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Highly selective oxygen reduction to hydrogen peroxide on transition metal single atom coordination

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Shifting electrochemical oxygen reduction towards 2e\textsuperscript{−} pathway to hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), instead of the traditional 4e\textsuperscript{−} to water, becomes increasingly important as a green method for H\textsubscript{2}O\textsubscript{2} generation. Here, through a flexible control of oxygen reduction pathways on different transition metal single atom coordination in carbon nanotube, we discovered Fe-C-O as an efficient H\textsubscript{2}O\textsubscript{2} catalyst, with an unprecedented onset of 0.822 V versus reversible hydrogen electrode in 0.1 M KOH to deliver 0.1 mA cm\textsuperscript{−2} H\textsubscript{2}O\textsubscript{2} current, and a high H\textsubscript{2}O\textsubscript{2} selectivity of above 95% in both alkaline and neutral pH. A wide range tuning of 2e\textsuperscript{−}/4e\textsuperscript{−} ORR pathways was achieved via different metal centers or neighboring metalloid coordination. Density functional theory calculations indicate that the Fe-C-O motifs, in a sharp contrast to the well-known Fe-C-N for 4e\textsuperscript{−}, are responsible for the H\textsubscript{2}O\textsubscript{2} pathway. This iron single atom catalyst demonstrated an effective water disinfection as a representative application.
Molecular oxygen (O$_2$) can be electrochemically reduced to water (H$_2$O) via a 4e$^-$ pathway, or hydrogen peroxide (H$_2$O$_2$) with 2e$^-$ transferred in aqueous solutions. The former pathway is preferred in fuel cell applications to maximize the energy conversion efficiencies$^{1-3}$, and the latter one represents a green synthetic method for H$_2$O$_2$ $^{4-7}$. Compared to the traditional energy, capital, and waste intensive anthraquinone process$^{8,9}$, electrochemical synthesis of H$_2$O$_2$ becomes a promising alternate with significant advantages including: (1) mild reaction conditions under room temperature and ambient pressure; (2) renewable electricity as the energy source without fossil fuel consumptions; and (3) green precursors starting with water and air. Although a variety of highly active catalysts driving the 4e$^-$ oxygen reduction reaction (ORR) have been developed to improve the performance of fuel cells$^{10-14}$, there are less known catalysts that can selectively reduce O$_2$ to H$_2$O including noble metals$^{15-19}$ and carbon materials$^{20-29}$. A molecular level understanding of the elementary reaction steps could provide important guidance to the design of ORR catalysts for different pathways. The critical knob for searching efficient ORR catalysts relies on the proper binding strengths between the reaction site and O species$^{27-29}$. Taking the selective ORR to H$_2$O$_2$, where the O–O bond in O$_2$ needs to be preserved, as an example here, a too-strong interaction between the reaction site and O species could easily dissociate the O$_2$ molecule and direct the selectivity towards H$_2$O, while a too-weak one may create a high reaction barrier to overcome$^{27,29}$. Therefore, a materials platform with flexible tunability in electronic structures is highly desired for systematic control of ORR pathways as well as improvements in catalytic activities.

Transition-metal (TM) single atom motifs coordinated in well-defined carbon matrix, with a variety of tuning knobs such as the different metal atom centers and the varied adjacent coordinative dopants, have been attracting considerable interests in heterogeneous catalysis field$^{30-33}$. This is mainly due to their unique electronic properties compared to their bulk metal counterparts for extraordinary activities, as well as their capability in tuning the binding strength with reaction intermediates for boosting desired catalytic pathways$^{34-36}$. One representative example is the Ni single atom catalyst in our previous CO$_2$ reduction studies where the binding with CO was significantly weakened on isolated Ni atomic sites compared to that of bulk Ni surface to facilitate CO evolution$^{37,39}$. With potentially a wide range of tunability in binding with O species via different TM single atom coordination, this class of materials as a powerful platform thus provides us with great opportunities in exploring highly selective and active catalysts for H$_2$O$_2$ generation, as well as a flexible control of ORR pathways.

Here we report the TM single atom coordination motifs for a full range control of ORR pathways from the 2e$^-$ reduction selectively to H$_2$O towards the 4e$^-$ to H$_2$O. A series of TM single atoms including Fe, Pd, Co, and Mn are anchored into carbon nanotube (TM-CNT) vacancies (Fe-CNT, Pd-CNT, Co-CNT, and Mn-CNT, respectively) with neighboring C, O, or N coordination for pathway tuning. Among the different TM-CNTs, Fe-CNT presents the state-of-the-art performance towards H$_2$O$_2$ generation in terms of activity and selectivity. An unprecedented onset potential to reach 0.1 mA cm$^{-2}$ H$_2$O$_2$ generation current is achieved at only 0.822 V versus reversible hydrogen electrode (vs. RHE) in 0.1 M KOH on rotating ring-disc electrode (RRDE), while a maximum H$_2$O$_2$ selectivity of more than 95% is delivered in both alkaline and neutral pH. With the O$_2$ mass transport facilitated by a gas diffusion layer (GDL) electrode, the H$_2$O$_2$ generation rate by Fe-CNT can reach to 43 mA cm$^{-2}$ with a 95.4% selectivity under only 0.76 V. By switching the neighboring O with N coordination, the 2e$^-$ ORR pathway is successfully shifted towards 4e$^-$ of H$_2$O, demonstrating a wide range of reaction tunability in this materials platform. Density functional theory (DFT) calculations suggest that the catalytically active C and Fe sites in Fe–C–O and Fe–C–N motifs are responsible for the H$_2$O$_2$ and H$_2$O pathways, respectively. In a variety of Fe–C–O motifs calculated, the incorporation of Fe atoms significantly improves their catalytic activities for H$_2$O$_2$ generation compared to those with only O dopants. As a prototype demonstration of potential applications, this high-performance H$_2$O$_2$ generation catalyst enables an effective water disinfection of >99.9999% bacteria removal at a treating rate of 125 L h$^{-1}$ m$^{-2}$ electrode.

**Results**

**Synthesis and characterizations of single atom catalysts.** A small quantity of TM cations (∼0.1 at%) were first dispersed onto commercial surface-functionalized CNTs as the carbon matrix suspended in water (Supplementary Fig. 1), followed by freeze-dry and thermo annealing under Ar flow at 600 °C (Methods, Supplementary Note 1 and Supplementary Figs. 2–3)$^{38}$. All four types of TM-CNT samples, including Fe, Pd, Co, and Mn, have shown similar structures in Fig. 1 by transmission electron microscopy (TEM) and aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM). No nanoparticles or clusters were observed in the bright field TEM images by different scales (Fig. 1a–d; Supplementary Figs. 4–7), suggesting a well dispersion of TM atoms. Isolated TM atoms can be resolved by HAADF-STEM due to their high Z contrast compared to those neighboring light elements such as C or O$^{32}$. While all four isolated metal atoms were observed as the white dots in Fig. 1e–h, Pd-CNT presents the most distinguishable single atoms due to its heaviest atomic mass compared to the other three metal elements. Although no obvious TM signals were detected by X-ray photoelectron spectroscopy (XPS, Supplementary Fig. 8) due to the low mass loading, synchrotron-based X-ray absorption spectroscopy (XAS) on the K-edge of Fe$^{40}$, Pd$^{41}$, Co$^{42}$, and Mn$^{43}$ can instead provide direct evidence of the valence states and coordination environments$^{38}$. The X-ray absorption near-edge structure (XANES) spectra in Supplementary Fig. 9 indicate the partial-oxidation states of these metal dopants where the pre-edge peaks are located between the corresponding metal foils and metal oxides. This is mainly due to the strong M–C and M–O bonds via which the electrons from the metal atomic centers are partially depleted to the neighboring C and O sites, in a good agreement with the simulated charge density distributions and Balder charge analysis (Supplementary Table 1)$^{44}$. In addition, the oxidation state of coordinated Fe is lower than simply adsorbed Fe on CNT, suggesting the different chemical environment between the adsorption case and coordination case (Supplementary Note 2, Supplementary Fig. 10). The corresponding Fourier transforms of extended X-ray absorption fine structure (EXAFS) for each metal are plotted in Fig. 11–L. It is noted that the signals from bulk metal foils are dominated by M–M bonds, i.e., 2.17 Å for Fe–Fe, 2.55 Å for Pd–Pd, 2.18 Å for Co–Co and 2.31 Å for Mn–Mn, respectively$^{40-43}$. In contrast, M–C or M–O bonds at ~1.4–2.0 Å are the major features in M-CNTs, reinforcing the isolated distribution of these TM single atoms in the carbon matrix. A shoulder peak at 2.05 Å is observed for Mn-CNT, which is corresponding to the Mn–O coordination$^{43}$.

Due to the capabilities in both three dimensional (3D) imaging and chemical composition measurements at the atomic scale, atom probe tomography (APT) becomes a complementary characterization to STEM and XAS to reveal additional information about the atomic structure in catalysts$^{37,45-48}$. Fe-CNT was analyzed as a representative of other M-CNTs. We used a
sandwich” approach for the sample tip preparation (Fig. 2). We drop-casted dispersed Fe-CNT onto a nickel-coated substrate, sandwiched in between two 25-nm gold layers deposited by sputter-coating; the gold serves as a marker for the original surface of the CNT powder (Fig. 2a, Supplementary Fig. 11). The Au-CNT-Au sandwich is itself enclosed in layers of sputter-deposited Ni, to give sufficient material supports for APT tip preparation. Focused ion beam (FIB) procedures are applied to cut the sample into pieces, with a corresponding cross-section structure shown in the SEM image of Fig. 2b. Preparation of an APT-compatible needle-shaped specimen is carried out by FIB as shown in Fig. 2c. APT was then performed on a Cameca LEAP 4000 HR as detailed in the Methods, with a total of 9 million atoms collected. The reconstructed tomography of the sample tip is presented in Supplementary Movie 1, with the projected 2D image shown in Fig. 2d. Each dot represents the position of the ion detected by mass spectrometry, with a maximum detection efficiency of 38% (reflectron atom probe). Au layer as a marker in yellow is observed in the upper left corner, indicating the catalyst region for analysis. A few hundreds of isolated $^{56}$Fe atoms (identified only from the 56 Da peak due to molecular fragment overlaps at the other Fe isotopes and charge states) were well dispersed across the sample tip and highlighted in green. A smaller region attached to the Au marker was selected for detailed analysis as shown by the 2D contour map of carbon atom distribution (Fig. 2e), where the shape of a CNT was resolved. Fe atoms were distributed uniformly along the CNT as shown in the corresponding 2D projection (Fig. 2f), with no neighboring Fe atoms observed with a distance less than 3 Å. This is in consistent with STEM and XAS characterizations and further confirms the atomic dispersion of Fe in CNT. While a closer observation around Fe atoms is not able to provide the exact atomic structures due to the loss of ion signals during the detection process as well as the APT resolution (0.1–0.3 nm), it could still give us important hints of the possible coordination environment: the side view suggests a few atomic layers where Fe single atoms were anchored; the top view of one atomic layer, although with vacant space since a portion of atoms were not detected, shows that the isolated Fe atoms may have neighboring coordination with both C and O, suggesting a possible coordination of Fe–C–O motifs which will be further discussed in our theoretical calculations.

Electrocatalytic ORR characterizations. The ORR performances were evaluated in 0.1 M KOH by casting a thin catalyst layer onto rotation ring disk electrode (RRDE), with the collection efficiency...
pre-calibrated by the redox reaction of $\text{[Fe(CN}_6\text{)]}^{4-}/\text{[Fe(CN}_6\text{)]}^{3-}$ (Supplementary Fig. 12, Methods). The potential of reference electrode was double confirmed by purging pure H$_2$ gas onto a physically and electrochemically polished polycrystalline Pt wire or Pt rotation disc electrode at a reasonable rotation speed (Supplementary Fig. 13, Methods). The ORR peak of Fe-CNT was observed in the cyclic voltammetry in O$_2$-saturated electrolyte, in contrast with the double layer current when O$_2$ was switched to N$_2$ (Supplementary Fig. 14). Figure 3a shows the polarization curves of M-CNTs for their performance screening at a constant catalyst loading of 0.1 mg cm$^{-2}$, together with the H$_2$O$_2$ generation current detected by the Pt ring electrode (Methods). Note that the possible H$_2$O$_2$ decomposition on metal oxides compared to the generation should be negligible (Supplementary Note 3). The corresponding H$_2$O$_2$ selectivity and electron transfer numbers were plotted in Fig. 3b as a function of potential. The background performance of CNT support (O content of 4.5%) showed similar H$_2$O$_2$ selectivity compared to previous studies (Fig. 3a, b)$^{27}$, which was significantly improved or decreased with TM single atoms incorporated. Note that the O contents in CNT were barely changed after the doping of metal atoms (Supplementary Fig. 8), ruling out its contribution to the changes of H$_2$O$_2$ selectivity. In addition, we excluded the possibility that the ratio between C and O might be influenced by adsorbed carbon dioxide and oxygen gas from air (Supplementary Fig. 15). Among those different TMs, Fe-CNT presents the best H$_2$O$_2$ generation.

![Fig. 2 Atom probe tomography of Fe-CNT catalyst.](image-url)
Fig. 3 ORR performance of M-CNT catalysts cast RRDE in 0.1 M KOH. a Linear sweep voltammetry (LSV) of CNT background and Fe-, Pd-, Co-, Mn-CNT catalysts recorded at 1600 rpm and a scan rate of 5 mV s$^{-1}$, together with the detected H$_2$O$_2$ currents on the ring electrode (upper panel) at a fixed potential of 1.2 V vs. RHE. b Calculated H$_2$O$_2$ selectivity and electron transfer number during potential sweep. c Stability measurement of Fe-CNT at a fixed disk potential of ~0.71 V. The ring electrode was refreshed several times by rapid scan at negative potentials to remove the accumulated PtOx in continuous operation. d, e LSV and corresponding H$_2$O$_2$ selectivity comparison on Fe-CNT, Fe-N-CNT, and forming gas reduced Fe-CNT (Red. Fe-CNT) catalysts
Theoretical calculations. The above experiments suggested that the product selectivity of ORR could be related with the coordination motifs of Fe–C–O or Fe–C–N in those single atom catalysts. While based on current experimental techniques it is still challenging to directly resolve all of the exact atomic structures, density functional theory (DFT) calculations of different configurations (a total of 18 configurations as shown in Fig. 4a) become of great importance to understand the origin of selectivity change, and for rational design of new catalysts in the future. We used a two-dimensional graphene to model the CNT support used here, since the difference in binding free energies of reaction intermediates at CNT with a diameter larger than 20 nm and at the two-dimensional graphene is <0.1 eV. We considered carbon mediated at CNT with a diameter larger than 20 nm and at the since the difference in binding free energies of reaction intermediates (a total of 18 configurations) becomes of great importance to understand the origin of selectivity change, and for rational design of new catalysts in the future. We used a two-dimensional graphene to model the CNT support used here, since the difference in binding free energies of reaction intermediates at CNT with a diameter larger than 20 nm and at the two-dimensional graphene is <0.1 eV. We considered carbon mediated at CNT with a diameter larger than 20 nm and at the
Fig. 5 Disinfection performance of Fe-CNT in neutral pH. a Schematic of electrochemical synthesis of H$_2$O$_2$ for water disinfection, with green inputs such as sunlight, air, and water. b, c LSV of Fe-CNT catalyst on RRDE at 1600 rpm in 0.1 M PBS (pH 7.2) with the corresponding H$_2$O$_2$ selectivity under different potentials. d LSV of Fe-CNT catalyst on GDL electrode (0.5 mg cm$^{-2}$ mass loading) in an H-cell electrolyzer. e Bulk electrolysis at a constant current density of 20 mA cm$^{-2}$ in 0.1 M PBS containing ~10$^7$ c.f.u. mL$^{-1}$ E coli bacteria. The H$_2$O$_2$ concentration of 1613 ppm at 210 min was determined from a bacteria-free control experiment. f CCD photos of overnight cultured plates with spread droplets taken from different time slots during the electrolysis. Dilution factor is labeled at the right bottom corner of each image. No bacteria colonies were observed after 2-h treatment. g The disinfection efficiency as a function of treatment time. The error bar represents two identical cultured plates.
**Water disinfection by Fe-CNT catalyst.** A wide range of practical applications could be realized with this low-cost Fe-CNT catalyst for highly efficient H$_2$O$_2$ generation. Since H$_2$O$_2$ has been widely used in killing bacteria$^{60}$, one promising field is the delocalized or green-route water disinfection with accessible inputs including sunlight for electricity, air for O$_2$, and water as shown in the schematic in Fig. 5a. Here we performed a prototype experiment to test the catalyst’s disinfection effectiveness. Neutral pH needs to be used instead of alkaline solutions to mimic the practical applications, therefore the ORR selectivity of Fe-CNT was first evaluated in 0.1 M PBS electrolyte using RRDE as shown in Figs. 5b and 5c. H$_2$O$_2$ generation starts at ~0.53 V and maintains a high selectivity above 90% from 0.5 to 0.3 V. The practical electrolysis was performed in an H-cell where Fe-CNT catalyst was casted onto a GDL electrode (0.5 mg cm$^{-2}$ catalyst loading), with the catalytic performance plotted in Fig. 5d. The potential to deliver a 20 mA cm$^{-2}$ current constant for H$_2$O$_2$ generation remained unchanged over the course of electrolysis (Fig. 5e). Around 1613 ppm H$_2$O$_2$ was generated within 210 min of electrolysis as determined by the colorimetric quantification method, representing an average Faradaic Efficiency of 90.8%. With those performance metrics obtained, electrolyte with Escherichia coli (E. coli) was then used as a model system at a bacteria concentration of ~10$^7$ colony forming units (c.f.u.) mL$^{-1}$. The disinfection process was monitored by picking up several droplets within the 20 mA cm$^{-2}$ chronopotentiometric measurement, followed by serial dilution and spread plating onto LB agar for overnight culture$^{61,62}$. The dark-field CCD images of agar plates with cultured bacteria colony are shown in Fig. 5f, with the calculated killing rate plotted in Fig. 5g. Fe-CNT demonstrates a rapid disinfection efficiency for E. coli, delivering a 43% bacteria inactivation in 5 min and more than 99.9999% in 120 min (equals to a 125 L h$^{-1}$ electrode processing rate) with no recovery observed (Supplementary Fig. 32). We further suspended E. coli bacteria into 2-h electrolyzed 0.1 M PBS solution (ca. 1000 ppm of generated H$_2$O$_2$ concentration) with the image of overnight cultured plate shown in Supplementary Fig. 29, which clearly excludes any effects of disinfection from applied potential. This device can be further upgraded into a flow cell with tunable water flow rate and current density for a well-balanced water disinfection rate and efficiency for specific applications in the future.

**Discussion**

Our experimental and theoretical results highlight that the TM single atom coordination motifs can effectively tune the ORR pathways and product selectivity. Among different catalysts examined, Fe–C–O coordination was identified as highly active and selective motif for O$_2$ reduction to H$_2$O$_2$. Given the many
SEM images of the tip profile was performed using Cameca IVAS 3.16.4 software, with reconstructions based on Ni K-edge spectra were acquired in fluorescence mode with a 32-element Ge detector. The H2O2 concentration-absorbance curve was calibrated by mixing known amount of commercial H2O2 solution with 1 mM Ce(SO4)2. The absorption at 320 nm wavelength was measured on a Cary 5000 UV-Vis-NIR spectrometer (Agilent) and used to determine the Ce4+/Ce3+ concentration (Supplementary Fig. 18). To fit the linear range of calibration curve, the electrolyte collected was further diluted by 10 to 100 times in 0.5 M H2SO4.

**Electrochemical measurements.** A BioLogic VMP3 work station was employed to record the electrochemical response. Certain amounts of KOH (Reagent Grade, Sigma-Aldrich or KHP04/KOH (ACS Grade, Sigma-Aldrich) was dissolved in Millipore water to prepare the 0.1 M electrolyte. The rotation ring disk electrode (RRDE) measurements were run at 25 °C in a typical three-electrode cell. A platinum foil (99.99%, Beantown Chemical) and a saturated calomel electrode (SCE, Cal Instruments) were used as the counter and reference electrode, respectively. A RRDE assembly (A6ER1PTPK, Pinnacle Instruments) containing a rotation disk electrode (Φ = 5.0 mm) and a Pt ring (Φ = 15.0 mm) was used, with a theoretical collection efficiency of 25%. Experimentally, the apparent collection efficiency (N) was determined to be 24.1% in the ferrocyanide/ferricyanide half reaction system at a rotation rate of 3000 rpm and 2200 rpm on the RRDE. To prepare M-CNT cast working electrode, typically, 3.3 mg of as-prepared M-CNT catalyst was mixed with 1 ml of ethanol and 10 μl of Nafion 115 solution (5%, Sigma-Aldrich), and sonicated for 20 min to get a homogeneous catalyst ink. 6 μl of the ink was pipetted onto glassy carbon disk (0.196 cm² area, 0.1 mg/cm² mass loading), got vacuum dried prior to usage. As the catalyst can be dispersed very well in ethanol solutions, uniform catalyst coating can be made on the disc electrode without obvious pin holes or uncovered edge. All potentials measured against SCE was converted to the reversible hydrogen electrode (RHE) scale in this work using E (vs. RHE) = E (vs. SCE) + 0.244 V = 0.595pH, where pH values of electrolytes were determined by using 320 PerpHect Log Meter (Thermo Scientific, i.e., 13.0 for 1 M KOH and 13.0 for 1 M KCl). This RHE electrode was further corrected to freshly prepared RHE prior to usage (Supplementary Fig. 13), in good agreement with the calculated values. The diffusion limited current of our catalyst is at around 3 mA cm⁻² and is higher than that of bare glassy carbon, which may due to the low density of active sites on mirror polished glassy carbon electrode. A gradual degradation of the catalyst was observed during the continuous RRDE stability test, which was mainly due to the surface oxidation of Pt ring electrode constantly operated at high potential (1.2 V, Fig. 3c) and can be readily recovered by rapid cyclic voltammetry at low potentials to reduce PtO₂. H₂O₂ selectivity was calculated using the following equation: H₂O₂ (‰) = (200 × I₂ ring - I₁ disk) / I₁ disk and the electron transfer number (n) at the disc electrode during ORR was calculated using n = I₁ disk / I₂ ring, where I₁ disk is the ring current, I₂ ring is the disk current and N is the collection efficiency.

**Bulk H₂O₂ production in 1 M KOH was carried out in a customized H-cell electrolyzer with 0.5 cm⁻² Fe-CNT air bubbled onto a 1×2.5 cm² Fricenberg GDL electrode (Fuel Cell Store) as ORR cathode, with the anode of 0.2 mg cm⁻² IrO₂/GDL for water oxidation. A Fumasep FAA-3-PK-130 anion exchange membrane (Fuel Cell Store) was employed to separate the chambers. H₂O₂ concentration was quantified by cerium sulfate titration based colorimetric method (2Ce⁴⁺ + H₂O₂ → 2Ce³⁺ + H₂O + 2H⁺). The H₂O₂ concentration-absorbance curve was calibrated by mixing known amount of commercial H₂O₂ solution with 1 mM Ce(SO₄)₂. The absorption at 320 nm wavelength was measured on a Cary 5000 UV-Vis-NIR spectrometer (Agilent) and used to determine the Ce⁴⁺/Ce³⁺ concentration (Supplementary Fig. 18). To fit the linear range of calibration curve, the electrolyte collected was further diluted by 10 to 100 times in 0.5 M H₂SO₄.

**Computational details.** Density functional theory calculations were performed using the Vienna Ab Initio Simulation Package (VASP) 6.5.6. We used BEEF-vdW exchange-correlation functional, which has been shown to accurately describe dimers, small aromatic hydrocarbons and weakly bound adsorbates. We used a 200 eV energy cutoff, a convergence criteria for self-consistent iteration and ionic relaxation to be 500 eV, 10⁻⁴ eV and 0.05 eV Å⁻¹, respectively. Bulk graphene unit cell was optimized using (12 × 12 × 1) k-points mesh, resulting in C-C distance to be 1.424 Å. (7 × 7) supercell consisting of 98 carbon atoms with 15 Å of a vacuum perpendicular to the graphene plane was employed to model carbon material, and we considered up to six carbon vacancies. Various sites for a single metal atom adsorption were assessed, and the effects of oxygen or nitrogen near the single metal atom were taken into account as well. For the adsorption calculations, (2 × 2 × 1) k-points mesh was utilized.

**Simulations** of OOH adsorption on the catalysts, where the possible catalytic active site is either the single metal or nearby carbon sites. For single atom catalysts, the single metal atom is significantly under-coordinated compared to their bulk counterparts resulting in markedly strong binding of adsorbates, and it is highly likely that the site is pre-occupied by other adsorbates, such as O or OH, under the ORR conditions. In this situation, no site adsorption energy is determined the most relevant coverage of the metal atom at 0.7 V vs RHE by constructing a surface Pourbaix diagram (Supplementary Figs. 29-31). For carbon site adsorptions, we considered all carbon sites near the single metal atom and reported the most stable binding free energies.

**Pourbaix diagram.** A free energy diagram of ORR to H₂O₂, we corrected the calculated electronic energies by adding zero-point energy, enthalpy and entropy of adsorbate at 300 K obtained from a harmonic oscillator approximation using Atomic Simulation Environment. Since O₂ molecule is poorly described by standard DFT functionals, we calculated the energies of gas-phase H₂O and H₂ molecules, and used the calculated electronic formation free energies of H₂O and H₂. To take into account the effect of the electrode potential, computational hydrogen electrode (CHE) method was employed. In this method the chemical potential of proton
and electron pair $\mu^+(-e^-)$ is equal to one half of that of gas-phase hydrogen molecule (1/2μH2) at standard conditions, and the effect of the electrode potential is included by shifting the electron free energy by $-\Delta U_{\text{elec}}$, where $e$ and $U_{\text{elec}}$ are elementary charge and electrode potential, respectively.

### Water disinfection

A standard lab bacterial Escherichia coli strain was kindly provided by Howard Berg’s laboratory. *E. coli* was cultured to stationary phase in LB broth for 14 h at 37°C, harvested by centrifugation at 800 g, washed three times with 0.1 M PBS solution and suspended in 0.1 M PBS to $7.1 \times 10^{7}$ c.f.u. mL$^{-1}$. The electrochemical disinfection measurements were run at 25°C in a H-type glass cell separated by a Fumasep FBM bipolar membrane (Fuel Cell Store). 25 mL of the prepared *E. coli* in 0.1 M PBS was injected into the cathodic chamber, with a 1 cm$^2$ Fe-CNT/CDL (0.5 mg cm$^{-2}$ catalyst loading) serving as the working electrode. A chrono-potentiometric measurement at a fixed current density of 20 mA cm$^{-2}$ was performed to ascertain water disinfection. Another control experiment was run in 25 mL of bacteria-free electrolyte to calculate the overall H2O2 concentration and generation rate. The pH value was noted to maintain ~7.2 before and after the continuous electrolysis in PBS buffer. Bacterial concentrations and killing rates were measured at different time points during electrolysis using standard spread plating techniques. Each sample was serially diluted and each dilution was plated in triplicate on LB agar plates, and incubated at 37°C for 12 h. The images of overnight cultured plates were taken with a custom-built dark-field imager equipped with a CCD camera (Point Grey Chameleon).

### Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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Author contributions

This project was conceptualized by K.J. and H.W. and supervised by H.W.; K.J. performed experimental work with the help of C.X. and H.W.; S.B. and S.S. designed and performed computational work with the discussion with J.K.N.; A.J.A performed APT characterization; Y.H. and E.S. helped on XAS tests; W.L. performed HAADF-STEM characterization; D.S. helped on E. coli experiments. K.J., S.B., S.S. and H.W. wrote the manuscript with the discussion with all authors.

Additional information

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Competing interests: A.U.S. provisional patent application, No. 62/779,590, entitled "Tuning of transition-metal single atom coordination for selective oxygen reduction towards hydrogen peroxide", has filed based on the technology described in this work on December 14, 2018 by K.J. and H.W. at Harvard University. The remaining authors declare no competing interests.

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