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A Ni single-atom catalyst for advanced environmental disinfection based on electrochemical production of hydrogen peroxide†

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With the increasing attention to environmental hygiene and air quality, the disinfection of bioaerosols has become a highly focused research area. Therefore, identifying a safe and efficient disinfection method to maintain indoor air quality is of critical importance. Hydrogen peroxide (H_2O_2) has garnered attention for environmental disinfection due to its broad-spectrum bactericidal properties and low toxicity. Herein, we employed the electrocatalytic 2e^- oxygen reduction reaction (ORR) to produce H_2O_2 and directly applied it for bioaerosol disinfection. In detail, our density functional theory (DFT) calculations demonstrated that a Ni single-atom catalyst with N and O coordination resulted in a partial transfer of electrons from the Ni atoms to the coordinated oxygen atom, which optimized the $^*\text{OOH}$ binding energy and enhanced 2e^- oxygen reduction activity to produce H_2O_2 . Guided by the DFT calculations, we designed a Ni single-atom catalyst with a $\text{Ni}-\text{N}_4-\text{O}$ structure for 2e^- ORR to produce H_2O_2 . This catalyst achieved high H_2O_2 selectivities of 95% and 85% under alkaline and neutral conditions, respectively, and displayed a H_2O_2 production rate as high as 316.8 mmol per g metal per h in an H-type electrolytic cell. Finally, in our environmental disinfection system, the produced H_2O_2 was atomized into a small space for disinfection, achieving a high disinfection rate of 87% at 4 minutes and nearly 100% at 6 minutes. This study highlights the great potential of single-atom catalysts in the field of environmental disinfection.

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1. Introduction

Numerous pathogenic microorganisms suspended in the air or adhering to surfaces can pose a threat to human health upon inhalation or contact with the skin and mucous membranes, potentially causing damage to tissues and organs. Examples include tuberculosis, smallpox, measles, SARS, and avian influenza, all of which are transmitted through aerosols suspended in the air. To effectively curb airborne transmission, thorough sterilization of bioaerosols containing pathogens is crucial. Ensuring safety and effectiveness during disinfection processes is paramount in preventing the airborne spread of pathogens. Hydrogen peroxide (H_2O_2) is an environmentally friendly and versatile oxidant widely used in disinfection, bleaching, waste treatment, and chemical synthesis.^{1–3} However, to date, H_2O_2 generated through electrochemical processes has primarily been used in water disinfection, with limited application in space disinfection. Choi *et al.*

demonstrated that a 0.5% concentration of aerosolized hydrogen peroxide disinfectant effectively removes pathogens from environmental surfaces. Aerosolization *via* a nebulizer can generate H_2O_2 vapor at ambient temperatures.⁴ Wood *et al.* used relatively low levels of H_2O_2 vapor to deactivate pathogens in indoor environments.⁵ Their results indicate that exposure to low levels of H_2O_2 vapor for four to seven days (with average air concentrations of 5–10 ppm) effectively deactivates anthrax spores on various materials.

To date, H_2O_2 production still heavily relies on the anthraquinone process established by Riedl *et al.* in 1939.^{6–8} The process relies on the catalytic or oxidative reaction of anthraquinone molecules in organic solvents on nickel-based or palladium-based catalysts, generating severe chemical pollution. In addition, the transportation and storage of high-concentration H_2O_2 solutions are critical due to their instability and hazards.^{9,10} Therefore, developing a small-scale, safe, economically efficient, and environmentally friendly method for synthesizing H_2O_2 is crucial.^{11,12} With technological advancements, electrochemical synthesis of H_2O_2 *via* the two-electron (2e^-) oxygen reduction reaction (ORR) has emerged as an alternative to traditional processes.^{13,14} Berl first reported on the electrochemical generation of H_2O_2 *via* 2e^- ORR, commercializing it as the Huron-Dow process in 1991.¹⁵

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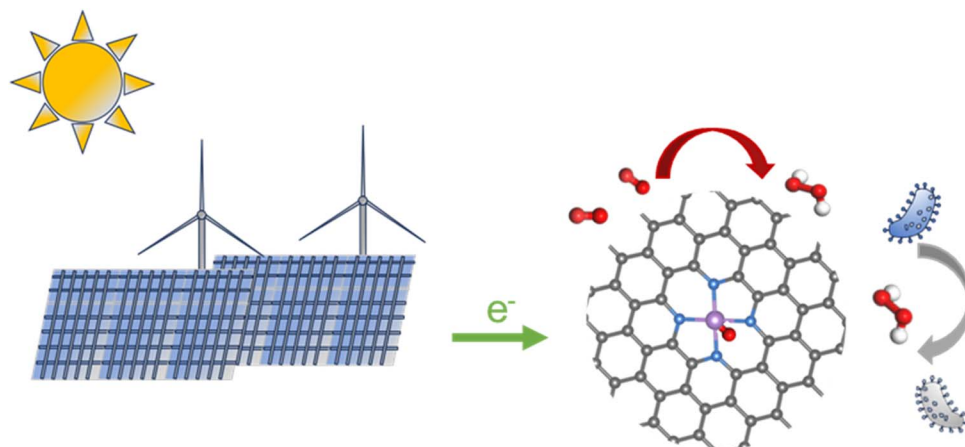


Fig. 1 Schematic of the electrochemical generation of H_2O_2 for environmental disinfection, powered by renewable energy.

Recently, variants of the electro-Fenton process (a variation of the Huron-Dow process) have been developed and widely applied in water purification.^{16–19} Therefore, electrochemical synthesis of H_2O_2 holds considerable potential for further application development and research.

This work demonstrates a Ni single-atom catalyst for advanced environmental disinfection based on the electrochemical production of hydrogen peroxide. As shown in Fig. 1, the strategy aims to utilize renewable energy sources (such as solar energy and wind energy) to provide electrical energy for electrochemical devices to drive the 2e^- oxygen reduction reaction (ORR) for producing H_2O_2 . The produced H_2O_2 is then applied for environmental disinfection. In detail, our density functional theory (DFT) calculations suggest that the Ni single-atom catalyst with N and O coordination leads to a partial transfer of electrons from Ni atoms to the coordinated oxygen atom, which can optimize the $^*\text{OOH}$ binding energy and enhance the 2e^- ORR activity to produce H_2O_2 . From the DFT calculations, we synthesized a Ni single-atom catalyst with a $\text{Ni-N}_4\text{-O}$ structure for 2e^- ORR, which showed excellent H_2O_2 selectivity and high H_2O_2 production rate. In our environmental disinfection system, the produced H_2O_2 was atomized into a small space for disinfection, which achieved a high disinfection rate of 87% at 4 minutes and nearly 100% at 6 minutes for disinfection.

2. Materials and methods

2.1 Preparation of M-OCB

Metal-doped oxidized carbon black was achieved through ion adsorption and hydrothermal reaction methods. Initially, 20 mg of oxidized carbon black (OCB) was dispersed in 10 mL of water to form a suspension, which was then sonicated for 30 minutes. Subsequently, 220 mg of 2,5-pyridinedicarboxylic acid was added to the suspension and sonicated for another 30 minutes until a uniform dispersion was achieved. Finally, 11.5 mg of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added and the mixture was sonicated for 2 hours. Next, the prepared suspension was transferred into a 50 mL hydrothermal reaction vessel and reacted at 180 °C for 6

hours. After cooling the reaction vessel to room temperature, the solid product was collected by centrifugation, dried overnight in a vacuum oven, and subsequently ground into a powder. The powder was then placed in a tube furnace and heated under an Ar gas flow at a rate of 60 standard cubic centimeters per minute (sccm) to 350 °C, and then maintained for 1 hour to obtain the final product, $\text{Ni-N}_4\text{-O}$. Different percentages of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used to prepare 3%, 5%, and 10% $\text{Ni-N}_4\text{-O}$ by varying the amount added. Additionally, $\text{Fe-N}_4\text{-O}$, $\text{Co-N}_4\text{-O}$, and $\text{Cu-N}_4\text{-O}$ were synthesized using the same method.

2.2 Rotating ring-disk electrode (RRDE) measurements

A three-electrode configuration electrochemical workstation (Ivium, Netherlands) was used at room temperature, with data collected by a CHI 760E electrochemical workstation (CH Instruments, Ltd). The electrode setup included Ag/AgCl as the reference electrode, platinum wire as the counter electrode, and a rotating ring-disk electrode (RRDE) as the working electrode. The disk electrode was a glassy carbon disk with a diameter of 4 mm (geometric area of 0.1256 cm^2), while the ring electrode was platinum (geometric area of 0.1866 cm^2). Prior to measurements, the catalyst ink was prepared by mixing 5 mg of catalyst with 625 μL of deionized water, 625 μL of anhydrous ethanol, and 30 μL of 5 wt% Nafion under sonication for 1 hour until a homogeneous catalyst ink was obtained. Subsequently, 7 μL of the ink was drop-cast onto a polished disk electrode, and dried naturally at room temperature to form a uniform thin film, providing approximately 0.189 mg cm^{-2} of catalyst loading on the disk electrode surface. All electrochemical measurements were conducted in 0.1 M KOH or 0.1 M PBS solutions saturated with O_2 or N_2 . Conversion between the Ag/AgCl electrode and the reversible hydrogen electrode (RHE) was performed using formula (1).

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.1976 + 0.0592 \times \text{pH} \quad (1)$$

Before conducting measurements, a CV pre-scan is necessary to activate the platinum ring electrode. The scan range is 0 to

1 V vs. RHE (reversible hydrogen electrode), with a scan rate of 100 mV s⁻¹ and 20 cycles, until a stable state is achieved. Throughout the measurement process, continuous O₂ flow is required to maintain an oxygen atmosphere at the electrolyte surface and equilibrium O₂ concentration in the electrolyte. For the LSV (linear sweep voltammetry) curves of various catalysts, the scan rate is 10 mV s⁻¹, and the potential range is 0 to 1 V vs. RHE (without *IR* correction). The ring electrode potential is set at 1.2 V vs. RHE to oxidize the H₂O₂ generated by the disk electrode. The RRDE rotation speed is set to 1600 rpm. Subsequently, N₂ is purged for at least 15 minutes to achieve N₂-saturated electrolyte conditions for the background current measurement. Polarization curves are corrected by subtracting the background current measured in N₂-saturated electrolyte from the current measured in the O₂-saturated electrolyte. The collection efficiency *N* is calibrated at different speeds using the Fe(CN)₆³⁻/Fe(CN)₆²⁻ redox method. Based on measurements, *N* is determined to be 36.9% (Fig. S1†), which is close to the theoretical value of 37%.

The H₂O₂ selectivity calculation formula is as follows:

$$\text{H}_2\text{O}_2 = \frac{200 \times \frac{I_{\text{ring}}}{N}}{|I_{\text{disk}}| + \frac{I_{\text{ring}}}{N}} \quad (2)$$

where *I*_{ring} is the ring current, *I*_{disk} is the disk current, and *N* represents the collection efficiency.

The number of electrons transferred can be calculated using the following formula:

$$n = \frac{4 \times |I_{\text{disk}}|}{|I_{\text{disk}}| + \frac{I_{\text{ring}}}{N}} \quad (3)$$

The Tafel slope formula is as follows:

$$\eta = \alpha + b \log(J_K) \quad (4)$$

Here, α is a constant, η is the applied potential, *b* is the Tafel slope, and *J*_K is the electrochemical current density for H₂O₂ generation.

In 0.1 M KOH solution, cyclic voltammetry (CV) scans were conducted in the non-faradaic region to measure the electrochemical capacitance and electrochemical active surface area based on the double-layer capacitance curve. The scan rates ranged from 10 to 120 mV s⁻¹. As shown in Fig. S2 and Table S2,† the double-layer capacitance was determined from the slope relationship between the current density and scan rate. The catalyst stability was measured using cyclic voltammetry (CV) with a potential range of 0–1 V vs. RHE over 6000 cycles, approximately lasting 16.5 hours.

The five catalysts were tested by cyclic voltammetry (CV) in electrolytes saturated with O₂ and N₂, respectively, to detect the performance of the catalysts (Fig. S3†). It can be seen that in an N₂ atmosphere, different catalysts have similar curves, indicating that they have similar double-layer capacitances. In an O₂ atmosphere, the O₂ reduction peaks of these five catalysts

generally appear at 0.7–0.8 V vs. RHE, but the reduction peak of Fe–N₄–O is not obvious.

2.3 Production of H₂O₂ in an H-type electrolysis cell

H₂O₂ production was conducted using an H-type electrolysis cell. An anion exchange membrane, FAB-PK-130, separated the anode and cathode compartments to prevent oxidation of H₂O₂ at the anode. To facilitate subsequent disinfection applications, the cathode compartment was filled with PBS buffer solution, ensuring the electrolyte was harmless to bacteria, while the anode compartment contained 0.1 M KOH solution. O₂ was introduced into the cathode compartment under vigorous stirring, maintaining a gas flow of 20 Standard Cubic Centimeters per Minute (sccm) during measurements to ensure O₂ saturation, while stabilizing the liquid surface. A hydrophobic carbon paper (2 × 2 cm²) was used as the working electrode, onto which 1 mg of catalyst was spray-coated, achieving a catalyst loading of 0.25 mg cm⁻² on the carbon paper. The catalyst-coated carbon paper was dried naturally at room temperature, ensuring uniform distribution of the catalyst. Ag/AgCl and Pt foils were employed as reference and counter electrodes, respectively, and placed in the cathode and anode compartments. Samples were taken every hour, and their concentrations were measured *via* colorimetric reaction. Additionally, polarization curves were recorded for catalyst-coated carbon paper and pristine hydrophobic carbon paper in the H-type electrolysis cell, with a scan rate of 5 mV s⁻¹ and a scan range of 0–1 V vs. RHE (without *IR* compensation).

2.4 Density functional theory calculations

Spin-polarized density functional theory (DFT) calculations were performed using the VASP software to optimize structures and obtain electronic properties. The RPBE(*U*) method was selected to evaluate the catalyst's free energy, incorporating spin polarization. The plane-wave energy cutoff was set to 500 eV with a Gaussian smearing width of 0.05 eV using projector augmented waves (PAW) pseudopotentials. The optimization of the bulk transition metals employed an 11 × 11 × 11 Monkhorst-Pack *k*-point mesh. The kinetic energy cutoff was set to 700 eV, and a Gaussian smearing method with an energy width of 0.02 eV was applied. The energy of each single atom was optimized within an asymmetric supercell with dimensions of 19 Å × 20 Å × 21 Å to better represent their degenerate states using the Γ -point. These isolated (Tm) SA were embedded into a graphene (Gr) supercell consisting of 48 carbon atoms, with a 7 × 7 × 1 *k*-point sampling. Geometric relaxation continued until Hellman–Feynman forces converged to 0.01 eV Å⁻¹. Convergence tests were carried out during the calculation to ensure the reliability of the results.²⁰

2.5 Bioaerosol disinfection testing

Pseudomonas aeruginosa was cultured in LB broth at 37 °C with shaking for 12 hours. The bacterial concentration was determined to be 2 × 10⁹ CFU mL⁻¹ using the dilution method. The culture was then diluted with PBS buffer to a concentration of 2 × 10⁷ CFU mL⁻¹ for the experiment. A predetermined

concentration of H_2O_2 solution, prepared using electrochemical methods, was loaded into a nebulizer for the disinfection experiment. Aerosol generation was performed using an aerosol generator (ZR-1050, Qingdao Zhongrui Intelligent Instrument Co., Ltd, China) at a standard flow rate of 10 L min^{-1} for 30 minutes to ensure uniform distribution of bacteria in the air. After stopping aerosol generation, aerosolized H_2O_2 was immediately applied for disinfection. Bacterial sampling was conducted using a six-stage Andersen sampler (ZR-2000, Qingdao Zhongrui Intelligent Instrument Co., Ltd, China) with a standard flow rate of 28.3 L min^{-1} . The sampler collects bio-aerosols of different particle sizes: $>7 \mu\text{m}$, $7.0\text{--}4.7 \mu\text{m}$, $4.7\text{--}3.3 \mu\text{m}$, $3.3\text{--}2.1 \mu\text{m}$, $2.1\text{--}1.1 \mu\text{m}$, and $1.1\text{--}0.65 \mu\text{m}$. Subsequently, the collected bacterial samples were plated onto culture dishes and incubated overnight at 37°C . The next day, the colony counts on the plates from different sampling times were observed to assess the efficacy of H_2O_2 produced *via* electrochemical methods for disinfection.

3. Result and discussion

3.1 Theoretical calculations

Catalysts play a key role in our proposed environmental disinfection system. We employed theoretical calculations to guide the design of highly efficient catalysts for 2e^- ORR. In the 2e^- ORR process, the step from O_2 to $^*\text{OOH}$ plays a crucial role, and

the selectivity of the 2e^- ORR is fundamentally determined by the adsorption strength of the $^*\text{OOH}$ and $^*\text{O}$ intermediates: to achieve high catalytic activity, the adsorption of $^*\text{OOH}$ should be enhanced; to achieve high catalytic selectivity, the adsorption of $^*\text{O}$ (the dissociation product of $^*\text{OOH}$) should be weakened. We performed DFT calculations to predict the kinetics of the oxygen reduction reaction for different Ni single-atom configurations. Nine possible models were selected ($\text{Ni-N}_4\text{-O}$, $\text{Ni-N}_1\text{O}_3$, Ni-O_4 , Ni-N_4 , $\text{Ni-N}_3\text{S}$, Ni-N_3 , $\text{Ni-N}_3\text{O}_1$, NiN_2O_2 , $\text{Ni-N}_4\text{O}_2$), and we calculated the adsorption energies of $^*\text{OOH}$, $^*\text{O}$, and $^*\text{OH}$ on four structures. We established correlations between $\Delta G(^*\text{OOH})$ and the limiting potentials for 2e^- ORR and 4e^- ORR to describe the scaling relations.²¹

Fig. 2a shows the activity volcano plot for 2e^- ORR of the nine different Ni single atoms. According to DFT calculations, $\text{Ni-N}_4\text{-O}$ is observed to be closest to the peak of the limiting potential volcano compared to other configurations, exhibiting high selectivity for the formation of H_2O_2 . In other words, the remaining coordination structures tend to dissociate the $^*\text{OOH}$ intermediate to produce $^*\text{O}$, which preferentially leads to H_2O generation *via* the 4e^- ORR pathway. To more accurately describe the ORR reaction, we examined the relationship between $\Delta G(^*\text{OH})$ and the limiting potential for 4e^- ORR; the limiting potential of $\text{Ni-N}_4\text{-O}$ is far from the equilibrium potential for 4e^- ORR. This indicates that $\text{Ni-N}_4\text{-O}$ has low activity for the reduction of O_2 to H_2O . Fig. 2b displays the

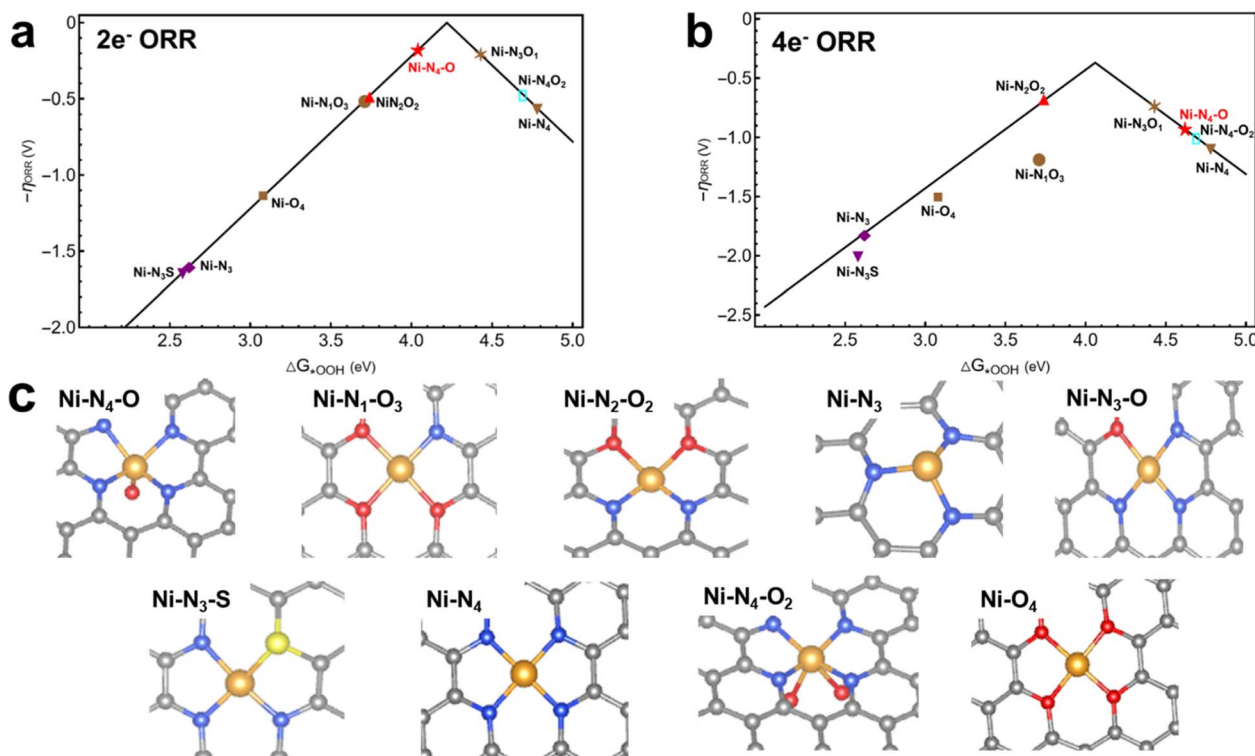


Fig. 2 Theoretical prediction of electrocatalysts for ORR selectivity with different Ni coordination. (a) Volcano plot of the 2-electron reduction reaction of O_2 . (b) Volcano plot of the 4-electron reduction reaction of O_2 (with the limiting potential plotted as a function of $\Delta G_{^*\text{OOH}}$). The equilibrium potentials of $U_{\text{O}_2/\text{H}_2\text{O}_2}$ is 1.23 V. (c) Simulated model of the single-atomic Ni moiety showing different types of coordination environments.

activity volcano plot for $4e^-$ ORR of the nine different Ni single atoms, showing that Ni-N₄-O is distant from the vertex of the $4e^-$ ORR volcano plot. This collectively indicates that Ni-N₄-O exhibits higher activity in the $2e^-$ ORR reaction, while having lower activity in the $4e^-$ ORR reaction, suggesting that the adsorption energy of this catalyst for intermediates is more suited for the $2e^-$ ORR reaction pathway. Considering the influence of the hydrogenation reaction, in order to explore the impact of Ni-N₄-OH on the catalytic activity, the relationship between $\Delta G(^*OOH)$ and $\eta(ORR)$ was studied, as shown in Fig. S5.† Fig. 2c presents the nine different Ni coordination configurations. To further clarify the advantages and uniqueness of this optimal Ni configuration, it was compared with other different elements (Fe, Co, Cu) with the same configuration. As shown in Fig. S6,† on the $2e^-$ ORR pathway, it is observed that Ni-N₄-O is closest to the peak position of the limiting potential volcano plot.

3.2 Synthesis and characterization of the catalysts

According to the theoretical calculations, we synthesized a Ni single-atom catalyst for $2e^-$ ORR. Commercial carbon black was oxidized using concentrated nitric acid to introduce surface defects and oxygen-containing functional groups. Subsequently, pyridine-2,5-dicarboxylic acid and Ni(NO₃)₂·6H₂O were sequentially added and dispersed under sonication to achieve a uniform distribution. The mixture was then transferred to a hydrothermal reactor for the reaction. After cooling, the reactor contents were centrifuged to collect the precipitate, which was then dried overnight in an oven. The dried material was ground into a powder, and subsequently annealed in an Ar atmosphere at 350 °C for 1 hour to obtain the desired Ni-N₄-O catalyst.

As shown in Fig. S10,† scanning electron microscopy (SEM) images display intact carbon black particles, indicating that the morphology of the carbon black particles was not disrupted

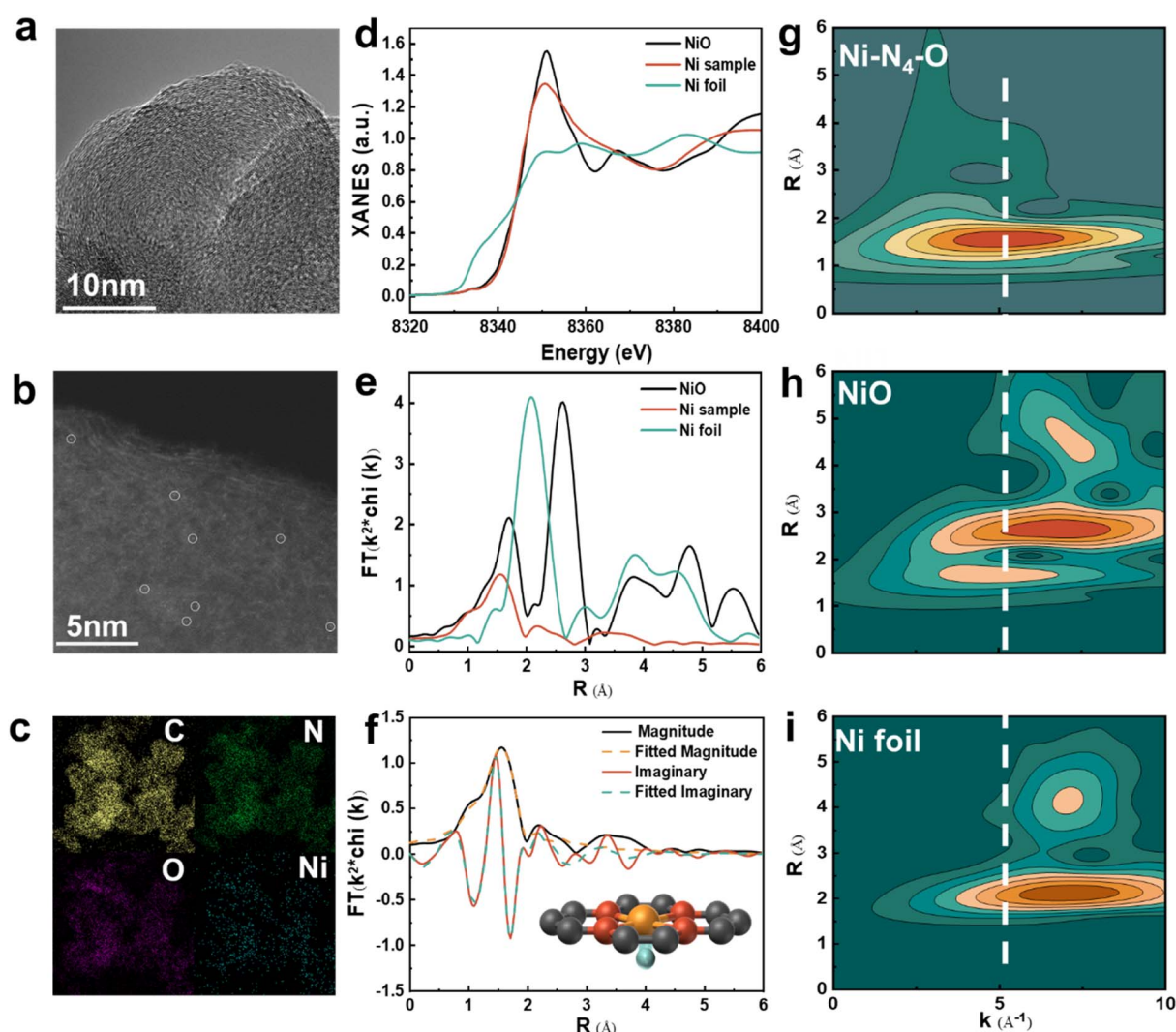


Fig. 3 Analysis of the coordination environment of Ni-N₄-O. (a) TEM image of Ni-N₄-O. Scale bar: 10 nm. (b) AC HAADF-STEM image of Ni-N₄-O. (c) EDS elemental mapping of Ni-N₄-O, suggesting uniform distributions of C, N, O, and Ni elements. (d) Ni K-edge XANES spectra for the NiO, Ni sample and Ni reference materials. (e) *R*-space EXAFS of Ni K edge. (f) Ni L₃ edge EXAFS fitting of Ni-N₄-O and the schematic atomic interface model. (g) Wavelet transforms of Ni-N₄-O, (h) NiO and (i) Ni foil.

during the reaction. Transmission electron microscopy (TEM) images reveal onion-like and defective graphene layers within the OCB particles Fig. 3a and S11,[†] serving as an effective coordination matrix for single-atom transition metals. No obvious metal clusters were observed in the TEM images. As shown in Fig. 3b, AC HAADF-STEM was able to directly observe that Ni atoms exist as isolated single atoms within the material (marked with red circles). Energy-dispersive X-ray spectroscopy (EDS) mapping images in Fig. 3c depict the distribution of various elements in the catalyst, demonstrating the uniform distribution of Ni elements within the carbonaceous matrix without forming distinct clusters, indicating the presence of Ni predominantly in the form of single atoms in the catalyst.

The X-ray diffraction (XRD) patterns of these five catalysts show two broad peaks in the ranges of 20–30° and 40–45°, corresponding to the (002) and (100) planes of graphite carbon, respectively (Fig. S12[†]). Notably, no diffraction peaks attributable to the Ni species were observed in the XRD patterns, indicating the highly dispersed Ni atoms within the material, consistent with the EDS results. Raman spectra (Fig. S13[†]) of Fe-N₄-O, Co-N₄-O, Ni-N₄-O, Cu-N₄-O, and OCB samples exhibit D and G bands, with the calculated intensity ratio I_D/I_G used to assess the degree of graphitization of carbon,²² which are 1.007, 1.01, 1.04, 1.03, and 1.009, respectively. Ni-N₄-O displays a higher I_D/I_G ratio, suggesting the presence of sufficient defects. Fig. S14[†] shows the functional groups present in OCB and Ni-N₄-O.

X-ray photoelectron spectroscopy (XPS) (Fig. S15[†]) was employed to further investigate the surface composition and electronic states of the catalysts. The O 1s spectrum can be deconvoluted into three typical peaks: C–O (532.05 eV), C–O–C (533.7 eV), and C–OH (536.8 eV).²³ The Ni 2p spectrum exhibits peaks corresponding to Ni²⁺ (875.8 eV) and Ni³⁺ (858.3 eV), along with their respective satellite peaks.²⁴ The N 1s spectrum can be resolved into five configurations: metallic nitrogen (399.2 eV), pyridinic nitrogen (398.4 eV), pyrrolic nitrogen (399.8 eV), graphitic nitrogen (400.7 eV), and oxidized nitrogen (403.1 eV).^{25,26} The content percentages (%) from the decomposed N 1s spectra of Ni-N₄-O are shown in Table S4.[†] The C 1s spectrum comprises three main peaks corresponding to C–C (284.8 eV), C–O (285.7 eV), and C=O (286.6 eV). Additionally, inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to determine the Ni loading in Ni-N₄-O to be 1.18 wt% (Table. S1[†]).

To determine the fine structure of the sample, extended X-ray absorption fine structure spectroscopy (EXAFS) was employed to investigate the local coordination environment of Ni. From the Ni K-edge X-ray absorption near-edge structure (XANES) spectrum shown in Fig. 3d, the intensity of the white line at the Ni L₃ edge for Ni-N₄-O is higher than that of Ni foil, indicating that Ni atoms are in an ionic state. Fig. 3e displays the Fourier transform EXAFS (FT-EXAFS) curve for Ni-N₄-O, with the main peak located at 1.56 Å. In comparison with Ni foil, the prepared sample shows no Ni–Ni scattering path, suggesting that the Ni species exist in an isolated single-atom states. NiO exhibits two main peaks in the FT-EXAFS at 1.71 Å and 2.63 Å, attributed to typical Ni–O and Ni–Ni scatterings of NiO,

respectively. By fitting the EXAFS spectra, the precise coordination environment of Ni is determined for Ni-N₄-O (Fig. 3f and Table S5[†]). The fitting analysis of the Ni L₃ edge reveals Ni–O bond lengths of 2.11 Å with a coordination number of 1.1, and Ni–N bond lengths of 2.04 Å with a coordination number of 3.8. The fitting results of the Ni L₃ edge in Ni foil are shown in Fig. S16,[†] Ni–Ni bond length is 2.48 Å and the coordination number is 12.

Wavelet transform EXAFS (WT-EXAFS) was applied to the Ni L₃ edge EXAFS oscillations to further confirm the atomic dispersion of the Ni species in Ni-N₄-O. From the wavelet contour plots of the NiO (Fig. 3h) and Ni foil (Fig. 3i) standards, the intensity peaks at 7.3 Å^{−1} and 7 Å^{−1} are most likely associated with Ni–Ni and Ni–O, respectively. In contrast, the WT contour plot of Ni-N₄-O (Fig. 3g) shows the maximum intensity peak at 5.3 Å^{−1}, significantly different from the former, thereby ruling out the presence of aggregated Ni foil or NiO in the sample. Therefore, these results conclusively demonstrate the isolated and hyper-coordinated characteristics of Ni species of Ni-N₄-O structure.

3.3 Electrocatalytic ORR performance

To evaluate the electrochemical performance of the catalysts, a three-electrode configuration was employed in a room temperature five-neck cell to assess the 2e[−] ORR performance of all samples in 0.1 M KOH. The electrolyte was saturated with O₂ in a 0.1 M KOH solution, with a potential range set from 0 to 1 V vs. RHE. The Pt ring electrode was maintained at 1.2 V vs. RHE to oxidize H₂O₂ produced on the disk electrode, quantified by the ring current. To explore the influence of the metal content on the catalyst performance, Ni-N₄-O catalysts with different Ni concentrations of 3%, 5%, and 10% were prepared specifically for studying their performance in 2e[−] ORR. Fig. 4a depicts the LSV curves of these catalysts with varying Ni content. Analysis of the current densities on both the disk and platinum ring electrodes revealed that at 0.2 V vs. RHE, the disk current density of 10% Ni-N₄-O (3.47 mA cm^{−2}) exceeded that of 3% Ni-N₄-O (3.012 mA cm^{−2}) and 5% Ni-N₄-O (2.95 mA cm^{−2}), prepared specifically for studying their performance in 2e[−] ORR. Fig. 4a depicts the LSV curves of these catalysts with varying Ni content. Analysis of the current densities on both the disk and platinum ring electrodes revealed that at 0.2 V vs. RHE, although the disk current density of 10% Ni-N₄-O (3.47 mA cm^{−2}) exceeded that of 3% Ni-N₄-O (3.012 mA cm^{−2}) and 5% Ni-N₄-O (2.95 mA cm^{−2}), 3% Ni-N₄-O showed the highest ring current (0.114 mA). Despite the minor differences in the H₂O₂ selectivity and electron transfer numbers between the 3% and 5% Ni-N₄-O catalysts, as shown in Fig. 4b and S5,[†] the surprising finding is the significant performance gap observed with the 10% Ni-N₄-O catalyst compared to the aforementioned two catalysts. This conclusion indicates that the incorporation of Ni doping in the catalyst favors the 2e[−] ORR pathway, but the enhanced H₂O₂ selectivity is not solely determined by the Ni content, as the results suggest that a higher Ni content does not necessarily yield better performance. To deeply explore the influence of

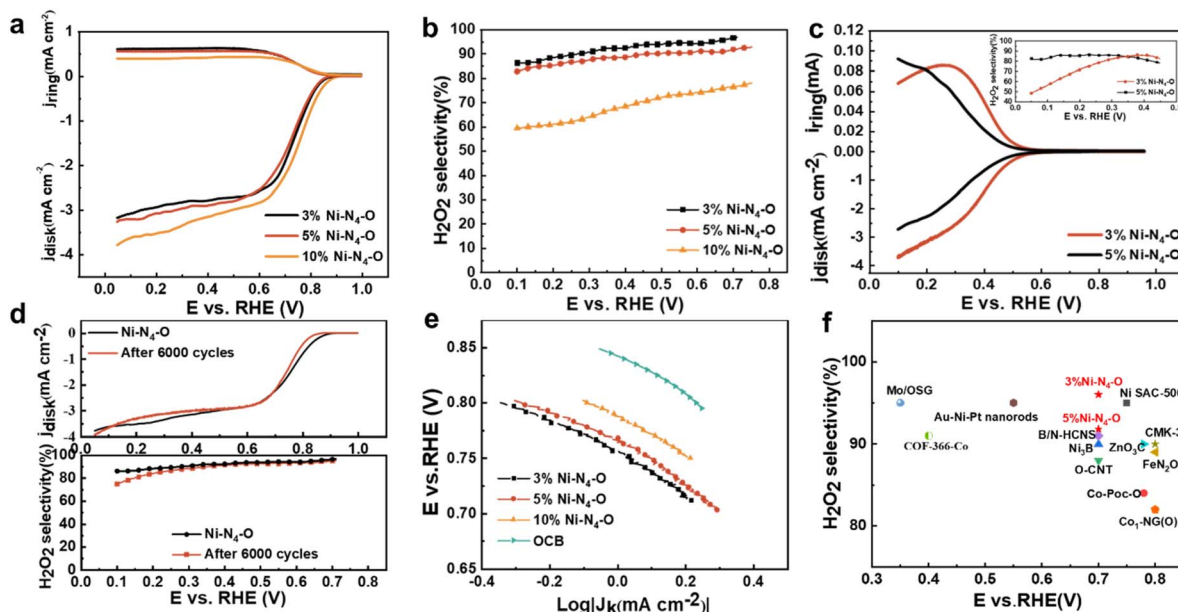


Fig. 4 Evaluation of the two-electron ORR activity and selectivity of all catalysts using RRDE. (a) Liquid state voltammetry (LSV) curves for different Ni elemental contents. (b) H₂O₂ selectivities based on the RRDE. (c) LSV curves at different Ni loadings in 0.1 M PBS buffer. (d) LSV curves and H₂O₂ selectivity before and after stability tests. (e) Tafel slopes of different Ni elemental content catalysts derived from the kinetic current for H₂O₂ production. (f) 2e⁻ ORR selectivity of Ni-N₄-O in comparison with recently reported catalysts.

the main group center on the performance of catalysts, taking 5 wt% metal element content as the standard, performance tests were individually carried out on five catalysts: Fe-N₄-O, Co-N₄-O, Ni-N₄-O, Cu-N₄-O, and OCB. The performance data, including the LSV curves, H₂O₂ selectivity, and electron transfer numbers, are illustrated in Fig. S9 and Table S3.†

Due to the widespread application of H₂O₂ in disinfecting bacteria, a promising area involves utilizing electrochemical methods to generate appropriate concentrations of H₂O₂ using only O₂ and H₂O. This approach enables the disinfection of biological aerosols, such as bacteria in air, which has not been previously explored. To ensure the accuracy of disinfection experiments and confirm that bacterial death results from electrochemically produced H₂O₂, it is essential to use neutral pH solutions instead of alkaline solutions to simulate practical applications. Therefore, using a rotating ring disk electrode (RRDE) in 0.1 M PBS electrolyte, the 2e⁻ ORR performance of the Ni-N₄-O catalyst was evaluated, as shown in Fig. 4c. The LSV performance of the catalysts with 3% and 5% Ni content in 0.1 M PBS buffer solution was tested, revealing surprising results. Despite the more challenging kinetics of the H₂O₂ generation under neutral conditions compared to alkaline conditions, the 5% Ni-N₄-O catalyst maintained over 80% high selectivity within the measurement range of 0.1–0.4 V vs. RHE. In contrast, the H₂O₂ production from the 3% Ni-N₄-O catalyst was slightly lower. Fig. 4d shows the stability of the material within the 0.2–1 V vs. RHE range. There is minimal difference in the ring-disk current and H₂O₂ selectivity before and after CV cycling, maintaining excellent performance, indicating the robust stability of the Ni-N₄-O catalyst. Fig. 4e displays the Tafel slopes of the seven catalysts, showing that 3% and 5% Ni-

N₄-O exhibit lower Tafel slopes compared to the other catalysts, suggesting their favorable kinetics for H₂O₂ generation, which is consistent with our experimental findings. Electrochemical double-layer capacitance (*C_{dl}*) measurements were used to calculate the electrochemical active surface area (ECSA) of the catalysts, as shown in Fig. S2.† Ni-N₄-O exhibits a larger *C_{dl}* value and more active sites compared to the other catalysts. Through the aforementioned performance tests, Ni-N₄-O catalysts can achieve widespread practical applications and efficiently produce H₂O₂. In conclusion, the activity and selectivity of Ni-N₄-O surpass many of the catalysts reported to date^{27–34} (Fig. 4f).

3.4 Practically feasible H₂O₂ production via H-type electrolysis cell

To accurately assess the selectivity, activity, and electrocatalytic synthesis capability of the Ni-N₄-O catalyst for H₂O₂ production, we employed the potassium titanyl oxalate titration method to measure the actual yield of H₂O₂. The generation of H₂O₂ takes place in an H-type electrolysis cell, as depicted in Fig. S17,† where continuous O₂ sparging of the electrolyte occurs under vigorous stirring conditions. A catalyst loading of 1 mg was supported on 2 × 2 cm pre-treated carbon paper (providing 0.5 mg cm⁻² catalyst loading) as the working electrode in the H-type electrolysis cell, with polarization curves of the hydrophobic carbon paper in 0.1 M PBS buffer displayed in Fig. S18.† Continuous electrolysis for H₂O₂ synthesis was conducted at a current density of 4.2 mA cm⁻² (0.25 V vs. RHE). As shown in Fig. 5a, an H-type electrolytic cell was used for the experiment on the production of H₂O₂. During this process,

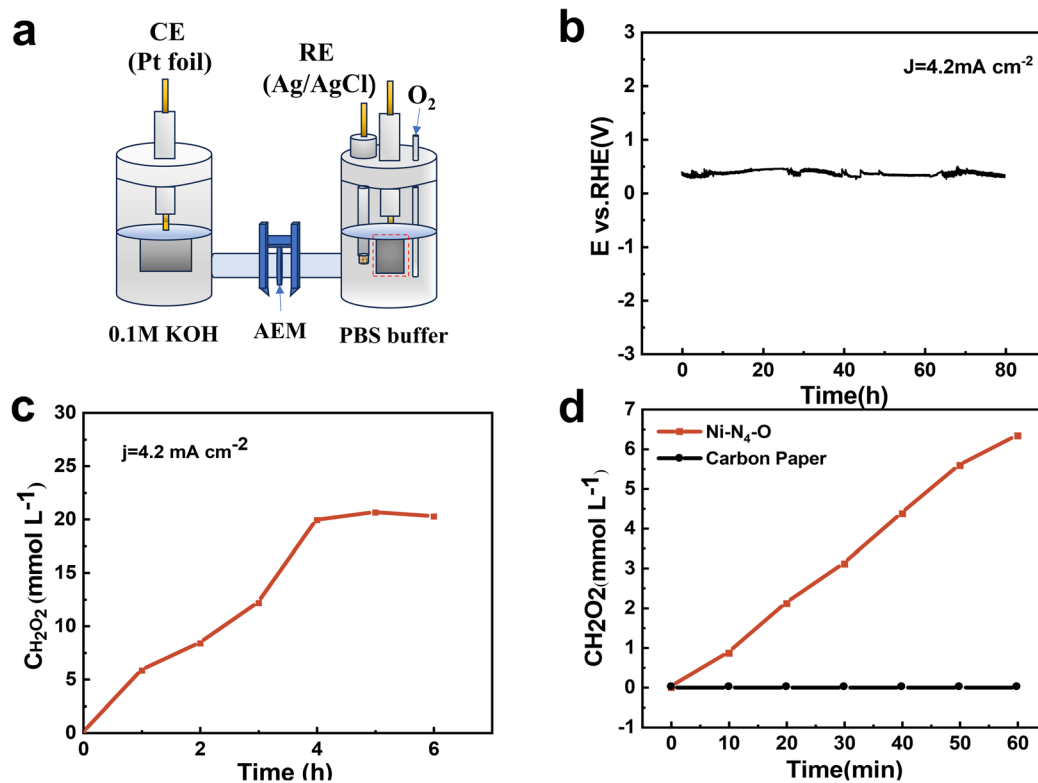


Fig. 5 (a) Schematic of the H-type electrolytic cell. (b) Chronopotentiometry stability test of the catalyst under the condition of the H-cell electrolytic device. (c) Amount of generated H₂O₂ at a current density of 4.2 mA cm^{-2} . (d) Comparison of H₂O₂ production performance between blank carbon paper and carbon paper loaded with catalyst over one hour.

under vigorous stirring, the cathodic electrolyte was continuously purged with O₂. As shown in Fig. 5b, during the continuous current period (80 hours), the voltage remained stable, staying around 0.35 V all the time, which proves the excellent stability of this catalyst. Continuous measurements over 6 hours showed that as the electrolytic time increased, the sample solution (a mixture of chromogenic reagent and electrolyte solution) gradually turned yellow. Measurements with a UV-visible spectrophotometer indicated a gradual increase in absorbance. The specific changes in the H₂O₂ concentration are depicted in Fig. 5c, revealing that the catalyst remarkably maintained excellent H₂O₂ production performance even in neutral buffer conditions, achieving a yield of $19.92 \text{ mmol L}^{-1}$ within 4 hours. The H₂O₂ concentration remained relatively constant at 5 and 6 hours, suggesting a decrease in the rate of H₂O₂ production, possibly due to reaching a dynamic equilibrium between production and decomposition at higher H₂O₂ concentrations.³⁵ Following the 16.5 hour stability test, the electrolyte was extracted. Through colorimetric reactions, observing that the sample solution turned a deep brown color, the measured H₂O₂ concentration reached $27.592 \text{ mmol L}^{-1}$. To ensure experimental accuracy, a comparison was made between the bare hydrophobic carbon paper and Ni-N₄-O-loaded carbon paper for 1 hour H₂O₂ production experiments (both conducted at 0.25 V current density). The electrolyte was sampled every 10 minutes for concentration measurement, and the experimental

results are shown in Fig. 5d. Through colorimetric reactions, it was observed that the solution of the bare carbon paper samples remained nearly transparent, whereas the solution of the Ni-N₄-O-loaded carbon paper samples visibly turned yellow, indicating minimal H₂O₂ production from bare carbon paper and a measurable production of $6.336 \text{ mmol per L H}_2\text{O}_2$ within 1 hour from the Ni-N₄-O-loaded carbon paper. Considering the electrolyte volume (50 mL) and catalyst mass (1 mg), this translates to an impressive $316.8 \text{ mmol per g metal per h H}_2\text{O}_2$ concentration. Up to now, the carbon-based catalyst has a relatively high yield for H₂O₂ (Table S6†).

3.5 Electrochemically generated H₂O₂ is used for space disinfection

The Ni-N₄-O catalyst exhibits impressive performance in the electrochemical synthesis of H₂O₂, which can be widely applied for effective bacterial eradication. Previous studies have demonstrated that H₂O₂ produced electrochemically by Fe-CNT can deactivate 43% of bacteria within 5 minutes and over 99.9999% within 120 minutes, with no observed recovery.³⁶ This underscores the bactericidal efficacy of H₂O₂. To further evaluate its practical application, we propose an innovative experimental setup, where H₂O₂ generated electrochemically is used for disinfecting biological aerosols in air. Fig. 6a depicts the actual experimental arrangement for bio-aerosol disinfection. The room dimensions are 1.95 m in

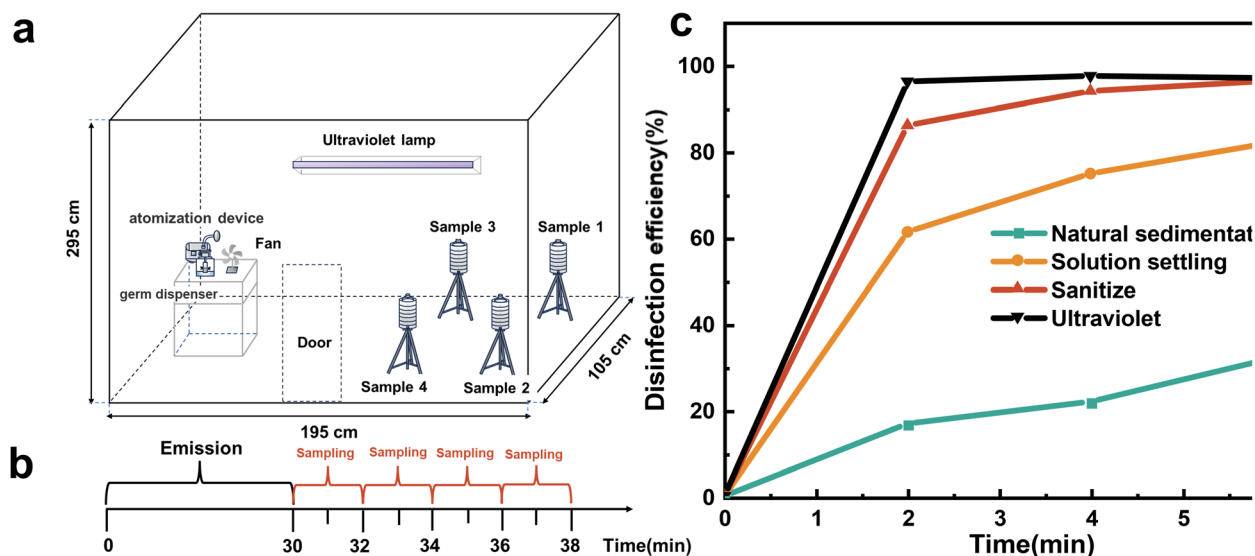


Fig. 6 Sample positioning, timeline, and disinfection efficiency in a small room. (a) Three-dimensional model of a small room. (b) Temporal bioaerosol measurement timeline. (c) Comparison of disinfection efficiency under different disinfection methods.

length, 1.05 m in width, and 2.75 m in height, equipped with a ceiling ventilation system, which was sealed with tape to isolate the effect of H_2O_2 from the ventilation system. To ensure experimental accuracy, thorough cleaning and disinfection of the room were conducted before each experiment, involving hypochlorous acid disinfectant spraying and 1 hour UV disinfection. As illustrated in the schematic diagram in Fig. S19,† Andersen samplers were evenly placed before the aerosol generator at spaced intervals, maintaining a certain distance from the inoculation point. Fans were positioned in front of the aerosol generator and nebulizer to disperse the aerosolized bacterial suspension and H_2O_2 solution into the air, allowing molecular diffusion throughout the room. Fig. 6c outlines the experimental procedure, which consists of two phases: environmental setup, disinfection and sampling. During the first phase, a bacterial aerosolization experiment was conducted for 30 minutes to achieve a heavily contaminated environment. Upon completion, the aerosol generator was turned off, and immediate disinfection with H_2O_2 and subsequent sampling were carried out four times for 2 minutes each. After all sampling sessions were completed, the Andersen samplers were removed from the room. The collected Petri dishes were then placed in a 37 °C constant temperature incubator for 24 hours to enumerate the bacterial colonies. In this experiment, the concentration decay of bioaerosols is influenced by natural sedimentation rates and disinfection efficiency. To ensure rigor, two control experiments were performed: one involving only bacterial aerosolization to observe the natural sedimentation rates, and another involving aerosolization of a PBS solution to observe sedimentation rates under humidification conditions. The sampling times and methods for these control experiments mirrored those of the disinfection experiment. To verify that the *in situ* generated H_2O_2 has excellent disinfection efficacy, comparisons were

made with the UV irradiation disinfection experiments, as depicted in Fig. 6d. UV irradiation showed the most significant disinfection effect, achieving a 96.5% kill rate within 2 minutes. Additionally, PBS solution aerosolization caused more pronounced bacterial sedimentation compared to natural sedimentation, possibly due to gravitational effects on aerosols entrained in water vapor. Notably, the aerosolized H_2O_2 solution resulted in a more significant decay of bioaerosols compared to the aerosolized PBS solution, with nearly no viable *Serratia marcescens* collected at 4 minutes, indicating that the aerosol decay partly resulted from H_2O_2 disinfection. This highlights the feasibility of using electrochemically generated H_2O_2 for air disinfection experiments. The setup can be further upgraded to a flow electrolysis cell with adjustable water flow rates and current densities, enabling convenient generation of H_2O_2 at appropriate concentrations tailored to specific scenarios, thereby providing more efficient disinfection outcomes.

4. Conclusion

By selecting transition metal atoms, carriers, and non-metallic binders and through hydrothermal reactions, single-atom catalysts containing different main group centers can be prepared. Performance testing revealed that $\text{Ni-N}_4\text{-O}$ exhibits outstanding performance in 2e^- ORR of H_2O_2 , significantly surpassing other catalysts. Under both alkaline and neutral conditions, $\text{Ni-N}_4\text{-O}$ achieved H_2O_2 selectivities of 95% and 85%, respectively. In a 1 hour electrolysis experiment, carbon paper loaded with $\text{Ni-N}_4\text{-O}$ achieved a high yield of $6.338 \text{ mmol L}^{-1}$, maintaining sufficient stability throughout a continuous 16.5 hour electrolysis process, with a final yield measured at $27.592 \text{ mmol L}^{-1}$. Combined experimental and theoretical studies indicate that the excellent catalytic

performance of Ni-N₄-O in 2e[−] ORR can be attributed to the N,O-hypercoordinated environment. Furthermore, the H₂O₂ generated after a period of electrolysis in an H-type electrolysis cell was applied to air disinfection, demonstrating effective disinfection results. The kill rate reached 87% at 4 minutes and approached 100% at 6 minutes. This experiment can further utilize a flow electrolytic cell, controlling the flow rate of deionized water and current density, to produce pure H₂O₂ solutions of different concentrations without additional solutes. This work provides a promising pathway for the rational design of 2e[−] ORR catalysts to address issues in industrial H₂O₂ synthesis, and may offer new insights for the green production of H₂O₂ from renewable biomass for spatial disinfection.

Data availability

Data will be made available on request.

Conflicts of interest

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

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