as well as the ratio of N, P and S of these three catalysts are similar with each other. The above results demonstrate that the outstanding ORR performance of Co1-N<sub>3</sub>PS/HC is attributed to atomic dispersion of Co species and unique structure of active center with synergistic N, P and S coordination, as further supported by the remarkable enhancement of Co1-N3PS/HC on mass activity (MA) and turnover frequency (TOF) in comparison to other reported single-atom ORR catalysts (Table S8).

The tolerance to methanol crossover and durability of electrocatalysts are of great importance for practical applications. The methanol tolerance of Co1-N3PS/HC was evaluated by injecting methanol solution during the chronoamperometric measurement. As shown in Figure 4g, Co1-N3PS/HC still maintains a stable current density after methanol injection. In contrast, the commercial Pt/C exhibits a sharp jump of current density ascribed to the occurrence of methanol oxidation. These results reveal that Co1-N3PS/HC possesses excellent tolerance to methanol crossover. Moreover, we conducted accelerated durability test (ADT) to investigate the long-term durability of Co1-N3PS/HC. As shown in Figure 4h, no obvious decay in halfwave potential of Co1-N3PS/HC is observed even after 10000 continuous cycles, revealing that Co1-N3PS/HC exhibits a superior long-term durability. After durability tests, the hollow polyhedral morphology of the used Co1-N3PS/HC still remains (Figure S45), and the XRD pattern of the used Co<sub>1</sub>-N<sub>3</sub>PS/HC is similar with that of the fresh Co<sub>1</sub>-N<sub>3</sub>PS/HC (Figure S46), demonstrating outstanding structural robustness. Further observations in EDS mapping and AC HAADF-STEM image reveal that the atomic dispersion of Co species in Co<sub>1</sub>-N<sub>3</sub>PS/HC is well preserved (Figure S47 and Figure 4h). These results disclose that Co<sub>1</sub>-N<sub>3</sub>PS/HC has an excellent stability.

We also evaluated acidic ORR performance of Co<sub>1</sub>-N<sub>3</sub>PS/HC in 0.5 M H<sub>2</sub>SO<sub>4</sub>. As shown in Figure 5a, Co<sub>1</sub>-N<sub>3</sub>PS/HC exhibits excellent acidic ORR performance in term of outstanding an E<sub>1/2</sub> of 0.790 V, which is comparable to that of the commercial Pt/C (0.798 V). Furthermore, Co<sub>1</sub>-N<sub>3</sub>PS/HC shows better acidic ORR kinetics with a larger  $J_k$  of 25.8 mA cm<sup>-2</sup> at 0.775 V and a smaller

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Tafel slope of 43 mV dec<sup>-1</sup> compared with Pt/C with a  $J_k$  of 10.0 mA cm<sup>-2</sup> at 0.775 V and a Tafel slope of 87 mV dec<sup>-1</sup> (Figure 5b and 5c). It can be seen that Co<sub>1</sub>-N<sub>4</sub>/HC and NPS/HC show obviously poor acidic ORR performance, suggesting the excellent acidic ORR performance of Co<sub>1</sub>-N<sub>3</sub>PS/HC is attributed to atomically dispersed Co active sites and unique atomic configuration with N, P and S synergistic coordination. As displayed in Table S9, the acidic ORR performance of Co<sub>1</sub>-N<sub>3</sub>PS/HC outperforms those of most of the previously reported non-precious acidic ORR electrocatalysts.



**Figure 5.** Electrocatalytic acidic ORR performance of Co<sub>1</sub>-N<sub>3</sub>PS/HC. (a) ORR polarization curves of Co<sub>1</sub>-N<sub>3</sub>PS/HC and reference catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub>. (b) Comparison of  $J_k$  at 0.775 V and  $E_{1/2}$  of Co<sub>1</sub>-N<sub>3</sub>PS/HC and reference catalysts. (c) Tafel plots of Co<sub>1</sub>-N<sub>3</sub>PS/HC and reference catalysts. (d) ORR polarization curves of Co<sub>1</sub>-N<sub>3</sub>PS/HC before and after 10000 potential cycles in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

The LSV curves of Co1-N3PS/HC at different rotation rates were recorded and the corresponding K-L plots were obtained (Figure S48 and S49). The electron transfer number of Co<sub>1</sub>-N<sub>3</sub>PS/HC in acidic media was estimated as 3.93-4.02 based on K-L equation. Moreover, we carried out the RRDE tests, which demonstrates the H<sub>2</sub>O<sub>2</sub> yield of Co<sub>1</sub>-N<sub>3</sub>PS/HC maintains below 2.7 % in the potential range from 0.1 to 0.6 V associated with the high electron-transfer number of 3.945-3.955 (Figure S50). In comparison, the H<sub>2</sub>O<sub>2</sub> yield of Pt/C remains below 2.2 % and the corresponding electron transfer number is calculated as 3.955-3.970. The above results well suggest Co<sub>1</sub>-N<sub>3</sub>PS/HC undergoes a high-efficient 4e<sup>-</sup> catalytic process. In addition to excellent acidic ORR activity, Co1-N3PS/HC also exhibits great tolerance to methanol. As shown in Figure S51, there is no obvious change in CV curves of Co1-N3PS/HC after the injection of methanol. For comparison, the typical oxygen reduction peak becomes weaker and an inverse peak associated with methanol oxidation appears in the CV curves of the Pt/C when methanol is added into acidic electrolyte (Figure S52). The great stability for ORR electrocatalysts in acidic media is urgently needed. As shown in Figure 5d, Co1-N3PS/HC exhibits an enhanced stability with a small  $E_{1/2}$  loss of only 12 mV in half-wave potential after 10000 potential cycles test in 0.5 M H<sub>2</sub>SO<sub>4</sub>, compared with the typical PANI-derived Fe-N-C with a  $E_{1/2}$  loss of 80 mV after 5000 cycles.<sup>[16]</sup> The above results well reveal that Co<sub>1</sub>-N<sub>3</sub>PS/HC delivers excellent acidic ORR performance. After potential cycles in acidic media, the structure and atomic dispersion of Co species of Co<sub>1</sub>-N<sub>3</sub>PS/HC catalyst well maintain (Figures S53-S55), suggesting the excellent stability in acidic media.



**Figure 6.** Zn-air battery performance of Co<sub>1</sub>-N<sub>3</sub>PS/HC. (a) Schematic diagram of Zn-air battery. (b) Discharge polarization curves and power density plots of Co<sub>1</sub>-N<sub>3</sub>PS/HC and Pt/C based Zn-air battery. (c) Specific discharging capacities of Co<sub>1</sub>-N<sub>3</sub>PS/HC and Pt/C based Zn-air battery at 10 mA cm<sup>-2</sup>. (d) Galvanostatic discharge-charge cycling curves of Co<sub>1</sub>-N<sub>3</sub>PS/HC based Zn-air battery.

To demonstrate the potential application of Co1-N3PS/HC catalyst in energy conversion devices, we employed Co1-N<sub>3</sub>PS/HC as the catalyst of air cathode and Zn foil as the anode with 6 M KOH electrolyte to assemble the Zn-air battery (Figure 6a). Co<sub>1</sub>-N<sub>3</sub>PS/HC based Zn-air battery shows an open-circuit voltage of 1.47 V, which is higher than that of Pt/C+RuO<sub>2</sub> based Zn-air battery (Figure S56). And a higher discharge current and an obvious shrunken discharge-charge voltage gap are accomplished in the Co1-N3PS/HC based Zn-air battery compared to the values of Pt/C+RuO<sub>2</sub> based Zn-air battery, indicating the higher activity of the Co1-N3PS/HC catalyst enabling better rechargeability (Figure S57). As shown in Figure 6b, Co1-N3PS/HC based Zn-air battery also exhibits an excellent maximum powder density of 176 mW cm<sup>-2</sup> at a current density of 280 mA cm<sup>-2</sup>, which are both higher than those (117 mW cm<sup>-2</sup>, 183 mA cm<sup>-2</sup>) of Pt/C based Zn-air battery. The specific capacity of the Co1-N3PS/HC based Zn-air battery achieves as high as 786 mA h g<sup>-1</sup> at the discharge current density of 10 mA cm<sup>-2</sup>, which is larger than that (744 mA h g<sup>-1</sup>) of Pt/C based Zn-air battery (Figure 6c). As listed in Table S10, the Zn-air performance of Co1-N3PS/HC as the catalyst of air cathode surpasses most of reported catalysts. As shown in the inset of Figure 6c, two Co<sub>1</sub>-N<sub>3</sub>PS/HC based Zn-air batteries in series can easily power a blue light-emitting diode (LED) panel displaying "Zn air". Moreover, we carried out galvanostatic charge and discharge measurements to evaluate the rechargeability and cyclic stability of Co1-N3PS/HC based Zn-air battery. As shown in Figure 6d, no obvious increase in the charge/discharge

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voltage gap is detected even after 50 h charge/discharge cycling test, indicating the excellent rechargeability and long-term cyclic stability of the  $Co_1-N_3PS/HC$  based Zn-air battery.

#### Conclusion

In summary, we demonstrate that ORR performance of Co single-atom catalyst can be tuned and optimized by precise control of atomic configuration of active sites based on DFT calculations and electrochemical analysis. Guided by DFT calculations, a two-step pyrolysis strategy is developed to fabricate single-atom Co sites catalyst with the optimized Co-N<sub>3</sub>PS active moiety. The atomic configuration of Co<sub>1</sub>-N<sub>3</sub>PS/HC is confirmed by a series of advanced characterization techniques, including XPS analysis, AC HAADF-STEM and XAFS measurements. Co1-N3PS/HC exhibits highly efficient ORR reactivity and remarkable ORR kinetics as well as good methanol tolerance and excellent stability in both alkaline and acid media, which outperforms the commercial Pt/C and most of known non-precious electrocatalysts. Furthermore, Co1-N<sub>3</sub>PS/HC based Zn-air battery shows outstanding battery performance and long-term charge/discharge durability. demonstrating the great potential application. According to the designed control experiments and DFT calculations, we confirm the crucial role of optimized electronic density of atomically dispersed Co active centers induced by unique N, P and S atoms synergistic coordination in the remarkable enhancement on ORR performance. This work advances the scientific understanding of the correlation between the electronic density of atomic sites and ORR performance, which will provide new opportunities for rational design and optimization of catalysts.

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# RESEARCH ARTICLE

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The correlation between atomic configuration induced electronic density of singleatom Co active sites and oxygen reduction reaction (ORR) performance has been established by combing density functional theory calculations and electrochemical analysis. Directed by this correlation, we design the synthesis of MOFs-derived single-atom Co catalyst that comprises an optimal Co<sub>1</sub>-N<sub>3</sub>PS active moiety supported on hollow carbon polyhedron (Co<sub>1</sub>-N<sub>3</sub>PS/HC), which exhibits superior alkaline and acidic ORR performance. Yuanjun Chen,<sup>[a],‡</sup> Rui Gao,<sup>[b],‡</sup> Shufang Ji,<sup>[a]</sup> Haijing Li,<sup>[c]</sup> Kun Tang,<sup>[d]</sup> Peng Jiang,<sup>[a]</sup> Haibo Hu,<sup>[d]</sup> Zedong Zhang,<sup>[a]</sup> Haigang Hao,<sup>[b]</sup> Qingyun Qu,<sup>[a]</sup> Xiao Liang,<sup>[a]</sup> Wenxing Chen,<sup>[e]</sup> Juncai Dong,<sup>[c]</sup> Dingsheng Wang, <sup>[a],\*</sup> Yadong Li<sup>[a]</sup>

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Atomic-level modulation of electronic density of metal-organic frameworksderived Co single-atom sites to enhance oxygen reduction performance