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Oxygen-coordinated Co-N-C for High-efficiency H₂O₂ Electrosynthesis

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Abstract

Atomically dispersed Co-N-C is a promising material for H₂O₂ selective electrosynthesis via a two-electron oxygen reduction reaction. However, the performance of typical Co-N-C materials with routine Co-N₄ active center is insufficient and needs to be improved by further. This could be done by fine-tuning its atomic coordination configuration. Here, we report a single-atom electrocatalyst (Co/NC) that comprises a specifically penta-coordinated Co-N-C configuration (O-Co-N₂C₂) with Co center coordinated by two nitrogen atoms, two carbon atoms, and one oxygen atom. Using a combination of theoretical predictions and experiments, we confirm that the unique atomic structure slightly increases the charge state of the cobalt center. This optimizes the adsorption energy towards *OOH intermediate, and therefore favors the two-electron ORR relevant for H₂O₂ electrosynthesis. In neutral solution, the as-synthesized Co/NC exhibits a selectivity of over 90% over a potential ranging from 0.36 to 0.8 V, with a turnover frequency value of 11.48 s⁻¹; thus outperforming the state-of-the-art carbon-based catalysts.

Introduction

Hydrogen peroxide (H₂O₂) is a high-value green and highly efficient oxidant which is being widely and increasingly used for chemical and medical applications both in industry and for household usage.^[1] Despite the growing demand, H₂O₂ is almost exclusively manufactured by using the energy-intensive anthraquinone process^[2]. An attractive alternative route for direct on-site production of H₂O₂ is through two-electron oxygen electroreduction (ORR)^[3-5].

For safe and eco-friendly electrosynthesis of H₂O₂, efficient catalysts are vital.^[6]

Benefiting from the desirable features of atomically isolated metal centre, the end-on type of adsorption of O₂ on single-atom catalysts (SACs), reduce the possibility of O–O bond splitting; thereby facilitating the selective production of H₂O₂ production.^[7-8] By maximizing the atom utilization efficiency, the SACs of metal-nitrogen doped carbon (M-N-C) with tunable geometry and electronic structures are considered as promising candidates for ORR. Till now, various M-N-C materials (M=Co, Ni, Mo, etc.)^{[9] [10-11] [12] [13] [14] [15]} that have been explored for efficient H₂O₂ production in alkaline solution. However, H₂O₂ is intrinsically unstable in an alkaline solution due to the decomposition catalyzed by OH⁻.^[16-17] To suppress the decomposition of H₂O₂, an extra inhibitor is necessary^[18-20]. In neutral or acidic solution, the performance of M-N-C is still insufficient with high overpotential or low selectivity^[21].

Density functional theory (DFT) calculations reveal that the metal center with OOH* adsorption energy (ΔG_{OOH^*}) of 4.2 eV is optimal for H₂O₂ production via 2 e⁻ ORR.^[18] However, none of the state-of-the-art M-N-C catalysts with routine M-N₄ matrix achieve the optimal adsorption energy necessary for H₂O₂ production.^[22] The predicted binding energy of OOH* intermediate over typical Co–N₄ catalyst is near the top of the volcano accounting for favorable two-electron ORR.^[18] Correspondingly, a precise atomic-level regulation of the electronic structure of Co-N-C to slightly decrease the charge of the metal center could further weaken the adsorption of the intermediate therefore boosting H₂O₂ production.^[23] For example, the ΔG_{OOH^*} of Co-N₄ (3.9 eV) could be increased to 4.1 or 4.5 eV by incorporating

one or two C-O-C groups in the second coordination sphere, to improve the selectivity of two-electron ORR to form H₂O₂.^[18,24] By modifying first coordination sphere, the fabricated catalyst with CoN₂O₂ moiety presents a selectivity of >95% for acidic H₂O₂ electrosynthesis, due to the structure dependent shift of active sites from the center Co atom to the O-adjacent C atom.^[25] However, both of them suffer the trade-offs associated with improving the selectivity on one hand but decreasing the activity.

In this work, an atomically dispersed catalyst (Co/NC) comprising of an optimal Co-N-C moiety (O-Co-N₂C₂) is successfully synthesized via a template casting approach. The local structure and coordination environment of Co single atoms is explicitly studied using advanced synchrotron x-ray characterization, along with theoretical modeling. Due to electronic modulation by the coordinated oxygen atom, and associated redistribution of the spin and charge densities of Co center; there is a catalytic performance enhancement observed. A H₂O₂ selectivity over 90% is achieved with lower overpotential in both acidic and neutral electrolyte toward ORR.

Results and Discussion

The overall synthetic scheme to prepare Co/NC is illustrated in Figure 1a. Metal atoms are first adsorbed on the surface on a mesoporous silica nanospheres (MSN)^[26] via impregnation. Due to the nature of the polymerization of ethylenediamine (EDA) and carbon tetrachloride (CCl₄)^[27], the carbon precursor with abundant nitrogen is introduced into the mesopores of MSN. During the pyrolysis step, the doped nitrogen in carbon skeleton binds with the metal to form the atomically dispersed M-N-C

sites.^[28]

Despite the high annealing temperature (900 °C), a relatively high percentage of nitrogen is incorporated (more than 5.0 at.%; Table S1) for the finally obtained NC, Co/NC or CoPc. The specific surface areas for NC, CoPc and Co/NC obtained from N₂ adsorption isotherms (Figure S1) are 809, 833 and 671 m² g⁻¹ with total pore volumes of 2.15, 2.23 and 2.00 cm³ g⁻¹ (Table S1). According to the Barrett–Joyner–Halenda (BJH) method based on the desorption branches, all samples show similar pore size distribution (PSD) in Figure S1b. The template replication leads to the formation of mesopores with diameters centered at about 7.6 nm, while the wide peak of PSD at 49 nm should be ascribed to the stacking pore.

Additionally, seen in scanning electron microscopy (SEM) images (Figure 1b and S2), are both NC and Co/NC which exhibit a uniformly monodispersed morphology with a mean size of about 80 nm (inset Figure 1b and S2e). The size is smaller than that of template MSN (115 nm in Figure S2d), due to the thermal shrinkage of carbon skeleton^[29]. In contrast, without support of the template, the spherical carbon skeleton of CoPc suffers collapse to form small sheets (Figure S2c).

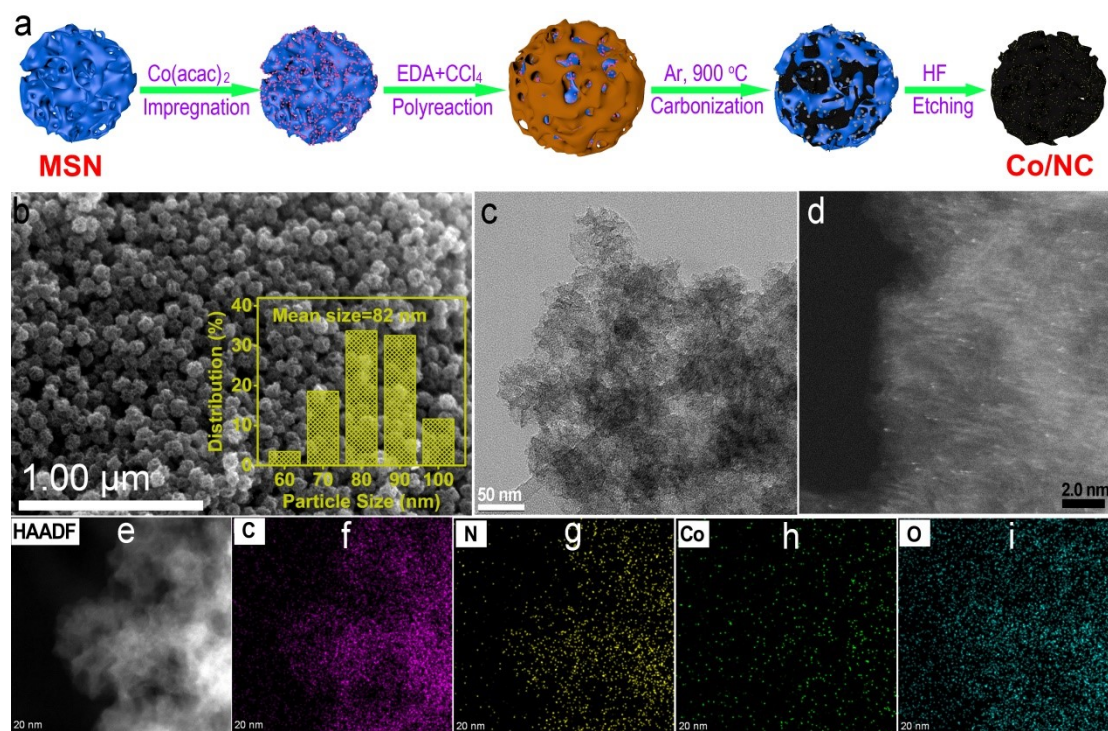


Figure 1. Preparation and textural structure of Co/NC. (a) Schematic illustration for making Co/NC. (b) SEM image and (inset) corresponding particle size distribution. (c) TEM image and (d) High resolution HAADF-STEM images. (e-i) HAADF STEM image and EDS mapping.

Images from transmission electron microscopy (TEM) are given in Figures 1c and S3. Using the high-angle annular dark field (HAADF) detector in scanning TEM (STEM), the acquired Z-contrast image in Figure 1d show widely distributed bright spots with a lateral size in the atomic range. This implies the presence of atomically dispersed Co in Co/NC. The X-ray energy dispersive spectroscopy (EDS) mapping (Figure 1e-i) reveals that C, N, and Co elements are uniformly distributed on Co/NC without aggregation.

The X-ray diffraction (XRD) patterns (Figure S4) of all the prepared samples exhibit a broad characteristic diffraction peak of the carbon (002) at about 26° ,

suggesting a low degree of graphitization. This is further validated by Raman spectroscopy in Figure S5. The peak located at 1365 cm^{-1} (D band) is attributed to disordered sp^3 carbon, whereas the peak located at 1584 cm^{-1} (G band) is related to graphitic sp^2 -hybridized carbon. The similar $I_{\text{D}}/I_{\text{G}}$ ratio (0.97) suggests that the graphitization of carbon matrix has not changed for Co/NC or CoPc. Measured by inductively coupled plasma optical emission spectrometry (ICP-OES), the overall Co content is listed in Table S1 is 0.66 and 0.74 wt.% for Co/NC and CoPc, respectively.

The surface chemical state is identified by x-ray photoelectron spectroscopy (XPS). In the deconvoluted N 1s XPS spectra (Figure S6), the metal free NC shows four peaks centered at 398.2, 399.9, 401.0, and 402.8 eV. These could be assigned to the pyridinic (Py-N), pyrrolic (Pyr-N), graphitic-like (G-like), and oxidized type (N-O) nitrogen, respectively. In addition to these typical peaks for nitrogen doped carbon, one more peak of cobalt-coordinated (Co-N) nitrogen at 398.9 eV is observed for both Co/NC and CoPc. This suggests the existence of Co-N-C structure. The Co 2p spectra are presented in Figure 2a. In comparison to CoPc, the Co 2p peak of Co/NC upshift to a higher binding energy and the spin-orbit splitting (15.96 eV) of Co/NC is larger than that of CoPc (15.49 eV). This indicates the lower charge density state of the cobalt atoms in Co/NC.^[18]

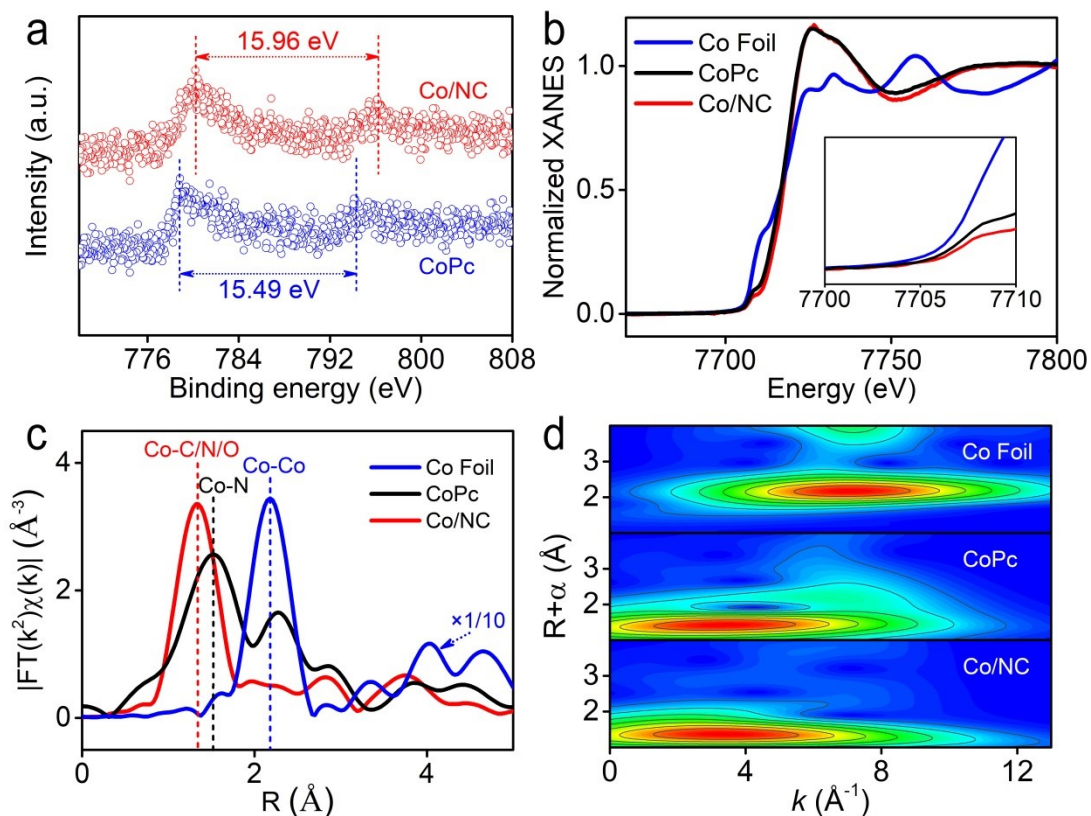


Figure 2. Electronic and coordination structure. (a) Co 2p XPS spectra of Co/NC and CoPc. (b) XANES spectra of Co K-edge for Co/NC and CoPc in comparison with the reference Co foil (inset: expanded view of Co K-edge pre-edge). (c) The FT k^2 -weighted EXAFS spectra. (d) WT-EXAFS spectra.

To elaborate the electronic and coordination environment on Co, the samples are further examined by synchrotron X-ray absorption spectroscopy. The Co K-edge X-ray adsorption near-edge structure (XANES) spectrum in Figure 2b suggest that the Co/NC contained near-edge structures similar to those of the CoPc but totally different from those of the Co foil reference. And in the rising edge (inset Figure 2b), a shift to higher energy is observed for Co/NC when compared with CoPc. These observations suggest that the Co in Co/NC is more positively charged and is consistent with the XPS results.

Figure 2c shows the Fourier transform extended X-ray absorption fine structure (FT-EXAFS) curves. The peak at 1.5 Å for CoPc is assigned to the Co-N bond formed during the pyrolysis of cobalt phthalocyanine. Whereas, Co/NC exhibits a peak at 1.3 Å, which is shorter than the Co-N bond (1.5 Å) in CoPc. After EXAFS fitting (Figure S7), the coordination number can be directly obtained and listed in Table S2. As predicted^[30], the Co center in Co/NC is in a penta-coordinated geometry with two N atoms, two C atoms, and one O atom (bridge-bonded to the Co center and one adjacent C atom) to form an O-Co-N₂C₂ structure.

For CoPc, an average Co-N coordination number of 4.0 ± 1.8 is obtained, suggesting the existence of typical Co-N₄ structure. Besides, no Co-Co bond is identified in the k^2 -weighted FT-EXAFS and k^3 -weighted Wavelet transformed spectra (Figure 2d) indicates that the Co atom in Co/NC is atomically dispersed. Thus compared to the CoPc, the Co/NC has penta-coordinated Co center in relatively electron-lack state.

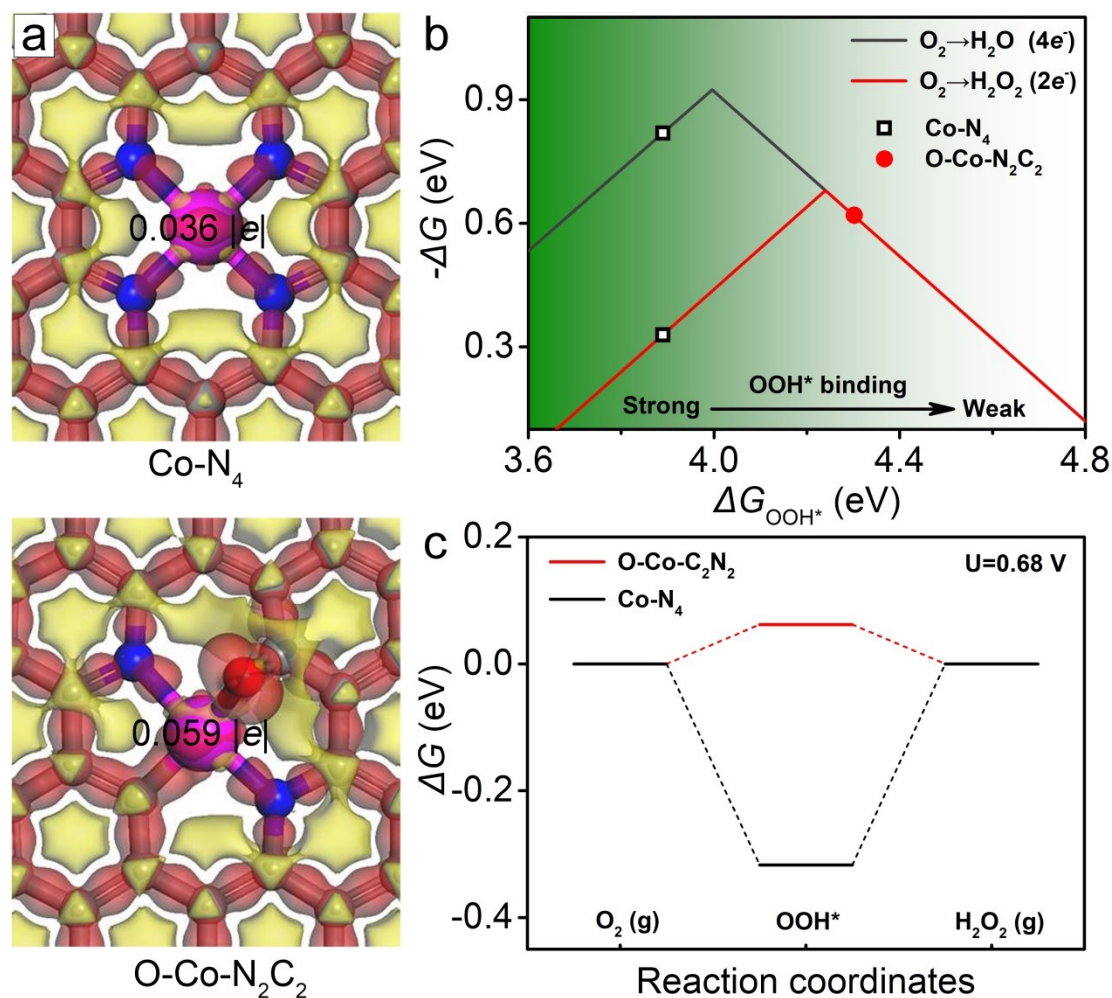


Figure 3. Theoretical simulations. (a) Deformation densities of O–Co–N₂C₂ and Co–N₄, respectively. The red and yellow isosurfaces (0.06 Bohr⁻³) correspond to charge accumulation and depletion regions. (b) Calculated catalytic activity volcanoes of ORR via the 4e⁻ (gray) or 2e⁻ (red) pathway. (c) Calculated reaction energetics of the ORR to produce H₂O₂ at the equilibrium potential.

Density functional theory (DFT) is first performed to compare the catalytic activity and selectivity of H₂O₂ production on O–Co–N₂C₂ and Co–N₄. On the basis of the optimized structures (Figure S8), the charge state of the cobalt atom for O–Co–N₂C₂ is 0.059 e⁻, which is more positive than the value of 0.036 e⁻ for Co–N₄ (Figure 3a). This is in good agreement with the XPS and XANES results. And

compared with the conventional Co-N₄, the Co center in O-Co-N₂C₂ with slightly decrease of the charge is expected to boost H₂O₂ production during ORR.^[23] As a reliable ORR descriptor, the volcano plot reveals that the optimal binding free energy of *OOH (ΔG_{OOH^*}) value for an ideal $2e^-$ pathway is 4.2 eV.^[18,25]

The DFT simulation in Figure 3b reveals that ΔG_{OOH^*} of the electron-deficient Co in O-Co-N₂C₂ is 4.3 eV, more peak-closed than Co-N₄ (3.9 eV). The weaker OOH* binding suggests that the prepared Co/NC with O-Co-N₂C₂ moieties is more prefer to $2e^-$ ORR. At the equilibrium potential for H₂O₂ production (U = 0.68 V vs RHE), the rate determining step (RDS) at O-Co-N₂C₂ site is the first electron transfer from O₂ to *OOH. This requires a driven energy of 0.062 eV, which is much lower than the RDS energy (0.32 eV) for OOH* protonation on Co-N₄ (Figure 3c). These results indicate that the penta-coordinated O-Co-N₂C₂ is intrinsically more active and selective than conventional tetra-coordinated Co-N₄ for H₂O₂ production.

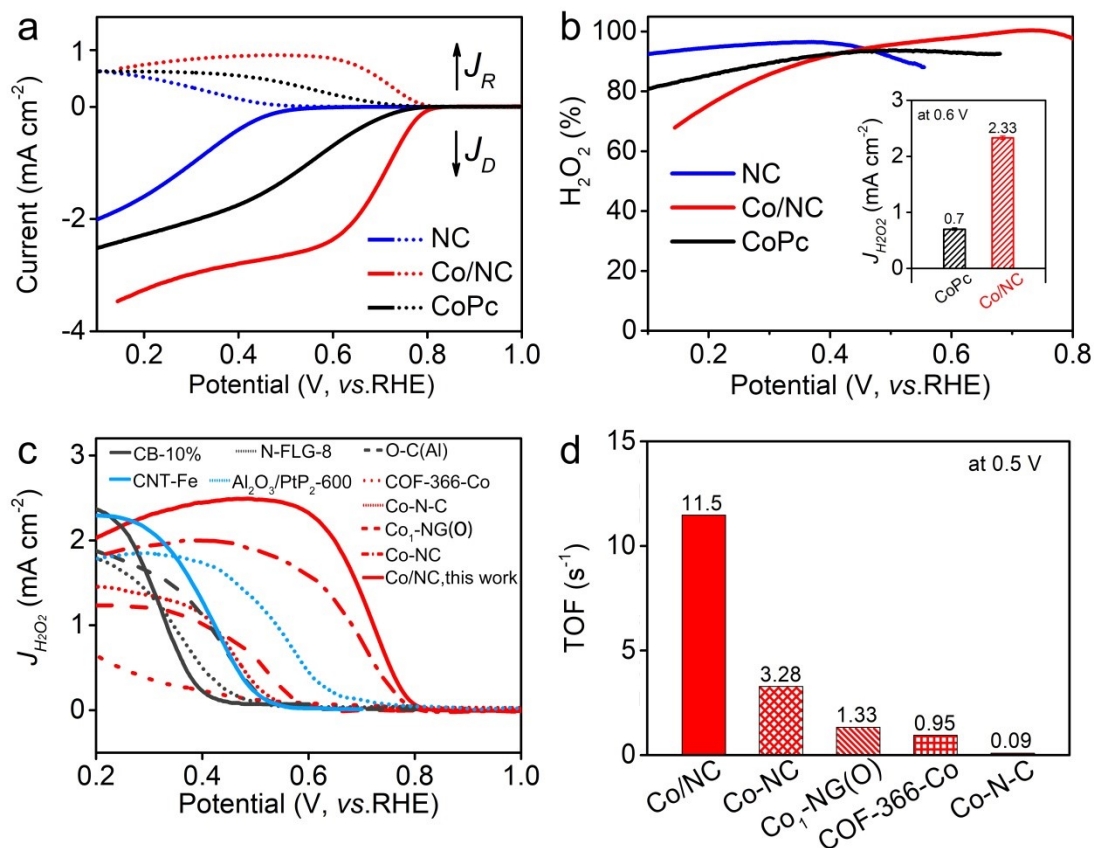


Figure 4. Electrocatalytic performance in neutral electrolyte (PBS, pH=7.0). (a)

The disk and ring current density normalized by the geometric area of disk electrode is collected by RRDE at 10 mV s⁻¹. Scan rate is 1600 rpm. (b) The calculated H₂O₂ selectivity. Inset is the H₂O₂ current density at 0.6 V. (c) Comparison of the current density for H₂O₂ production at different potential. Detailed cited references can be found in Table S3 in the Supplemental Information. (d) Comparison of the TOF value with the reported Co SACs for H₂O₂ production at 0.5 V.

We perform electrochemical ORR evaluation on a rotating ring-disk electrode (RRDE) at room temperature in 0.1 M PBS (pH=7.0) electrolyte. Cyclic voltammetry (CV) measurements (Figure S9) showed that the cathodic peak for the reduction of oxygen by Co/NC occurred at the potential of 0.71 V relative to the reversible hydrogen electrode (RHE). The ring current (J_R) collected at 1.15 V monitors the

H₂O₂ formed at disk electrode. The effect of the catalyst loading amount on the ORR performance for Co/NC is first investigated (Figure S10). Increasing the catalyst loading amount improves the ORR activity with declined H₂O₂ selectivity.

To achieve high H₂O₂ current, a catalyst loading amount of 10 μg cm⁻² is selected. As shown in Figure 4a, the Co/NC catalyst, which has an electron-deficient cobalt center induced by the oxygen coordination, is able to catalyze the 2e⁻ ORR and shows a superior activity for H₂O₂ production in comparison to CoPc. The potential (*E*_{ORR}) required to reach the current density of 1.0 mA cm⁻² is 0.72 V versus RHE for our Co/NC is better than the state-of-the-art catalysts (Table S3).

At the potential range from 0.36 to 0.8 V versus RHE (Figure 4b), the H₂O₂ selectivity on Co/NC is higher than 90%. This indicates that ORR is dominated by two-electron pathway with H₂O₂ as the final product. Figure S11 shows the ORR polarization curves at various rotating speeds. Calculated from the slopes of Koutecky-Levich (K-L) plots, the electron transfer number at the potential over 0.45 V is close to 2.0. This is in agreement with the RRDE results of two-electron ORR.

The ring current adjusted by collection efficiency (37.0%) for H₂O₂ production over Co/NC reaches 2.3 mA cm⁻² at 0.6 V versus RHE (inset Figure 4b). This is much higher than CoPc (0.7 mA cm⁻²). This finding agrees with the proposed DFT prediction and previous reports^[18, 31]: the relatively strong binding energy of *OOH for Co-N₄ would cause the break of O–O bond and result in the formation of *O and *OH intermediates. This would eventually reduce to H₂O via the 4e⁻. Impressively, the current density for H₂O₂ production through ORR of Co/NC is rather outstanding,

when benchmarked with the state-of-the-art catalysts (Figure 4c).

The active site of Co/NC is experimentally confirmed via thiocyanide (SCN^-) poisoning. It is known that SCN^- ion can strongly binds to the single metal atom sites, and make the central metal site inaccessible for ORR catalysis.^[25, 32] Along with the addition of 10 mM SCN^- , the remarkable depression of ORR activity with a significantly lower current density is observed (Figure S12). This result confirms that the center Co atom in Co/NC should be the origin of the activity associated with highly selective $2e^-$ ORR activity. This is in fact consistent with the DFT computation results. To reveal the intrinsic electrocatalytic activity, turnover frequency (TOF) values of each Co atom for H_2O_2 production is calculated and compared with the recently reported Co SACs^[9, 18, 22, 33]. At a potential of 0.5 V versus RHE, the TOF value of 11.48 s^{-1} achieved on Co/NC in this work is the highest one (Figure 4d).

In addition, we further determine the response towards H_2O_2 redox in Ar-saturated 0.1 M PBS (pH=7.0) containing 10 mM H_2O_2 . As shown in Figure 5a, all the prepared samples show an onset potential for H_2O_2 reduction at 0.70 V. However compared with the current density for O_2 reduction (Figure 4a), the current density for H_2O_2 reduction is less than 10% at the potential over 0.4 V (Figure S13), thus leading to the high selectivity for $2e^-$ ORR. This outstanding performance also suggests the potential usage of Co/NC for selective O_2 sensor^[34].

To investigate the durability for H_2O_2 yield and Faraday efficiency (FE), the Co/NC modified carbon paper is tested in an H-cell (Figure S14). The

chronoamperometric result (Figure 5b) shows that the current density remained stable for 10 h without discernible decay. The final concentration of H₂O₂ is determined by titration method confirms the FE of 84.2% throughout the entire process. An average H₂O₂ production rate of 3.57 mol h⁻¹ g_{cat}⁻¹ is thus obtained at 0.4 V versus RHE. After durability test, the Co in Co/NC maintains the primary chemical state as confirmed by XPS result (Figure S15), demonstrating the superior stability in neutral condition.

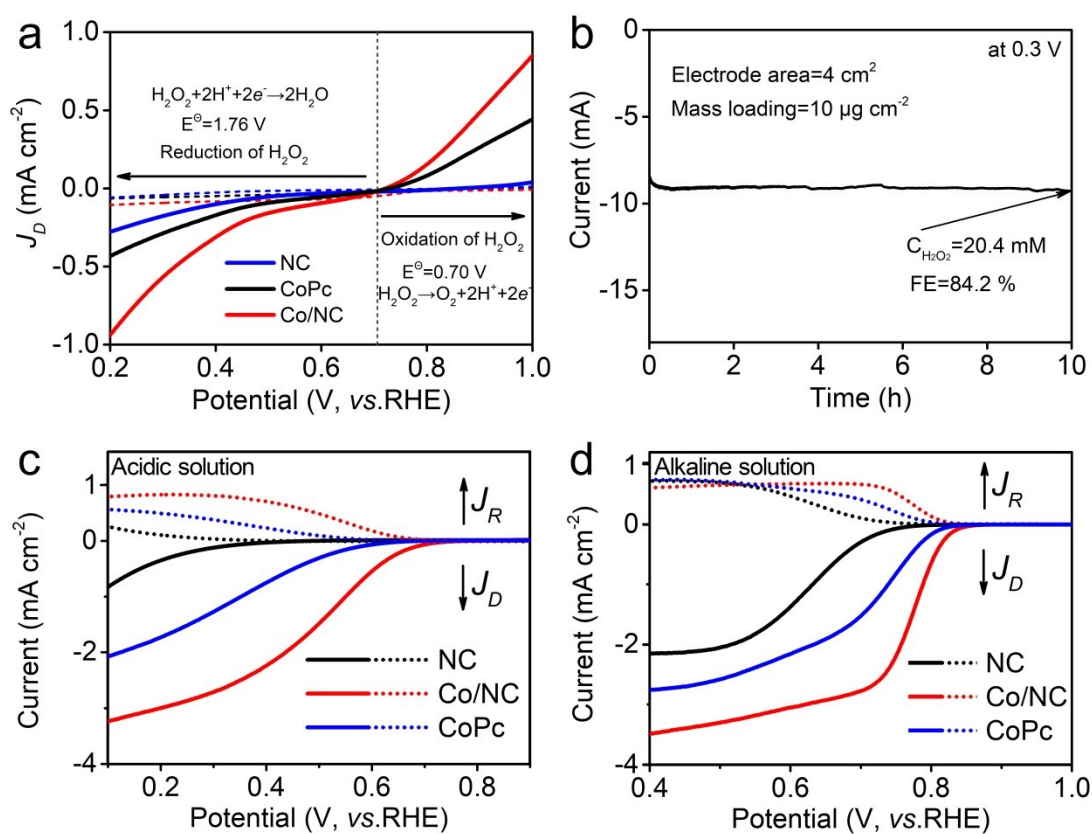


Figure 5. (a) The activity toward H₂O₂ redox reaction at a scan rate of 1600 rpm. Measurements in Ar-saturated 0.1 M PBS (pH=7.0) with and without 10.0 mM H₂O₂ are shown in solid and dash line, respectively. (b) Stability measurement of Co/NC at a constant potential of 0.4 V in 0.1 M PBS. (c) ORR polarization curves for the synthesized samples in the acidic (0.1 M HClO₄) and (d) alkaline (0.1 M KOH)

solution.

The catalytic ORR performances are also tested in acidic (0.1 M HClO₄, Figure 5c) and alkaline (0.1 M KOH, Figure 5d) conditions. Interestingly, our Co/NC also shows a significant amount of H₂O₂ production in acidic solution (Figure S16). In contrast, all samples present higher activity for ORR in alkaline conditions (Figure S17) than in neutral and acidic media with the enhanced disk current density at the same potential versus RHE. This trend is consistent with previous reports, and could be attributed to the role of proton affinity on the surface of carbon matrix at different pH electrolytes.^[21, 35] In all pH solutions, the metal free NC suffers from the highest overpotential and lowest current densities for H₂O₂ production. Both activity and selectivity are important metrics for catalyst design towards 2e⁻ ORR.^[36] Although the NC maintains the highest selectivity among the samples studied in alkaline solution (Figure S17a), the current for H₂O₂ production (1.3 mA cm⁻²) is less than the Co/NC (1.8 mA cm⁻²) at 0.6 V versus RHE (Figure S17b).

Conclusion

In summary, a new Co-N-C catalyst with penta-coordinated Co center was prepared for highly selective 2e⁻ oxygen reduction to H₂O₂. The local structure and coordination environment of Co single atoms is identified using HAADF-STEM and EXAFS. By combining electrochemical tests and theoretical calculations, the Co single-atom with the specific local coordination (O-Co-N₂C₂) is responsible for the outstanding activity ($E_{ORR}=0.72$ V at current density of 1.0 mA cm⁻²) and selectivity ($S_{H_2O_2}>90\%$ over the potential range from 0.36 to 0.8 V) towards neutral H₂O₂

electrosynthesis. This is at present the best catalytical performance for H₂O₂ electrosynthesis among reports available thus far. This work offers an approach for regulating local coordination environments of Co-N-C at the atomic-level. Findings will likely provide further understanding of the structure–property relationships of Co SACs for other catalytic reactions^[37-40].

Conflicts of interest

The authors declare no competing interests.

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