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Marginal defects modified graphene with S-C-N-C groups for highly selective oxygen reduction to H₂O₂

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Abstract

Developing efficient metal-free catalysts to achieve electrochemical synthesis of

hydrogen peroxide (H_2O_2) is crucial for substituting traditional energy-intensive anthraquinone process. Heteroatom-doped carbon materials have shown great potential toward 2e-pathway for catalyzing oxygen reduction to hydrogen peroxide (ORHP). However, conventional nanocarbon electrocatalysts show slow kinetics toward ORHP due to the weak binding strength with OOH^* intermediate, resulting reduction of O_2 to H_2O . Here, sulfur and nitrogen dual-doped graphene (SNC) electrocatalyst consisting of S-C-N-C functional group are synthesized through hydrothermal self-assembly and nitridation processes with thiourea as sulfur source. In S-C-N-C functional group, pentagon-S and pyrrolic-N are covalently grafted onto the edge of graphene and produce marginal carbon ring defects, which provide highly active sites for catalyzing ORHP. The obtained SNC catalysts deliver an outstanding ORHP activity and selectivity for H_2O_2 production, while retaining remarkable stability. The experimental and computational results reveal that marginal S-C-N-C functional groups afford an appropriate adsorption strength with OOH^* intermediate and a low reaction barrier as well, which are essential for the activity of ORHP.

Keywords

Defect, hydrogen peroxide, electrocatalysis, graphene, metal-free

Introduction

Hydrogen peroxide (H_2O_2) is an omnipresent and extremely essential green oxidant that has been widely applied in various chemical industries and environmental remediation, especially for effluent disposal, industrial papermaking, textiles, medical industry, etc¹. Based on a research report by Global Market Insight, Inc., the H_2O_2

market size is forecast to exceed \$6.2 billion by 2026². Traditionally, the industrial product of H₂O₂ is mainly synthesized by anthraquinone oxidation process, which require complex technology and expensive palladium catalysts and generates an extensive volume of organic chemical wastes³. Recently, electrochemical synthesis of H₂O₂ through oxygen reduction reaction with two-electron transfer (2e-ORR) has attracted extensive attentions from both academia and industry. Compared to traditional anthraquinone process, it shows high energy efficiency, cost effectiveness, and environmental-friendly⁴. However, 2e-ORR process competes with the reduction of O₂ to H₂O via a four-electron (4e-) transfer, and thus highly requires efficient electrocatalysts that selectively promote oxygen reduction to hydrogen peroxide (ORHP). For the 2e-ORR route, noble metals and their alloy (Pd-Au, Pt-Hg, Pd-Hg, etc⁵.) are currently the most efficient catalysts for H₂O₂ production due to the electronic structure of Pt and Pd conformed to 2e-ORR process⁶. Unfortunately, the rarity and high cost of noble metals rigorously hamper their scalability. Therefore, it is highly urgent to seek active, stable, and earth-abundant alternatives to noble metal-based catalysts toward efficient electrocatalyze ORHP.

Owing to the low cost, controllable preparation and high conductivity, metal-free carbon materials have been intensively reported as promising candidates toward ORHP. Chiefly, oxidized carbon materials (such as oxidized carbon black⁷, oxidized CNTs⁸, oxygenated graphitic nanoplatelets⁹) have emerged as a type of promising catalyst for ORHP, due to the oxygen moieties improving the OOH* absorption capacity of the adjacent carbon atoms. Nevertheless, oxidized carbon materials generally suffer from

67 surface oxidization at high current, showing sluggish kinetics. Additionally,
68 heteroatoms (O, N, S, etc^{10,11}.) regulated carbon materials have garnered much attention,
69 in which these heteroatoms can bond or even substitute carbon atoms with strong
70 chemical bonding, introducing in-plane and out-of-plane defects to improve catalytic
71 activity. Heteroatoms with highly electronegativity can incorporate into carbon lattice
72 and enhance the distribution of π electrons, which create a net positive charge
73 surrounding carbon atoms, improving surface charge transfer kinetics¹². Nevertheless,
74 these anionic regulated carbon materials are commonly utilized for traditional 4e-
75 pathway to water because of the tendency for reducing OOH* to O* and OH*. More
76 recently, several studies have manifested that defective carbon materials could catalyze
77 ORHP, as the defects in carbon materials may act as reactive sites for oxygen adsorption
78 or reduction during the electrocatalytic process¹³. Unfortunately, the extraneous
79 topological defects are usually located in the basal plane of materials framework, which
80 do not predominate in the catalytic process, showing remarkable limited effect on
81 catalyzing H₂O₂. Meanwhile, the topological defects at edge afford diverse active sites
82 for intermediate adsorption and further boost catalytic reaction as well. Erecting edged
83 defects in nanocarbon catalysts is the crucial way to achieve both high catalytic activity
84 and selectivity. However, practical difficulties (e.g., rigorous synthetic conditions,
85 process complexity and difficulty, and hard configuration control) have severely limited
86 the development of defect modified carbon catalysts through heteroatoms doping.
87 Therefore, developing feasible heteroatoms doping schemes to construct edged defect-
88 enriched carbon structures for electrocatalytic ORHP becomes important yet

challenging.

Herein, sulfur and nitrogen dual-doped graphene (SNC) with unique marginal defects is synthesized by hydrothermal process and controllable chemical vapor deposition (CVD) with thiourea ($\text{CH}_4\text{N}_2\text{S}$) as sulfur source. During CVD process, the inherent S-C-N configurations of thiourea are partially retained and chemically grafted onto the edge of graphene, building S-C-N-C functional group eventually, which induces numerous edged graphitic defects into SNC lattice. In S-C-N-C functional group, marginal defects consist with pentagon-S and pyrrolic-N coordinated with carbon atoms, which significantly alter surface atoms and electronic structures of graphene precursors, providing broad active edges for ORHP. The defect-enriched SNC exhibits an excellent catalytic performance that delivers over 90% H_2O_2 selectivity at the 0.2-0.6 V vs. RHE (versus reversible hydrogen electrode) and 98.9% at 0.6 V vs. RHE, outperforming most state-of-the-art ORHP catalysts. The SNC catalyst also show excellent stability and retain 95% of initial activity after 50000 s continuous electrolysis. Density functional theory (DFT) calculations indicate that defective S-C-N-C functional groups afford desirable binding strength to OOH^* intermediates and diminish the energy barrier for O_2 to OOH^* , which confirms to be the active sites for ORHP. This general synthetic strategy provides a new insight to introduce marginal defects on metal-free electrocatalysts for application in advanced fields.

Results

Synthesis and characterization of SNC catalyst. The SNC electrocatalyst was synthesized through a two-step procedure, as schematically illustrated in **Figure 1a**.

111 Firstly, the solution of graphene oxide (GO) and thiourea were mixed for ultrasonic
112 homogenization and then proceed hydrothermal reaction, and the pristine GO sheets
113 were reduced to reduced graphene oxide (rGO). As a result, S-doped rGO (S-rGO) was
114 obtained. Subsequently, the SNC catalyst were acquired by annealing S-rGO precursors
115 with NH_3 in an Ar atmosphere. In addition, under the same synthesis process, S and N
116 co-doped graphene with sulfur powder as sulfur source (define as SSC) was synthesized
117 and used as a reference, together with monatomic sulfur and nitrogen doped rGO
118 (denoted as SC and NC, respectively) were also synthesized (Supplementary **Table 1**).
119 For comparison, a series of SNC with various CVD time and annealing temperature
120 were also prepared (Supplementary **Table 2**) (see “Methods” for more details).

121 Morphologies and structures of the SNC catalyst were characterized with scanning
122 electron microscopy (SEM) and transmission electron microscopy (TEM). The
123 synthesized SNC catalyst exhibits a curly appearance and lamellar structure with
124 abundant wrinkles and ripples (**Figure 1b**). The typical higher-resolution TEM (HR-
125 TEM) images elucidate that the wrinkled ultrathin flake consists of few-layered
126 graphene with characteristic d-spacing about 0.30 nm (**Figure 1c**). As illustrated in
127 **Figure 1d**, a spacing of 0.304 nm is further calculated with selected area electron
128 diffraction (SAED) pattern. Notably, the interplanar spacing is much smaller than the
129 theoretical thickness of monolayer graphene (0.335 nm)¹⁴, which can be further verified
130 by X-ray diffraction (XRD) patterns. As illustrated in **Figure 1e**, an asymmetric (002)
131 peak is exhibited along with a weak (100) peak, and these characteristics are typically
132 shown in defect-enriched graphene. SNC and SC exhibit a higher broad peak (25.7°)

than that of routine SSC and NC (25°), indicating that tighter graphene layer distance is actually obtained with the introduction of thiourea¹⁵. In addition, the effects of annealing temperature and CVD time on the layer spacing of SNC were also studied, and no significant diffraction angle shift was observed (Supplementary **Figure 1**).

Furthermore, the (002) peaks for SNC and SC sheets are more pronounced than that in SSC and NC, which suggests a larger crystallite size in the *c*-axis¹⁶. It is noteworthy to mention that the peak intensity of crystal surface (002) is positively correlated with annealing temperature and CVD time, and this tendency arises from graphitization intensified with overheating. Comparing with SSC and NC, SNC and SC exhibit a distinct (004) peak, which indicates more crystal face exposure, generating more active sites. This is also evident from the SEM image in Supplementary **Figure 2**, which reveals the morphology of SSC sheets is mostly hardened block, not conducive to the occurrence of electrocatalytic surface reactions. The high-angle annular dark-field scanning TEM (HAADF-STEM) images clearly demonstrate the flake-like structures of SNC are retained without aggregation or stacking after high-temperature annealing (**Figure 1f**). In addition, the energy dispersive X-ray spectroscopy (EDS) elemental mapping of C, N, O, and S overlap quite well, confirming both N and S have been uniformly doped into SNC framework.

Figure 1 | Synthesis process and morphology of SNC catalyst. **a**, Schematic illustration of the synthesis process. **b**, TEM image of SNC, scale bar, 100 nm. **c**, HR-TEM images of SNC with several (002) graphite surface, scale bar, 10 nm. **d**, Corresponding SAED displayed crystalline plane diffraction rings of (002), (100) and (004), scale bar, 5 $1/\text{nm}$. **e**, XRD patterns, inset is the diffraction angle migration for SNC and SC at (002) peak. **f**, HAADF-STEM image and corresponding EDS elemental mapping images, while sulfur and nitrogen atoms partially remain in the reduced graphene after annealing, scale bar, 5 nm.

To get a further cognition of chemical composition and electronic structure of SNC moieties, Raman spectra, electron paramagnetic resonance (EPR), and X-ray photoelectron spectroscopy (XPS) were conducted. As revealed in **Figure 2a**, the intensity ratio of D and G band (I_D/I_G) for SNC (1.147) is clearly higher than that of SC (1.098), NC (1.087), and SSC (1.054), suggesting that thiourea as sulfur source introduces more structural defects than that of sulfur powder. Additionally, increasing temperature could enhance the orderliness of SNC, while prolonging CVD time has the opposite effect (Supplementary **Figure 3**). The specific surface areas of SNC, SSC, SC and NC are 706, 1085, 579, 783 $\text{m}^2 \text{g}^{-1}$, respectively (**Figure 2b**), and the main pore size is centered at 3.5 nm (**Figure 2b**, inset). Interestingly, SNC and SC have lower specific surface area than that of SSC and NC, which may attribute to the larger grain size of graphene induced by thiourea, is evident in XRD patterns. In addition, the BET surface area of SNC under diverse process condition were quantitatively analyzed and the SNC catalyst annealed at 850 °C for 60 min obtains maximum surface area, which provides more electrocatalytic active sites for ORHP (Supplementary **Figure 4**). EPR spectroscopy was conducted to probe unpaired electrons in graphene matrixes (**Figure 2c**). Here, a broad signal at $g = 2.04$ is assigned to unpaired electrons, originated from nitrogen atoms, which can distribute extra electrons to adjacent carbon atoms via activate π -conjugated system. While a weak symmetrical EPR signal at $g = 2.10$ is identified as the dipole-dipole interaction, which corresponds to the inhomogeneous distribution of electrons, accompanying with high electronegativity nitrogen atoms bonding with carbon atoms^{17,18}. Comparing with SSC and NC, SNC and SC modified

with thiourea exhibit a lower EPR intensity at $g = 2.01$, which indicates fewer unpaired electrons are detected. Obviously, SNC and SC generate a stronger van der Waals interaction due to the decreased interplanar graphene spacing, which could accelerate electron transfer and capture more unpaired electrons.

The XPS survey spectrum shows characteristic peaks of C, N, O and S, and corresponding atomic concentrations are obtained (Supplementary **Figure 5**). No evident of other impure peaks is found. As revealed in **Figure 2d** and Supplementary **Figure 6**, the C 1s spectra are deconvoluted into sp^2 carbon, sp^3 carbon, heteroatom to carbon (C-O, C-N, C-S), C=O, O-C=O bonds at binding energies of 284.8, 285.4, 286.1, 287.0 and 289.1 eV, respectively. The sp^3 carbon can be regarded as carbon atom defects, which are different from the general sp^2 carbon structures, arising from the implantation of heteroatom. Apparently, SNC gives a highest sp^3 carbon purity than others, highlights more extrinsic defects induced. The control samples with various annealing temperature and CVD time were also subjected to XPS measurements. For C 1s, prolonging CVD time introduces more C-N bonds to substitute C=C components (Supplementary **Figure 7**), while higher temperature accelerates graphitization and restores partial defects of SNC¹⁹ (Supplementary **Figure 8**). The N 1s spectra (**Figure 2e**) are deconvoluted into four subpeaks assignable to pyridinic-N (398.3 eV), pyrrolic-N (399.9 eV), graphitic-N (401.3 eV), and N-O bonds (403.0 eV). Notably, compare to SSC and NC, SNC has a larger pyrrolic-N and less graphitic-N concentration, which indicates that N species in SNC are inclined to occur in the form of defective pentagon-C. The concentration of graphite-N is proportionate to the annealing temperature and CVD time; namely,

extending nitridation time or elevating temperature can generate more graphitic-N species in the basal of carbonic ring and eliminate the pyrrolic-N (Supplementary **Figure 9** and **10**). Additionally, extra stretching mode of C-N heterocycles emerged with prolonging CVD time, which were detected in the Fourier-transform infrared (FT-IR) spectra (Supplementary **Figure 11**).

As presented in **Figure 2f**, SNC, SSC, SC and NC exhibit S=O peak (534.1 eV) and oxygen-containing groups (O-C=OH, C-OH and C=O at 533.4, 532.2 and 531.0 eV, respectively) after annealing, which are distributed uniformly in carbon matrix²⁰. These results are also evidenced by the FT-IR spectra (Supplementary **Figure 12**). Meanwhile, compared with SC, SNC, SSC, and NC all possess reduced O-C=O bonds accompanied with an increase in C-O bonds, demonstrating that the carboxyl groups are partially eliminated with high-temperature nitridation process. Specially, the peak intensity of C-O at 532.2 eV gradually enhances with nitridation temperature increasing, which is attributed to the break of C=O bonds in carboxyl group at high-temperature²¹ (Supplementary **Figure 13**). Similarly, most of characteristic bonds for SNC annealing at various annealing temperatures become insignificant, which are perceived in FT-IR (Supplementary **Figure 14**). As revealed in **Figure 2g**, the fitted peaks around 164.0 and 165.4 eV are referred to the spin-orbit coupling of S 2p (thiophene-S and C=S), and sub-peaks at 168.4 and 169.6 eV are sulfur oxide species (-C-SO_x-, x=2,3)²². A small broad shoulder related with oxidized S is clearly observed in NC and no peaks are detected at the region of S 2p spin-orbit, demonstrating that sulfur in SNC is effectively introduced by thiourea. Specifically, compared to SSC, the S 2p in SNC shift toward to

higher binding energy, which can be attributed to the formation of thiophene-S, giving rise to these micro-displacements²³ (Supplementary **Figure 15**). Moreover, as nitridation temperature increasing, the content of O=S=O species obviously increases accompanied by the gradually decrease of -SO₃H groups, indicating that the hydroxy bonded coordinated with sulfur atom could be removed with high-temperature CVD process (Supplementary **Figure 16 and 17**).

Figure 2 | Compositional characterization. **a**, Raman spectra of graphene matrixes, inset is the corresponding I_D/I_G values. The 2D band is obviously enhanced in SNC and SC, implying the number of graphene layers are decreased compared to SSC and NC. The emergence of D+G band at 2920 cm^{-1} affirms the increased structure disorder. **b**, Isothermal curve of N₂ adsorption and desorption, inset is pore diameter distribution diagram. **c**, EPR spectra of graphene matrixes. **d**, High resolution of C 1s spectra with peaks deconvoluted into five subpeaks, while heteroatom refers to the C-S, C-N, and

C-O bonds in graphene matrixes. **e**, High resolution N 1s spectra. The SC shows unapparent characteristic peak in N 1s spectra. **f**, The deconvolution of O 1s spectra. **g**, S 2p spectra.

Next, to further unravel coordination features of SNC moieties, soft X-ray absorption near edge structure (XANES) and solid-state nuclear magnetic resonance (ssNMR) were applied. And commercial thiourea was investigated for comparison. As illustrated in **Figure 3a**, the peak around 285.5 eV is assigned to unoccupied π^* states originated from the out-of-plane bonds in the sp^2 bonding configuration; the signals above 292.0 eV corresponds to excited σ^* states from C-C in-plane bonds in a carbon ring structure⁹. Moreover, SNC and SC have an additional shoulder peak around 284 eV (left inset), which arises from vacancy defects and Stone-Wale (SW) defects induced with the incorporation of thiourea. Compared with SSC and NC, SNC and SC exhibit a weaker π^* states, also reflect the rich defects²⁴. The right inset in **Figure 3a** exhibits a minor resonance situated at 288.2 eV, revealing the presence of graphene interlayer states and transition to sp^3 hybridized states²⁵. In comparison to SSC and NC, SNC and SC demonstrates a weaker resonance at graphene interlayer states, which can be ascribed to the different charge transfer derived from dissimilar interlayer spacing²⁶.

The soft N K-edge XANES (**Figure 3b**) provides further information about graphene matrixes. The π^* resonance peaks located at 399.5, 400.8, and 402.4 eV are corresponding to pyridinic, pyrrolic, and graphitic-N species, respectively²⁷. The peak located at 408.6 eV is assigned to the general transitions from N 1s core level to C-N σ^* states²⁸. Moreover, SNC gives rise to a strongest $\sigma^*(C-N)$ at 408.6 eV, while SSC

with ammonia as monotonous nitrogen source shows weak C-N σ^* states, indicating these double nitrogen sources increase the occupation of σ^* states and enhance the C-N bonding as well. Notably, raw SC without nitridation shows weak π^* and $\sigma^*(\text{C-N})$ resonances in the 398-410 eV region; these features are assigned to the nitrogen species originated from thiourea. Thus, the pyrrolic-N in SNC is partly originated from thiourea, which accelerates 2e-ORR²⁹.

S K-edge spectra (**Figure 3c**) indicate that SNC and SC mainly contain thiophene-S (2472.8 eV) and sulfate (2481.2, 2479.2 and 2498.3 eV) structures³⁰. NC displays the feature of oxidized-S, consistent with S 2p spectra, which is derived from the sulfate groups retained during graphene oxidation process³¹. Notably, a slight deviation of photon energy between SNC and SSC is clearly observed in the inset, which contributes to the different valence states of sulfur; that is, SSC appears in the higher photon energy can be recognized to the higher electronic oxidation state of sulfur³². Compared with SSC, the intrinsic coordination configuration (S-C-N) of thiourea produces distinctive fine structures for SNC, which cause different photon energy. In accordance with Element analysis (EA), SSC owns higher concentration of O and lower S than those of SNC (Supplementary **Table 3**), highlighting that SSC is inclined to involve more oxidized-S species. Moreover, sulfur powder could sublime at high annealing temperature, and only part of sulfur atoms can substitute carbon atoms into graphene lattice, whereas thiourea with N and S coordinated structure are more easily preserved through two-step procedure.

Furthermore, ¹³C ssNMR was utilized to gain insights into chemical bonding of

SNC. As revealed in **Figure 3d**, SNC, SC and SSC have typical signals for sp^2 carbon (124.3 and 125.9 ppm)³³, whereas the resulting NC feature is not pronounced and only shows a weak signal of C=O species at 184.9 ppm, indicating that S-doping play a vital role in enhancing the graphitization. Compared with SSC, SNC has an additional sharp peak located at 128.6 ppm, which can be indexed to C=S bonds inherited from thiourea. Besides, the peak at 137.5 ppm is ascribed to the -SO₃H groups from sulfuric acid, consistent with the results of XANES and XPS spectra. Interestingly, in SNC, SC, and SSC, plentiful oxygen-containing groups like C-O-C (56.2 ppm), O-C-O (102.1 ppm) and hydroxyl (70.5 ppm) are almost completely eliminated with annealing; only robust carboxyl survives and exhibits an obvious peak at 164.3 ppm, which endow graphene with a certain auxiliary functionalization for 2e-ORR²⁰. In the ¹³C NMR spectroscopy of thiourea, the signal at 163.6-164.3 ppm is S-C-N configurations resided on original framework without annealing and nitridation. Additionally, SNC and thiourea display similar signals at 164.3 ppm, which are supposed to be carboxyl groups at the edge of graphene. Therefore, the S-C-N configurations in thiourea are partially preserved and chemically grafted onto graphene with two-step synthesis process, eventually developing into the S-C-N-C groups in SNC framework.

Figure 3 | Structural characterization. **a**, The XANES of C K-edge for graphene matrixes. Left inset is the region around 284-285 eV and right inset is the resonances between π^* and σ^* states. The sharp peak at 288.0 eV can be assigned to the π^* excitation of C-N in thiourea. **b**, The XANES of N K-edge. The peak at 402.2 is assigned to amino groups in thiourea. **c**, The XANES of S-K edge, inset is the micro-shift for SNC and SSC. The thiourea exhibits a feeble peak of sulphide at 2470.8 eV. **d**, The ^{13}C NMR spectroscopy. The feature around 164.0 ppm is assigned to S-C-N configurations from thiourea.

Microscopic morphology of SNC. Based on these results, we therefore pursued to verify the defect states of SNC via aberration-corrected scanning TEM (AC-TEM). In

the optical images, graphene ribbon rings circled by blue hexagons are explicitly identified. These onion ring like graphene structures are composed of concentric carbon layers, and cyan pentagon signs are on behalf of disordered grain boundaries (**Figure 4a**). As demonstrated in **Figure 4b**, the graphene ribbon rings are observed again, as well as in-plane nanosized holes together with ordered graphene structures appear alternately. Remarkably, the onion ring like structures are determined by the more graphene ribbons concentrically grow on the new edges, and the high-temperature ensure graphene conquer the barrier of nucleation, growing at a low chemical potential continuously³⁴. Compared with SNC, SSC shows regular atomic configuration with few defects (Supplementary **Figure 18**). Thus, the S-C-N configurations of thiourea deliver a profound effect on SNC frameworks, which renders disorder and substantial atomic rearrangement in SNC. As displayed in **Figure 4c**, carbon vacancy and irregular aromatic rings are observed in carbon lattice of SNC. Carbon single vacancy can be ascribed Jahn-Teller distortion, which generates missing carbon atom induced by additional unsaturated dangling bond, resulting in the formation of 5-9 ring³⁵ (**Figure 4c1**). We also observe the multiple vacancies arose from a row of carbon atoms partially missing, presenting folds and bumps in SNC, which morphologically result from several dangling bonds (Supplementary **Figure 19**). These non-hexagonal carbon rings are actual line defect, which mostly occur in the non-sp² hybridized orbitals, and generate 5-6-7 rings from local reconstruction (**Figure 4c2** and Supplementary **Figure 20**). Namely, these 5-6-7 rings can account for the curvature of the SNC layers, bringing about the fluffy sheet-like structure.

Of note, as illustrated in **Figure 4d**, several SW defects scatter in SNC. These are topological defects consisting of two five-atom and two seven-atom rings, through rotated a couple of C-C bond by 90° in the graphene, which can be perceived as a unique self-regulation to build stable structure of graphene lattice³⁶. Analogously, SW defect is further depicted in **Figure 4d1**, which is reconstructed from four hexagonal carbon rings. Moreover, theoretical and experimental studies suggest that the carbon atoms simultaneously linked by 5-7 rings in SW defects are active sites to facilitate the ORHP⁷. Interestingly, various apertures of in-plane holes in SNC lattice are observed (**Figure 4e** and Supplementary **Figure 21**). These holey structures arise from the loss of numerous carbon rings caused by thermal annealing, thus forming the in-plane holes. SNC flakes obtain 55-77 rings around the in-plane holes, which are extensive enough (about 3 nm in diameter) and can be regarded as defective edges (**Figure 4e1**). Compared with the defects in basal plane, these marginal 55-77 rings are most frequently observed defects in integrated graphene, which provide broad active edges for adsorption of OOH* intermediate³⁷. Moreover, the introduction of 55-77 rings lead the localized states transform to defect states, which open a local bandgap due to symmetry breaking and increase the density of state around the Fermi level (E_F) as well, facilitating local electron transfer³⁸. Impressively, we find a wrinkle-rich morphology with stripe phases and lattice phases in SNC, suggesting that more active sites are exposed with crumpling lattice plane (Supplementary **Figure 22 and 23**). Accordingly, SNC catalyst with high concentration of defects are successfully synthesized, while numerous marginal defects ensure great active area for electrocatalysis.

Figure 4 | AC-TEM images of SNC. **a, b**, The regions marked by blue and cyan respectively correspond to regularly hexagonal onion rings and disordered grain boundaries graphene. The region with yellow dotted line indicates that the graphene layers are abundant of in-plane holes with size less than 5 nm. **c, c1, c2**, Intrinsic defects are revealed in the yellow region, including (**c1**) carbon single vacancy (**c2**) and non-hexagonal rings. **d, d1**, Several SW defects observed in the basal plane of SNC framework. **e, e1**, Holey SNC with marginal 55-77 defects at the in-plane hole. Scale bar, 5 nm in **a–e**, 0.5 nm in **c1, c2, d1**, and **e1**.

Electrocatalytic ORHP characterization. To assess the ORHP activity and selectivity,

the as-prepared SNC catalyst was directly used as working electrodes and evaluated in an O₂-saturated 0.1 M KOH electrolyte by using a rotating ring-disk electrode (RRDE) device (see Method and Supplementary **Figure 24** for experimental details). SSC, SC, NC, and rGO were also measured for comparison. As displayed in linear sweep voltammetry (LSV) curves in **Figure 5a**, SNC renders a highest ring current density ($J_{\text{H}_2\text{O}_2}$, 0.73 mA cm⁻² at 0.1 V vs. RHE) and the most positive onset potential (defined as the potential at the current density of 0.1 mA cm⁻²) of 0.8074 V vs. RHE, indicating the highest ORHP catalytic activity among different graphene matrixes. Nevertheless, the $J_{\text{H}_2\text{O}_2}$ of SNC is slightly higher than that of SSC, SC, NC, and rGO (0.33, 0.54, 0.29 and 0.35 mA cm⁻²), implying that the 2e pathway is preferred for SNC catalyst. For comparison, the H₂O₂ selectivity and the number of electrons transferred (**n**) of graphene matrixes during ORR process were also calculated. SNC renders an outstanding H₂O₂ yield curve around ~90.5 to ~98.9% in the potential range of 0.2-0.6 V vs. RHE as determined by RRDE measurement (**Figure 5b**). In contrast, raw NC exhibits the poorest $J_{\text{H}_2\text{O}_2}$ (0.28 mA cm⁻²) and the lowest H₂O₂ yield ratio (35.7% at 0.6 V vs. RHE) because of the presence of graphitic-N and pyridinic-N, which favors 4e-ORR²⁹. Specially, with nitrogen introduction, the corresponding H₂O₂ selectivity increase from 77.8% for pure SC to 98.9% for SNC. This extreme improvement can be contributed the introduction of pyrrolic-N from CVD nitridation, in accordance with XPS N 1s analysis. Compared with SNC and SSC, the H₂O₂ yield of SNC is almost twice that of SSC, demonstrating the significance of thiourea as sulfur source. In detail, the H₂O₂ selectivity at 0.6 V vs. RHE follows the order of NC (35.7%) < SSC (43.1%)

$< \text{rGO (69.6\%)} < \text{SC (77.8\%)} < \text{SNC (98.9\%)}$, while the opposite trend for **n** is observed. Surprisingly, SNC yields the H_2O_2 selectivity of 98.9% with the **n** value of 2.02 (**Figure 5c**), indicating a nearly 2e-ORR process for H_2O_2 production. Additionally, rGO maintains a high H_2O_2 selectivity of $\sim 70\%$, which can be attributed to oxygen containing groups retained after annealing, accelerating 2e-ORR process^{9,20}. Although the selectivity of rGO is insufficient as ORHP catalysts, it still affords an advantageous precursor for subsequent doping. Notably, the ORHP performance of thiourea modified graphene matrixes (SNC and SC) are superior to the counterparts without thiourea involved (SSC and NC), clearly indicating that the activity and selectivity of these catalysts are dominated by defects, which match the XANES results. Thus, the defect-enriched SNC catalyst induced by thiourea can restrain 4e-ORR but expedite 2e-ORR pathway, signifying that SNC is the most suitable candidate for H_2O_2 production among these catalysts.

To gain more insight into kinetics of ORHP, further analysis of the Tafel slope was performed. The Tafel slope of SNC is 87 mA dec^{-1} , which is much lower than that of SSC (153 mA dec^{-1}), SC (110 mA dec^{-1}), NC (117 mA dec^{-1}), and rGO (168 mA dec^{-1}), signifying fast ORHP kinetics (**Figure 5d**). In addition, the ORHP activities of SNC prepared with various annealing temperatures and CVD time in control experiments were also evaluated (Supplementary **Figure 25 and 26**), and the SNC catalyst annealed at 850°C for 60 min affords faster kinetics with Tafel slope of 87 mA dec^{-1} and higher $J_{\text{H}_2\text{O}_2}$ of 0.73 mA cm^{-2} . Evidently, adjustment of temperature has a deep effect on H_2O_2 selectivity than that of CVD time (Supplementary **Figure 27 and 28**). Prolonging

nitridation times and increasing annealing temperature could engender the presence graphitic-N with high concentration, thereby leading to an apparent 4e-pathway on the adjacent carbon atoms. Particularly, the increase of graphitic-N proportion with CVD time prolonging is essentially arising from the nitrogen accumulation, while graphitic-N concentration with temperature increasing due to pyrrolic-N converted to graphitic-N species at high-temperature. Thus, prolonging CVD time and raising annealing temperature can increase the subjects of graphitic-N in SNC, which boost 4e-ORR rather than ORHP process.

In addition, the electrochemical double-layer capacitance (C_{dl}) measured via cyclic voltammetry (CV) at different scan rates was probed to estimate the electrochemical surface area (ECSA) and the corresponding intrinsic activity (**Figure 5e**). The C_{dl} and ECSA values of SNC are 1.78 mF cm^{-2} and 44.5 cm^2 , which are higher than those of SSC (0.82 mF cm^{-2} , 20.5 cm^2), SC (0.92 mF cm^{-2} , 23 cm^2), NC (0.78 mF cm^{-2} , 19.5 cm^2), and rGO (0.64 mF cm^{-2} , 16 cm^2) in 0.1 M KOH electrolyte, respectively (**Supplementary Figure 29**), suggesting the defect-enriched SNC systems ensure more electrocatalytically active sites exposed. Given the high ORHP activity and selectivity of SNC catalyst, we further analyzed their stability and durability to continuously catalyze the generation of H_2O_2 . As presented in **Figure 5f**, the LSV curves of SNC in 0.1 M KOH after 10000 cycles deliver a small decrease from ~ 2.42 to $\sim 2.36 \text{ mA cm}^{-2}$ at 0.1 V vs. RHE ; meanwhile, the average H_2O_2 selectivity (between 0.2 and 0.6 V vs. RHE) is almost unchanged just with a small decline from 93.4% to 92.1% , confirming the good durability. Besides, the stability of SNC catalyst was evaluated by long-term

testing. As presented in **Figure 5g**, SNC catalyst retains stable ring and disk current densities over 50000 s of continuous operation, demonstrating a superior recyclability and stability. Excellent structural integrity of SNC is confirmed by HR-TEM images taken after the stability test, and SNC still holds a fluffy sheet-like structure without obviously morphology change, which further confirms the robustness of the SNC catalyst (Supplementary **Figure 30**). Specifically, **Figure 5h** shows a comparison map of ORHP activity for SNC against other common catalysts, including metal-oriented systems and conventional carbon nanomaterials; SNC here demonstrates highest selectivity of 98.9% at 0.6 V vs. RHE, which outperforms most reported electrocatalysts (Supplementary **Table 4**), placing SNC at the top of all existing ORHP catalysts working in alkaline media.

Figure 5 | ORHP performance. a, polarization curves at 1,600 rpm together with the

corresponding H₂O₂ current on the ring electrode (dashed lines) and H₂O current on the disk electrode (solid lines) for graphene matrixes. The applied potential of ring electrode was set at 1.2 V vs. RHE. **b**, The corresponding H₂O₂ selectivity profiles at 0.2-0.6 V vs. RHE. **c**, H₂O₂ selectivity and **n** for different systems at 0.6 V vs. RHE. **d**, The corresponding Tafel plot of kinetic current of H₂O₂. **e**, CV cycles for SNC with varying scan rates from 20-300 mV s⁻¹. The inset is C_{dl} measurement in 0.1 M KOH. **f**, The polarization curves of SNC before and after 10000 CV potential cycles and inset is the H₂O₂ selectivity of SNC catalyst. **g**, Stability measurement of SNC at a fixed disk potential of 0.40 V vs. RHE. **h**, Comparison diagram of the selectivity for H₂O₂ electrosynthesis on SNC and other reported electrocatalysts in 0.1 M KOH electrolyte.

Theoretical calculation. The above experiments demonstrate that marginal defects modified SNC with S-C-N-C groups appreciably boost ORHP. DFT simulations were then conducted to understand the catalytic mechanism of the S-C-N-C functional groups toward ORR to H₂O₂ production. Two-dimensional graphene sheet was used as model system, where four types of SNC computational models were constructed, including pentagon-S, pyrrolic-N, and hexagon-S introduced at the edge planes of the graphene (**Figure 6a**). Initially, we tested the doping energy of all the possible N-doped sites nearby pentagon-S, and found A position has the relatively lowest doping energy, which is the most stable SNC models (Supplementary **Figure 31** and **Table 5**). Nevertheless, not all models create adsorption sites for OOH*. Accordingly, the adsorption energy of all carbon atoms (A-H sites) around S-C-N-C groups were calculated, in which A and B position were the most stable sites for SNC models due

to lowest OOH* adsorption energy (Supplementary **Table 6**). According to the Sabatier principle³⁹, the critical factors for O₂ conversion into H₂O₂ are the bind energy of active sites with OOH* intermediates (equation (1)) and desorption capacity of O₂ hydrogenated to OOH* (equation (2)).

Therefore, we used ΔG_{OOH^*} as the best descriptor to determine the ORHP activity on SNC. **Figure 6b** presents the volcano plots of the H₂O₂ formation with the limiting potential (U_L) of 0.70 V, which provides a general mechanism understanding at a wide pH range. Evidently, the U_L closer to 0.7 V reflects that the selected site of SNC is more likely to catalyze ORHP, and the corresponding free energy profiles of 2e-ORR affords lower overpotential for OOH* adsorption. Notably, most of the plots concentrate on the right side of volcano map, revealing that the binding capacity to OOH* of active sites eventually determine the ORHP performance. Among various possible configurations for SNC groups, Edge 2A exhibits a U_L of 0.64 V and improves the H₂O₂ activity towards the top of the volcano plot, comparable with the previously reported noble metal catalysts^{3,5}. Thus, we modeled Edge 4 (transforming the pentagon-S to hexagon-S in Edge 2) to examine the effect of OOH* adsorption by change the local electrons around sulfur atom. This conversion leads to the carbon ring doped with both nitrogen and sulfur atoms offsets z-axis from graphene base plane (Supplementary **Figure 32**), which induces the carbon active site become unstable, showing a lower U_L (0.53 V) and higher overpotential (0.17 eV) for OOH* adsorption (**Figure 6c**).

Surprisingly, Edge 2A yields the lowest energy barrier with an overpotential of 0.06 eV, suggesting the optimal electronic structure. Accordingly, the free-energy diagram of the intermediate states in 4e-pathway for different SNC models are also calculated, and the energy barrier for the formation of OOH* in 4e-pathway shows a similar trend with 2e-pathway (Supplementary **Figure 33**). We find that only Edge 1 located at the left leg of the volcano plot, which is limited by equation (2) due to the strong OOH* binding strength, thus generating a higher dissociation energy (3.13 eV) from OOH* to O* than other models, such as Edge 2 (1.16 eV), Edge 3 (2.06), and Edge 4 (1.77 eV). Furthermore, Edge 1A shows the highest energy barriers for O₂ to OOH* in both 2e- and 4e-pathway (0.25 and 0.98 eV, respectively), which lead to the O-O dissociation occurs during O₂ reduction, driving the 4e- pathway with H₂O as the major product.

To investigate the effect of oxidized-S species on the ORHP performance, we respectively replaced the positions of sulfur atoms in Edge 1 to 4 with C-SO₂ and C-SO₃ groups, and calculated the corresponding volcano plot at same sites (Supplementary **Figure 34, 35**). Obviously, for C-SO₂ and C-SO₃ groups modified SNC models, the U_L shows a gradual decrease as more oxygen atoms coordinated with pentagon-S, thereby exhibiting degraded ORHP activity (Supplementary **Table 7**). In addition, the introduction of oxygen atoms increases the energy of the bar configuration, leading to an unstable system with OOH* adsorption. Particularly, only Edge 2A exhibits undiminished U_L and preferable ΔG_{OOH^*} after adding oxygen atoms, revealing the good intrinsic activity. According to previous work²², O modified S-defect

sites have lower energy barrier for OOH* dissociate to O* than that of normal S-defect sites. Thus, the C-SO₂ and C-SO₃ groups in SNC is more beneficial to 4e-ORR.

To verify the pyrrolic-N is favorable for H₂O₂ production in S-C-N-C groups, we transformed pyrrolic-N to pyridinic-N configuration in Edge 1 and investigate the corresponding change of ΔG_{OOH^*} (Supplementary **Figure 36**). Of note, the Edge 1 doped with pyridinic-N transfers from the strongly bind side to weakly bind side, while the U_L decreases from 0.45 to 0.33 V, generating a relatively unstable system for OOH* adsorption. This is mainly due to the delocalized lone pair electrons carried by pyridinic-N, which motivate charge jump from π orbitals to antibonding orbitals during O₂ activation, and extensively weaken the O-O bonds as well as further facilitate OOH* intermediate dissociation into O* and OH*, impeding ORHP process⁴⁰. In addition, we respectively modified the graphene model with hexagon-SO₂, pentagon-SO₂, pyridinic-N, pyrrolic-N, graphitic-N, pentagon-S, hexagon-S, and SW defect, and investigated the corresponding the ORHP activity of these graphene matrixes (Supplementary **Figure 37**). Correspondingly, for pyrrolic-N and pentagon-S modified configurations, the calculated U_L is out the range of volcano plot, while pyridinic-N, graphitic-N, hexagon-S, hexagon-SO₂, and pentagon-SO₂ modified graphene have moderate binding energies for OOH*, which directly proves that SNC has better ORHP activity than SSC and NC (Supplementary **Figure 38**). Interestingly, only pyrrolic-N or pentagon-S modified graphene are limited in optimizing ORHP reaction kinetics, demonstrating the necessity of binary configurations. Thus, the pyrrolic-N and pentagon-S holistically coordinated structure in SNC framework can synergistically renders excellent 2e-ORR

activities.

To gain more intuitive insight into the bonding nature of the SNC catalyst adsorbed with O₂ molecule, we employed Crystal orbital Hamilton population (COHP) to analyze the bonding and anti-bonding states between OOH* intermediate and active sites. As displayed in **Figure 6d**, Edge 1A, 3A, and 4A have several distinct bandgaps near the E_F and respectively exhibit high overpotential of 0.25, 0.10, and 0.17 eV (**Figure 6c**), which are not favorable for ORHP. Edge 2A shows a wide energy band passing through the Fermi surface, indicating that more electron transfer occurs during active sites bonding with OOH*. To give a more quantitative explanation, the integrated COHP (ICOHP) was calculated by integrating the energy up to E_F. Specifically, Edge 1A has a highest ICOHP value (11.77), which contributes Edge 1A located at the left leg of the volcano plot individually; and the desorption of OOH* limited the binding strength, leading to the strongest bonding state. Interestingly, ICOHP positively correlate with ΔG_{OOH*} value, whereas Edge 2A deviates from this relationship and approaches the critical value (4.22 eV) of the ideal ORHP catalyst (Supplementary **Figure 39**). This deviation for Edge 2A attributes to the existence of bonding states occupied by electrons in E_F, which provides the least antibonding contribution with optimized binding strength toward OOH*, accounting for the best ORHP activity.

Moreover, we calculated Bader charge to analyze the charge transfer on active sites before and after the adsorption of OOH* intermediate. Compared with the sulfur and carbon atoms, the higher electronegativity of nitrogen atom (3.04 eV) could activate π-conjugated system and have a strong ability to withdraw electron, resulting in high local

charge density (**Figure 6e**, red triangle regions). Therefore, the electrons of Edge 3A adjacent to nitrogen atom are easily to be withdrawal, which produces a highest charge transfer (0.389 |e|) than other active sites. Edge 1A is the only site showing a negative Bader charge (-0.173 |e|), which indicates the corresponding carbon atom has excess electrons outside its nucleus and strongly binds with electronegative OOH*, consisting with the results of volcano plots and COHP. As anticipated, as pentagon-S replaced by hexagon-S, the corresponding charge transfer decreases from 0.139 |e| to 0.010 |e|, demonstrating the weak interaction between O₂ molecules and Edge 4A, which restrains the formation of OOH* intermediates. To further clarify the correlation between Bader charge and ORHP performance, we calculated the charge transfer of all the active sites with OOH* adsorption (Supplementary **Table 8**). Compared with bare sites, most of sites absorbed with OOH* have a higher charge transfer, only the sites of 1B and 4B show a subtle change (0.438 |e| to 0.456 |e| and 0.294 |e| to 0.333 |e|, respectively). Moreover, sites 1B and 4B also exhibit low limiting potential (0.30 and 0.25 V) and high overpotential values for OOH* adsorption (0.40 and 0.45 eV) (**Figure 6b and 6c**). Therefore, the charge transfer for site 1B and 4B change insignificantly after adsorption due to weak adsorption with OOH*. According to electrostatic interaction⁴¹, the binding strength between less positively charged carbon atoms and OOH* can be weakened, while Edge 2A adsorbed with OOH* shows a lowest charge transfer (0.41 |e|) than other SNC models, enhancing the desorption of OOH*.

Figure 6 | Theoretical analysis of different SNC configurations. **a**, The atomic structures of the examined SNC computational models. Gray, blue, yellow, and white balls denote carbon, nitrogen, oxygen, and hydrogen atoms, respectively. The carbon active sites labeled by the letters, in which A and B own the highest adsorption energies for OOH^* . **b**, Calculated volcano plot (solid line) for ORHP demonstrated with limiting potential U_L as a function of ΔG_{OOH^*} . The equilibrium potential for ORHP is 0.70 V and shown as the dashed green line. The golden squares present the activities of Pt-Hg, Cu-Hg, Ag-Hg, and Pd-Au alloys. **c**, Free energy profile of 2e-ORR pathway at $U =$

0.70 V for various SNC models and the corresponding overpotential. **d**, COHP between OOH* intermediate on Edge 1A, 2A, 3A, and 4A. The E_F is set at zero energy. Left side peak is anti-bonding state, right is bonding state. **e**, The Bader charge corresponding to S-C-N-C groups; the A sites marked with black. The blue and red region indicate electron-donating and electron-withdrawing areas, respectively.

Conclusions.

In summary, we have adopted SNC catalyst with S-C-N-C functional groups via hydrothermal self-assembly and controllable CVD nitridation. The S-C-N-C functional groups with marginal defects formed by the covalently grafting of pentagon-S and pyrrolic-N onto the edge of graphene, which account for the high activity of catalyzing ORHP. SNC presents excellent ORHP catalytic performance with maximum H_2O_2 yield ratio of 98.9% at 0.60 V vs. RHE and retains 95% of initial activity after 50000 s continuous reaction. DFT calculations reveal that the defective S-C-N-C functional groups in SNC afford desirable binding strength to OOH* intermediates and diminishes the energy barrier for O_2 to OOH*. This work systematically elucidates the mechanism of marginal defects on the performance of ORHP, which opens up an avenue for designing efficient metal-free electrocatalysts through defect engineering.

Methods

Preparation of SNC. GO was synthesized by using the improved Hummers method⁴².

An aqueous suspension of GO (2 mg mL^{-1}) was prepared by adding 0.15 g GO into 75 mL deionized water and sonicating for 10 h. Then, 10.6875 mg thiourea was added into the GO suspension and sonicated for another 30 min. The obtained solution was moved

to Teflon autoclave (100 mL volume) and heated 180 °C for 12 h. The subsequent product was freeze-dried to generate spongy column. Sponge column of S-rGO was then placed in the center of a standard 1-inch quartz tube furnace. After pumping and purging the system with Ar for 15 min, the temperature was risen at 15 °C min⁻¹ up to 850 °C with the introducing of NH₃ (50 sccm) and Ar (100 sccm) under a raised-up pressure (~ 2.85 Torr). The process maintained for 1h, and the ultimate creation SNC was cooled down to room temperature by quickly removing the sample from the hot region of furnace under the protection of Ar atmosphere.

Catalyst structural characterization. A FE-SEM (HITACHI, SU8010) and field emission gun TEM (JEOL, JEM-2100) were used to examine the morphologies and structures of the catalysts. X-ray powder diffraction (Rigaku, D/Max Ultima VI) was configured with a Cu-K α radiation source ($\lambda = 1.5418 \text{ \AA}$) and graphite monochromator at 40 kV voltage and 40 mA current. The Raman spectra were recorded on a confocal micro-Raman spectrometer (Horiba Jobin Yvon, LabRAM HR Evolution) with 532 nm laser excitation. The I_D/I_G ratio of samples were calculated by deconvoluting the Raman spectra using Gaussian peak fitting (Origin 2018) to allow a comparison of peak areas. The specific area was analyzed on a Quantachrome autosorb iQ₂ analyzer by N₂ adsorption-desorption isotherms using the Brunauer-Emmett-Teller (BET) method. The pore size distributions were determined by the Barret-Joyner-Halenda method. Room-temperature EPR spectra were obtained using an EMXPLUS10/12 paramagnetic resonance spectrometer, horizontal axis was convert to g value by $g = hv/\beta H$ ⁴³. The chemical compositions of samples were confirmed by XPS spectra (ThermoFisher)

with a monochromatic Al K α radiation. All XPS spectra were calibrated using C 1s line at 284.8 eV and Thermo Advantage V5.52 program were employed for surface componential content analysis. Elemental content measured by elemental analyzer (Elementar, Vario EL CUBE), the oxygen content was measured separately using a linear model. FT-IR were collected on a Thermo Nicolet is5 with a resolution of $\sim 1\text{ cm}^{-1}$, and the samples were tableted with KBr as support. The XANES measurements were undertaken on the soft X-ray beamline (BL20A1 for C K- and N K- edge) and intermediate X-ray beamline (BL16A1 for S K-edge) at the National Synchrotron Radiation Research Facility at Taiwan. The sample were pressed on indium foil and measured in X-ray fluorescence mode. The data were normalized to the incident photon flux and processed using the ATHENA software package⁴⁴. The Bruker AVANCE III 300 Spectrometer was conducted for Solid-state ^{13}C NMR analysis. HAADF-STEM images and EDS elemental mappings were carried out in FEI-Themis Z equipped with a Super-X EDS detector and operated at 300 kV. AC-TEM images were taken using an 80 KeV FEI-Themis Z equipped with a spherical aberration corrector.

Electrochemical measurement. All the electrochemical measurements were performed with a three-electrode cell system operated by a CHI 760E (CH instrument, USA) electrochemistry station and carried out in O₂-saturated 0.1 M KOH electrolyte. A RRDE loaded with catalysts, a platinum wire and an Ag/AgCl (saturated KCl) were used as the working electrode, counter electrode and reference electrode, respectively. The RRDE was (AFE6R2, Pine Research Instrumentation, USA) comprised by a glassy carbon rotation disk electrode (disk area: 0.2376 cm^2) and platinum ring (ring area:

0.2356 cm²), with a theoretical collection efficiency of 0.38. The rotating speed of working electrode was 1600 rpm throughout the tests. Synthetic catalyst ink was prepared by ultrasonically dispersing 2 mg of catalyst in solution containing 40 µL of 5 wt% Nafion solution and 0.4 mL of 1:1 (v/v) deionized water/ethanol. After sonication for 1h, 5 µL of the obtained suspension was loaded onto disk electrode, naturally dried prior to test. The area-based mass of loading electrocatalyst was 0.10 mg cm⁻².

Before tests, all the electrocatalysts were activated by CV cycles with a scan rate of 100 mV s⁻¹ in N₂-saturated and O₂-saturated 0.1 M KOH aqueous solution, the former aimed to detect background current. LSV was performed at a scan rate of 5 mV s⁻¹. All the potentials were calibrated to the RHE by equation (3). The ring electrode was set as a decomposition potential of 1.2 V vs. RHE to assemble the H₂O₂.

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.1976 \quad (3)$$

The selectivity of H₂O₂ and electron transfer number (n) were calculated based on the current of the disk electrode and ring electrode (equation (4) and (5)).

$$\text{H}_2\text{O}_2(\%) = 200 \times \frac{I_{\text{R}}/N}{I_{\text{D}} + I_{\text{R}}/N} \quad (4)$$

$$n = 4 \times \frac{I_{\text{D}}}{I_{\text{D}} + I_{\text{R}}/N} \quad (5)$$

where I_R is the ring current, I_D is the disk current and N is the collection efficiency.

The ECSA of the electrode was determined by measuring the C_{dl} of the catalytic surface, which is derived from the CV cycles (Scan rates were 20, 60, 100, 140, 180, 220, 260 and 300 mV s⁻¹) measured at the range of 0.86 to 1.06 V vs. RHE where no Faradaic current was generated. Based on the definition: ECSA = C_{dl} / C_s, we used a specific capacitance (C_s) value of 40 µF cm⁻².

Computational details. All the calculations were performed using Vienna ab initio

Simulation Package (VASP 6.2) with the projector augmented wave (PAW) pseudopotential method⁴⁵. The exchange-correlation potential was described by Perdew-Burke-Ernzerhof (PBE) functional⁴⁶ with generalized gradient approximation (GGA). The cutoff energy for the plane-wave was set to 500 eV. In the geometry optimization, the convergence criteria for the energy and force were 10^{-4} eV and 10^{-2} eV $\text{\AA}^{-1}$, respectively. A large vacuum spacing (more than 15 $\text{\AA}$) was taken to prevent mirror interactions. The Brillouin zones were sampled with $2\pi \times 0.02 \text{\AA}^{-1}$ spacing in reciprocal space by the Monkhorst-Pack scheme. Grimme's DFT-D3 van der Waals (vdW) corrections with the Becke-Jonson (BJ) damping was employed. The Gibbs reaction-free energy change (ΔG) for each step in the ORR was calculated using the computational hydrogen electrode (CHE) model⁴⁷,

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S + eU + \Delta G_{\text{pH}} \quad (6)$$

where ΔE , ΔZPE and ΔS are the binding energy change, zero-point energy change and entropy change between the reactant and product. U and e are the electrode potential and the number of electrons transferred, respectively. ΔG_{pH} is the free energy correction of pH calculated by equation (7):

$$\Delta G_{\text{pH}} = \ln 10 \times k_{\text{B}}T \times \text{pH} \quad (7)$$

Since RHE is taken as the reference, the pH was set to be zero in this calculation. The U_{L} is defined as the lowest potential at which all the reaction steps are downhill in free energy.

Data availability. The data that support the plots within these paper and other findings of this study are available from the corresponding author upon reasonable request.

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828 **Author contributions**

829 Z. M., Y. M., Y. Q., and X. F. conceived the experiment and scientific discussions. Z.
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832 paper. All the authors discussed the results and revised the paper.

833 **Competing interests**

834 The authors declare no competing financial interests.

835 **Additional information**

836 **Supplementary information** is available in the online version of the paper.

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