Single-Atom MnN₅ Catalytic Sites Enable Efficient Peroxymonosulfate Activation by Forming Highly Reactive Mn(IV)—Oxo Species

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ABSTRACT: Four-nitrogen-coordinated transitional metal (MN₄) configurations in single-atom catalysts (SACs) are broadly recognized as the most efficient active sites in peroxymonosulfate (PMS)-based advanced oxidation processes. However, SACs with a coordination number higher than four are rarely explored, which represents a fundamental missed opportunity for coordination chemistry to boost PMS activation and degradation of recalcitrant organic pollutants. We experimentally and theoretically demonstrate here that five-nitrogen-coordinated Mn (MnN₅) sites more effectively activate PMS than MnN₄ sites, by facilitating the cleavage of the O–O bond into high-valent Mn(IV)−oxo species with nearly 100% selectivity. The high activity of MnN₅ was discerned to be due to the formation of higher-spin-state N₅Mn(IV)=O species, which enable efficient two-electron transfer from organics to Mn sites through a lower-energy-barrier pathway. Overall, this work demonstrates the importance of high coordination numbers in SACs for efficient PMS activation and informs the design of next-generation environmental catalysts.

KEYWORDS: peroxymonosulfate activation, single-atom catalysts, coordination number, high-valent Mn(IV)−oxo species, high-spin state

INTRODUCTION

Heterogeneous peroxymonosulfate (PMS)-based advanced oxidation processes (AOPs) are powerful remediation technologies to treat recalcitrant organic contaminants in water. Catalysts with transition metals are efficient persulfate activators to produce free radicals (e.g., SO₄²⁻) that oxidize the target pollutants, but these radicals suffer from scavenging by background constituents and ultrashort lifetimes (∼10⁻⁸−10⁻⁹ s), which hinders their efficacy in complex matrices. High-valent metal−oxo (HVMO) species, as typical nonradical oxidative species generated in persulfate activation, are promising candidates for water purification, owing to their much longer lifetime (e.g., 7−10 s for Fe(IV)=O), higher steady-state concentrations (∼10⁻⁹ ≫ 10⁻¹²−10⁻¹⁵ M for radicals), ultrahigh oxidant utilization efficiency, and selective reactivity toward organics. However, HVMO species are usually generated in homogeneous systems catalyzed by transition metals that also produce other reactive species (e.g., OH and O₂), and this decreases the utilization efficiency of the oxidant (e.g., PMS). Therefore, it is important to develop transition metal-based heterogeneous catalysts that activate persulfate to efficiently generating HVMO species with high reactivity.

Single-atom catalysts (SACs) have emerged as promising heterogeneous catalysts for PMS activation due to their utmost atom utilization efficiency and high selectivity for diverse catalytic reactions. Especially, four-nitrogen coordinated SACs display significantly high selectivity in HVMO generation during PMS activation. For example, electron-depleted CuN₄/C−B was reported to boost PMS activation and form Cu(III)−OH reactive species for bisphenol A removal. Also, Fe(IV)−HVMO was found to be the major oxidizing species in FeN₄ single-site catalyzed PMS activation, and it exhibited selective reactivity for oxidizing organic contaminants of emerging concern.

The coordination number of M−N moieties in SACs strongly affects the geometric and electronic properties, as well as the catalytic activity of SACs. While SACs with a coordination number higher than four have been used for selective conversion of hydrocarbons and oxygen reduction reactions and play prominent roles in biomimetic and enzymatic oxidation reactions, the five-nitrogen coordinated SACs are seldom explored for persulfate activation.
except for Fe–N₅ SACs. This represents a fundamental knowledge gap and a missed opportunity for coordination chemistry using other transition metal SACs (such as Co, Mn, Cu, and Ni) to boost PMS activation and enhance the degradation of recalcitrant organic pollutants. For instance, while Mn SACs have been tested for HVMO-dominated persulfate activation, five-nitrogen coordinated Mn SACs have not. Herein, we experimentally and theoretically investigated the five-nitrogen coordinated Mn configuration (MnN₅) in PMS activation via the Mn–HVMO pathway. We also synthesized g-C₃N₄-supported MnN₅ to demonstrate the importance of high coordination numbers in SACs for efficient PMS activation and discerned how the high coordination number of Mn−N moieties enhances PMS-based AOPs to inform the design of next-generation catalysts.

**Experimental Section**

**Materials.** Dicyandiamide (DCD), manganese(III) acetylacetonate (Mn(acac)₃), ammonium chloride (NH₄Cl), 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diaminonitromethane salt (ABTS), PMS, and 2,2,6,6-tetramethylpiperidone (TEMP) were purchased from Sigma-Aldrich Chemical Co., Ltd. Methanol (MeOH), p-chlorophenol (4-CP), and furfuryl alcohol (FFA) were obtained from Sinopharm Chemical Reagent Co., Ltd.

**Synthesis of g-C₃N₄.** Graphitic carbon nitride (g-C₃N₄) was prepared by using DCD as the precursor. Typically, 5.0 g of DCD was heated to 550 °C with a rate of 2.5 °C/min and kept for 4 h in a muffle furnace. After cooling to room temperature, the yellow residual was ground to obtain g-C₃N₄.

**Synthesis of Mn SACs.** For the synthesis of MnN₅, NH₄Cl was selected to control the coordination environment of Mn single-atom sites on g-C₃N₄. Typically, 0.5 g of g-C₃N₄ and 0.25 mmol of Mn(acac)₃ were mixed with 8 mmol NH₄Cl molar weight in a mortar and thoroughly grinded. Then, the obtained sample was heated to 550 °C with a rate of 2.5 °C/min under an Ar atmosphere for 4 h in a tube furnace. Finally, the products were washed with ultrapure water to remove soluble Mn salts, dried at 60 °C for 12 h, and collected after grinding to obtain MnN₅. A series of samples MnN₅-x (x = 1, 2, and 3) were obtained corresponding to 4, 8, and 12 mmol NH₄Cl molar weight, respectively. If not specified, MnN₅-2 (labeled as MnN₅) was used in most of the investigations due to its optimal performance. MnN₅ was synthesized by a similar procedure but without the addition of NH₄Cl.

**Characterization.** The crystal phases and morphologies of catalysts were determined by Rigaku D/max-2200/PC X-ray diffraction (XRD) and Tecnai G2F20 transmission electron microscopy (TEM), respectively. N₂ adsorption–desorption isotherms were recorded on a Nova 2200e gas sorption analyzer (Quantachrome Instruments). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was conducted on a JEOL JEM-ARF200F atom resolution analytical microscope. X-ray photoelectron spectroscopy (XPS) analyses were performed on an Axis Ultra DLD system (Shimadzu/Kratos). Raman spectra were recorded on a Bruker Senterra R200-L dispersive Raman microscope at 532 nm. Zero-field-cooled (ZFC) and field-cooled (FC) measurements were executed by a magnetic property measurement system (MPMS, Quantum Design) under H = 1 kOe for temperature-dependent (2–400 K) magnetization measurements. The Mn contents in MnN₅-x catalysts were measured by an inductively coupled plasma mass spectrometer (Thermo Fisher Scientific). The X-ray absorption experiments were carried out at the XAS (X-ray absorption spectra) station (BL14W1) of the Shanghai Synchrotron Radiation Facility (SSRF). The electron storage ring was operated at 3.5 GeV. Si(311) double-crystal was used as the monochromator, and the data were collected using a solid-state detector under ambient conditions. The beam size was limited by the horizontal and vertical slits with an area of 1 × 4 mm² during XAS measurements. The X-ray absorption of a Mn foil at Mn K-edge was measured for energy calibration. The spectra analysis and fitting were performed by the software codes of Artemis and Athena.

**DFT Calculations.** All spin-polarized periodic calculations were carried out using the Vienna Ab initio Simulation Package (VASP). The remaining core electrons were described by the projector augmented-wave method. The 2s and 2p electrons in carbon, oxygen, sulfur, and nitrogen and the 3p, 3d, and 4s electrons in manganese were treated as valence electrons. The kinetic cut-off energy was set to 450 eV for all calculations. The surface models of MnN₄ and MnN₅ were built on g-C₃N₄ with a vacuum layer of 15 Å to avoid the interaction between contiguous period layers. The Monkhorst–Pack k-point mesh was set to 3 × 4 × 1 for both the surface and adsorbed models. The energy change and force convergence tolerance were chosen to be less than 10⁻⁵ eV atom⁻¹ and 0.02 eV Å⁻¹, respectively.

The Gibbs free energy is calculated using eq 1, where ΔE*, ΔE_ZPE, and ΔS represent the adsorption energy, zero-point energy variation, and entropy variation, respectively. Zero-point energy was obtained by the vibrational frequency calculation with a selective dynamics method because the vibrational contribution of MnN₄ and MnN₅ surfaces can be neglected in this process.

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\Delta G^* = \Delta E^* + \Delta E_{ZPE} - T \Delta S
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(Catalytic Performance. The tests of 4-CP removal (10 mg L⁻¹, 50 mL) in the activated PMS process were performed in a beaker. Around 25 mg of Mn SACs were first dispersed into the 4-CP solution and stirred for 30 min to reach adsorption–desorption equilibrium. Then, 15.4 mg of PMS was added to initiate the catalytic degradation process. An appropriate amount of the aqueous solution was taken at a given time interval, and the concentration of residual 4-CP was analyzed by high-performance liquid chromatography (Shimadzu LC-2010AHT). Residual PMS in the solution was detected by a reported ABTS method. The reactive oxygen species (ROS) in PMS activation systems were identified by a Bruker microEPR spectrometer. In the recycle tests, MnN₅ was collected after the reaction, and regenerated via elution with MeOH to thoroughly remove the adsorbed organic intermediates, and dried before the next run.

**Results and Discussion**

**Synthesis and Characterization of MnN₅ SACs.** Graphitic carbon nitride, with the well-defined tri-s-triazine framework, is frequently used as the support for isolated metal sites by calcining a mixture of metal sources and DCD, and this often produces MN₄ due to the formation of four-nitrogen coordinated precursors. To increase nitrogen coordination numbers, we introduced an external nitrogen source (NH₄Cl) during the CN-based synthesis process because the decomposition of NH₄Cl at temperatures above 520 °C generates...
gaseous HCl and NH\textsubscript{3}. HCl induces delamination and disintegration of bulk g-C\textsubscript{3}N\textsubscript{4}, while NH\textsubscript{3} enables amino groups’ anchoring on the metal sites to form extra coordinated structures.

Figure 1a illustrates the NH\textsubscript{4}Cl-mediated calcination approach to synthesize Mn SACs with a five-nitrogen coordination structure (MnN\textsubscript{5}). MnN\textsubscript{5} with different nitrogen contents (MnN\textsubscript{5-}x, x = 1−3) was synthesized by varying the NH\textsubscript{4}Cl doses (Table S1). The CN (NH\textsubscript{4}Cl) and MnN\textsubscript{4} control samples were also synthesized by a similar procedure without a Mn precursor and NH\textsubscript{4}Cl addition, respectively.

As shown by TEM images (Figures 1b and S1, S2), MnN\textsubscript{4} and MnN\textsubscript{5} displayed a lamellar structure, without visible nanoparticles. Only typical diffraction peaks of g-C\textsubscript{3}N\textsubscript{4} appeared in the XRD patterns of Mn SACs (Figure S3), ruling out the formation of Mn chlorides or Mn oxides. The absence of Mn chlorides was further proved by XPS measurements (Figure S4a), in which no Cl signal was detected on all catalysts. The atomically dispersive Mn species over the support of g-C\textsubscript{3}N\textsubscript{4} was evidenced by the HAADF-STEM equipped with a probe aberration corrector according to the bright spots of atomic scale (Figures 1c and S5). The element mapping images in Figure 1b further identified the uniform distribution of Mn atoms in the entire CN support. Furthermore, the mass content of Mn was comparable in all samples (2.7−3.0 wt %, measured by inductively coupled plasma atomic emission spectroscopy) (Table S2).

The structure of Mn−N coordination in MnN\textsubscript{4} and MnN\textsubscript{5} was proved by Raman spectra (Figure 1d). It displays no Mn−O coordination peak but new peaks at ~208.9, 357.4, and 472.5 cm\textsuperscript{-1}, which are attributed to the stretching or deformation vibration of out-of-plane Mn−N modes, further identifying the existence of Mn−N bonds in both catalysts.\textsuperscript{35,36} The downward shift of N 1s XPS binding energies in Mn SACs (Figure S6) in comparison to pristine CN provided further indication of the changes of nitrogen bonding structures.\textsuperscript{34,39} In comparison with CN, there was no evidence of Mn−C and Mn−O species in C 1s (Figure S7) and O 1s (Figure S8) XPS spectra of Mn SACs, unambiguously suggesting the formation of Mn−N coordination structures. The fine structures of Mn−N moieties in MnN\textsubscript{4} and MnN\textsubscript{5} were then compared by synchrotron X-ray absorption spectra. The Mn K-edge X-ray absorption near-edge structure (XANES) spectra (Figure 1e) show that the rising edges of the normalized K-edge for both catalysts are located much closer to that of MnO than that of Mn\textsubscript{3}O\textsubscript{4}, suggesting that Mn atoms are in an oxidation state with an average valence of about +2. This agrees with the XPS results, showing a distinct shake-up satellite peak of Mn\textsuperscript{2+} at 646.0 eV (Figure S9). The Fourier transform extended X-ray absorption fine structure (FT-EXAFS) spectra of MnN\textsubscript{5} (Figure 1f) had a solitary peak for the Mn−N shell at about 1.65 Å, which is similar to that of MnN\textsubscript{4} (Figure 1f) but significantly different from that of the Mn−Mn bond (Mn foil) at ~2.33 Å and the Mn−O bond (MnO) at ~2.72 Å, verifying atomically dispersed Mn−N moieties in both Mn SACs. The coordination number of Mn−N was calculated to be 5.19 ± 0.33 for MnN\textsubscript{5}, significantly higher than that of MnN\textsubscript{4} (4.34 ± 0.28) (Figure S10a,b and Table S3), inferring that the isolated Mn atoms were 4- and 5-fold coordinated by N atoms in MnN\textsubscript{4} and MnN\textsubscript{5}, respectively.
PMS Activation over MnN₅ Proceeded through a Mn(IV)–Oxo Dominated Pathway. The effect of nitrogen coordination numbers of Mn SACs on PMS activation activity was examined via degradation of 4-CP, a common recalcitrant organic pollutant. Before comparing the catalytic performances of these Mn SACs, the effect of the catalyst concentration on PMS activation was explored, as observed in Figure S11, thus determining an optimal catalyst dosage of 0.5 g L⁻¹. As shown in Figure 2a, almost 100% 4-CP (10 mg/L) was removed by adding MnN₅ and PMS (MnN₅/PMS) in 6 min, much faster than that with MnN₄ and PMS (73% removal). CN (NH₂Cl) and homogeneous Mn(II) ions (0.5 g L⁻¹), much higher than the Mn leaching contents listed in Table S4) exhibited very poor activity for PMS activation (less than 10% 4-CP removal) (Figure 2a), and all Mn SACs resulted in negligible 4-CP adsorption (Figure S12). The specific apparent rate constants (kₐ, min⁻¹ g m⁻²) (Figure S13) were calculated by normalizing the observed pseudo-first-order kinetic constants (kₐ,J) by their specific surface areas (SSAs) (Table S2 and Figure S14). The kₐ,J value of MnN₅ (0.022 min⁻¹ g m⁻²) was highest (inset of Figure 2a), 110- and 3.7-fold higher than that of g-C₃N₄ (0.0022 min⁻¹ g m⁻²) and MnN₄ (0.006 min⁻¹ g m⁻²), respectively. The intrinsic catalytic performance of MnN₅ was superior to that of many reported Mn-based catalysts and Cu/Fe SACs (Figure S15 and Table S5).¹,²,¹⁰⁻⁴⁵

More importantly, MnN₅ still retained high activity after six successive catalytic recycles (Figure S16), implying its long-term stability. MnN₅ was also more active than MnN₄ to remove various refractory pollutants via efficient PMS activation, including phenol, bisphenol A, sulfathiazole, and sulfamethoxazole (Figure S17). Furthermore, although the initial pH of the reaction solution changed from 3.5 to 10.5, the pH had a negligible influence on 4-CP removal in the MnN₅/PMS system (Figure S18a). The highly effective catalytic performance of MnN₅ was also observed in the complex water matrices (such as background inorganic and organic matters and real water environment—lake water), accompanied by 100% 4-CP removal within 15 min (Figure S18b), indicating the interference resistance of the MnN₅/PMS oxidation system. The kₐ,J values of all catalysts did not correlate with the contents of each surface N, C, and O species in the catalysts (Figures S19–S21 and Table S6), excluding the contribution of the nonmetallic sites to PMS activation. Thus, the atomically dispersed Mn–N moieties are the critical active sites for the outstanding performance of MnN₅ catalysts.

To understand the origin of the high activity of MnN₅, we first identified the pertinent reactive species in these two systems. Electron paramagnetic resonance (EPR) was conducted by using 5,5-dimethyl-1-pyrroline-N-oxide and TEMP as the probes of free radicals [sulfate radical (SO₄⁻)] and hydroxyl radical (OH)⁻ and singlet oxygen (¹O₂), respectively (Figure S22). Free radical signals did not appear in the EPR spectra of the MnN₅/PMS and MnN₄/PMS systems, which was corroborated by negligible inhibition on 4-CP removal upon the addition of excessive MeOH (500 mM), a typical scavenger of free radicals (Figures 2b and S23).⁶,³³ The removal efficiency of 4-CP experienced a very slight decrease in the presence of 10 mM p-benzoquinone (Figure S24a), implying a negligible contribution of O₂⁻⁻ in Mn SAC/PMS oxidation systems. Thus, the radical pathway of PMS activation could be ruled out. Although the characteristic triplet signals of TEMP·¹O₂ were observed in the EPR spectra (Figure 2c), and FFA (an ¹O₂ scavenger) mildly suppressed the 4-CP degradation, the contribution of ¹O₂ (frequently produced species with HVMO) was likely insignificant.⁵⁶ Considering the direct consumption of PMS by FFA, the degradation of 4-CP was also executed in the D₂O solvent due to the solvent-dependent lifetime of ¹O₂.⁴⁷ Figure S24b,c shows the minor difference between the 4-CP degradation rate in D₂O and H₂O solvents, demonstrating the negligible role of ¹O₂. In fact, the characteristic triplet signals of TEMP·¹O₂ in the MnN₅/PMS system were significantly lower than those in MnN₄/PMS (Figure 2c). Furthermore, the time-dependent evolution of ¹O₂ did not correlate with the 4-CP degradation (Figure S25), further corroborating the minor contribution of ¹O₂ to the 4-CP degradation in the Mn SAC/PMS systems.
Subsequently, the generation of high-valent Mn species was examined. As Mn(IV) species have been verified not to oxidize PMSO into PMSO₂ due to its poor reactivity of oxygen-atom transfer,⁴⁵,⁴⁸ PMSO oxidation and PMSO₂ production failed to prove Mn(IV) species in the MnN₅/PMS system (Figure S26), further indicating the absence of Mn(V)=O species. In the in situ Raman spectra of PMS (Figure 2d), MnN₅ decreased the Raman peak intensity ratio of 1061 cm⁻¹ (HSO₅⁻) to 981 cm⁻¹ (SO₄²⁻) from 2.24 to 1.78, and the peak of surface-complexed PMS species at ~839 cm⁻¹ appeared, corresponding to the interaction of PMS molecules with MnN₅. The simultaneous appearance of a new Raman peak at 746 cm⁻¹ could be assigned to the stretching vibration of Mn(IV)=oxo structures, suggesting that PMS molecules chemically bound to MnN₅ sites dissociated and transformed into Mn(IV)=oxo species.⁴⁷,⁵⁰ Similar phenomena were also observed in the MnN₅/PMS system (Figure S27), indicating that PMS activation pathways over the two catalysts were similar. Furthermore, the Mn(IV)=oxo stretching frequency (746 cm⁻¹) persisted under ambient conditions, disappeared immediately after the addition of 4-CP (Figure 2d), implying that Mn(IV)=oxo species have a strong oxidation capacity to induce a rapid electron transfer from 4-CP to Mn(IV)=oxo. Although the intensity of this peak (746 cm⁻¹) was weak due to the low Mn contents in Mn SACs, the Raman observation was in situ, and the difference among the Raman spectra was significant enough to discern the appearance and disappearance of such a peak, thus verifying the existence of the Mn(IV)=oxo species in the Mn SAC/PMS system.

As the dominant reactive species, the lifetime and reactivity of Mn(IV)=oxo for 4-CP degradation were further evaluated. The Mn(IV)=oxo-containing MnN₅, obtained by oxidizing MnN₅ with PMS in the absence of 4-CP (Text S1), were labeled as MnN₅-R0. The MnN₅-R0 stored for 1 day still could directly oxidize ~23.0% of 4-CP, resulting in higher removal than 4-CP adsorption on the fresh MnN₅ (~8.0%) and removal by the used catalyst (MnN₅-R, ~11.0%) (Figure S28a). This implies that Mn(IV)=oxo species produced from the interaction between PMS and Mn SACs had a relatively long lifetime,⁴⁸ which makes the off-line detection of Mn(IV)=oxo feasible. The formed Mn(IV)=O on the MnN₅ surface was thus identified by using ABTS, which is oxidized into ABTS⁺ through single-electron transfer.⁵¹ As seen in Figure S28b, fresh MnN₅ showed no reactivity with ABTS. However, in contrast to MnN₅-R (18%), MnN₅-R0 could rapidly convert ABTS (54%) into the organic cation radical of ABTS⁺, which had four characteristic adsorption peaks at 405, 640, 728, and 818 nm, further corroborating the formation of Mn(IV) species on the MnN₅-R0 surface and its dominant role in organic oxidation. The presence of Mn(IV)=oxo species on the catalyst surface was also corroborated by XPS analyses. In the Mn 2p XPS spectra of MnN₅-R0, the specific satellite peak at 646.0 eV for Mn(II) in pristine MnN₅ vanished (Figure 2e), accompanied by a shift of the Mn 2p₃/₂ peak at 641.2 eV to a higher binding energy (641.8 eV), which was normally assigned to Mn(IV).⁵² Simultaneously, a new signal at 529.5 eV appeared in the O 1s spectrum (Figure 2f), corresponding to the oxygen in Mn(IV)=oxo moieties, further proving the generation of Mn(IV)=oxo species during PMS activation. After the addition of 4-CP, the above characteristic XPS peaks of Mn(IV) and oxygen for Mn(IV)=O disappeared synchronously with the reappearance of the specific satellite peak at 646.0 eV for Mn(II). These above results excluded the contribution of free radicals, singlet oxygen, electron transfer via surface complexes, and Mn(V)=oxo and verified the existence and contribution of Mn(IV)=oxo species, thus sufficiently revealing that Mn(IV)=oxo species were the main contributors to rapid 4-CP oxidation in these Mn SAC/PMS systems.

We further quantitatively determined the contribution of possible reactive species (Mn(IV)=oxo and singlet oxygen) to 4-CP degradation by a kinetic analysis with a steady-state approximation (Text S2 and Figures S29, S30). When using FFA (5 μM) as a probe of O₂ and considering the reaction of PMS with FFA,⁴⁷ its steady-state concentrations ([O₂]ₜₜ) in the MnN₅ and MnN₅ systems were conservatively calculated to be 1.1 × 10⁻¹⁰ and 1.7 × 10⁻¹⁰ mM, respectively (Table S7). The much lower steady-state concentration of O₂ in the

Figure 3. Theoretical calculation of PMS adsorption and activation on MnN₅ and MnN₅ catalysts. (a) Adsorption of PMS (HSO₅⁻) on MnN₅ or MnN₅ sites of Mn SACs. The charge density difference of (b) MnN₅ and (c) MnN₅ sites after PMS adsorption. The light blue and light yellow iso-surfaces depict electron depletion and accumulation, respectively. (d) Free energy changes against reaction pathways of PMS activation at MnN₅ sites. (e) Comparison of free energy changes for PMS reductive activation at MnN₅ and MnN₅ sites.
Theoretical Verification of Superior Activity of MnN₅ Sites for PMS Activation. We then conducted density functional theory (DFT) calculations to explore PMS adsorption and activation over Mn SACs with well-defined four- or five-coordination-number structures (MnN₄ and MnN₅). On the surface of two catalysts, PMS (HO-OSO₅⁻) is chemically bound to the Mn sites by one peroxyl oxygen in a terminal end-on mode with large adsorption energies (E_{ads} < −0.5 eV, Figure 3a) to form Mn–O(\textit{H})OSO₅⁻, indicating that both Mn sites of MnN₄ and MnN₅ have strong PMS binding affinity.58 After adsorption, Mn–O(\textit{H})OSO₅⁻ is notably activated along with the significantly stretched O–O single bond from 1.39 to 1.48 Å and 1.50 Å for MnN₄ and MnN₅ sites, respectively (Table S8). The longer O–O bond on MnN₅ suggests a higher PMS activation capacity. The charge density difference mappings corroborate enhanced PMS activation on MnN₅ because more electrons are delocalized from Mn atoms to the bound oxygen of MnN₅ than that of MnN₄ (Figure 3b,c). Subsequently, the adsorbed PMS is dissociated into an intermediate state (\textit{Mn}(II)–OOO₅²⁻) by detaching a proton without an energy barrier for both MnN₄ and MnN₅ sites (Figure 3d). Then, the substantial electron donation from MnN₅ sites populates the peroxyl O atoms and affords a small energy barrier (+0.6 eV) for the dissociation of the O–O bond into N₃Mn(IV)═O (Figure 3e), in which the adsorption state was assigned as the first step. In contrast, N₃Mn(IV)═O formation from the intermediate state on MnN₄ sites is confronted with a large activation barrier (+1.19 eV) (Figure 3e). Thus, we estimated that a Mn SAC with five-nitrogen coordination is an efficient catalyst for PMS activation due to the energetically favorable generation of highly reactive N₃Mn(IV)═O species, which is consistent with the above experimental results.

Enhanced Reactivity of Mn(IV)–Oxo Species in the MnN₅/PMS System. Generally, the generation of Mn(IV)–oxo species is correlated with PMS consumption. Time-dependent PMS consumption over Mn SACs in the absence of organics was measured (Figure S31), and the specific PMS consumption rates were obtained by fitting the first-order kinetics (Figure S32), which were subsequently normalized by SSA (Figure S33). MnN₄ and MnN₅ showed similar specific PMS consumption rates with a difference of only 3.7% at an initial PMS concentration of 1.0 mg/L (Figure 4a), suggesting that the accelerated generation of Mn(IV)–oxo species was not the main reason for the high activity of MnN₅ (Figures 4a and S33–S36). We then first checked the enhanced intrinsic reactivity of the N₃Mn(IV)═O configuration by DFT calculations. In the process of 4-CP oxidation by Mn(IV)═O species, a molecule of 4-CP (C₅H₅OCl) spontaneously adsorbed on the Mn(IV)═O sites (I → II), inducing a slight decrease of free energies for both MnN₄ and MnN₅ systems (Figure 5a). The charge density difference results indicated more electrons localizing around the oxygen atoms in the Mn(IV)═O moieties (Figure S37), which favors the formation of a transitional intermediate (III) by a strong interaction between the oxygen and the positively charged carbon atom neighboring to chlorine in 4-CP. In this rate-determining step (II → III), the oxidation of 4-CP by N₃Mn(IV)═O encounters a much higher energy barrier of 0.80 eV (Figure 5a). Comparatively, the oxidation barrier is only 0.32 eV at N₃Mn(IV)═O sites. Furthermore, the transitional configuration (III) shows that the charge transfer from the adsorbed 4-CP to N₃Mn(IV)═O is 0.463 e (Figure 5b), higher than that of N₃Mn(IV)═O (0.437 e) (Figure 5c).

Figure 4. Significant contribution of Mn(IV)═O species and the spin state-dependent reactivity for 4-CP removal. (a) Correlation between specific PMS consumption rates \(k_{\text{SSA,PMS}}\) and specific activity \(k_{\text{SA,4-CP}}\) of different Mn SACs for 4-CP degradation at [PMS]ₐ = 1.0 mM. (b) Relationship between specific potential changes \(\Delta E_{\text{SSA}}\) and \(k_{\text{SA}}\) for 4-CP degradation. (c) Temperature-dependent magnetic susceptibility with the Curie–Weiss fittings for the Mn SACs-R0 (the catalyst reacted with PMS excluding pollutants, that is, Mn SACs containing Mn(IV)═O). (d) Relationship between the intrinsic reactivity of Mn(IV)═O species (slope of \(\Delta E_{\text{SSA}}\) – \(k_{\text{SA}}\) ) and \(\mu_{\text{eff}}\) of Mn SACs-R0 (\(\mu_{\text{eff}}\)–R0).

MnN₅/PMS system is consistent with the EPR results (Figure 2b). Subsequent kinetic analyses suggest that the contribution of \(^1\text{O}_2\) to the 4-CP degradation in the MnN₅/PMS system was below 0.01%. As Mn(IV)═O species in the MnN₅ system accounted for nearly 100% degradation of 4-CP (Table S7), the high activity of MnN₅ can be attributed to either accelerated generation or enhanced reactivity of Mn(IV)═O species, which needs further investigation.
The more favorable charge transfer and the much lower energy barriers suggest that the N₅Mn(IV)=O configuration has higher reactivity than N₅Mn(IV)=O to degrade 4-CP.

The enhanced reactivity of N₅Mn(IV)=O was corroborated by in situ open-circuit potential (OCP) tests via recording OCP values of Mn SAC electrodes with the increase of PMS dosages (Text S3). The OCP values of all Mn SAC electrodes increased sharply with the addition of PMS (Figure S41), the μₗ values (noted as μₗ-R0) for Mn SACs-R0 increased notably. All MnNₓ−R0 had larger magnetic moments (μₗ-R0 = 6.45−8.16 μB) than MnNₓ=R0 (5.75 μB) (Figure 4d), suggesting that the generated N₅Mn(IV)=O species had a higher spin state than N₅Mn(IV)=O. The μₗ-R0 values show a positive relationship with the intrinsic reactivity of Mn(IV)=O species (slope of ΔEₜₑ−Sₜ−kₐ) and kₐ values of Mn SACs (Figure 4d), implying the critical role of the spin state in the high reactivity of the generated Mn(IV)=O species. As the electron transfer from an organic molecule to the low-lying π* orbital of metal–oxo is in concert with spin-state crossing, high-spin Mn(IV)=O species enable a relatively low energy barrier route for oxidation, which is consistent with the above DFT analyses and OCP results.

The oxidation products of 4-CP were identified to explore the reactivity difference between N₅Mn(IV)=O and N₅Mn(IV)=O species (Text S4). As shown in Figure S41, the major products in Mn(IV)=O-mediated 4-CP oxidation were chlorinated oligomeric intermediates, such as dimeric substances (m/z = 219 and 253) and trimeric products (m/z = 345 and 379). The postulated transformation pathways of 4-CP by the Mn(IV)=O-mediated oxidation process are presented in Figure 6a. Chlorophenoxonium ions produced by 4-CP oxidation would form positively charged phenolic

![Figure 5](image)

**Figure 5.** Theoretical calculation of 4-CP oxidation reaction over Mn(IV)=O species. (a) Comparison for free energy changes against 4-CP oxidation reaction pathways on N₅Mn(IV)=O and N₅Mn-(IV)=O species. The corresponding intermediate structures are listed below the figure. The charge density differences of the optimized structure of the transition states (III) (b) N₅Mn(IV)=O and (c) N₅Mn(IV)=O=C₂H₅OCl. The light blue and yellow iso-surfaces depict electron depletion and accumulation, respectively.

The slope of the correlation curve, representing the increased tendency of the organic degradation rate at the same increase of ΔEₜₑ for Mn SACs, is an indicator of the intrinsic reactivity of Mn(IV)=O species generated in PMS activation. The slope value in the MnNₓ/PMS system was 4.33, significantly higher than that of MnNₓ/PMS (0.64), further proving the significantly enhanced intrinsic reactivity of N₅Mn(IV)=O species in the five-nitrogen coordinated Mn catalysts.

To further understand the basis of enhanced N₅Mn(IV)=O reactivity, we determined the magnetic property and spin state of Mn(IV)=O-containing Mn SACs (Mn SACs-R0), which were obtained by oxidizing Mn SACs with PMS in the absence of organic substances. The magnetic susceptibilities (χ), obtained by variable-temperature (2−400 K) magnetic susceptibility (ZFC and FC) measurements at 1000 Oe (Figure S39), obey the Curie−Weiss law (χ = C/(T − Θ)), where C and Θ separately represent the Curie constant and Curie−Weiss temperature. Then, the effective magnetic moment (μₗ = √8CμB) was obtained by linear fitting 

\[ T \]

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The theoretical calculation of 4-CP oxidation reaction over Mn(IV)=O species. (a) Comparison for free energy changes against 4-CP oxidation reaction pathways on N₅Mn(IV)=O and N₅Mn-(IV)=O species. The corresponding intermediate structures are listed below the figure. The charge density differences of the optimized structure of the transition states (III) (b) N₅Mn(IV)=O and (c) N₅Mn(IV)=O=C₂H₅OCl. The light blue and yellow iso-surfaces depict electron depletion and accumulation, respectively.
hydroxyl groups at para- and ortho-sites via instantaneous resonance transfer, suggesting these intermediates spontaneously undergo polymerization (PR) to generate chlorinated oligomeric products (Figure S41). The MnN₅/PMS system (Figure S41b) produced more trimeric \((m/z = 345 \text{ and } 379)\) and dimeric substances \((m/z = 253)\) than MnN₅/PMS (Figure S41a), suggesting the faster 2e⁻-transfer between \(\text{N}_5\text{Mn(IV)}\) and O-CP, which is consistent with the high reactivity of \(\text{N}_5\text{Mn(IV)}\) and O-CP. Based on the above DFT and experimental results, in comparison to MnN₅, MnN₅ enables more efficient PMS activation to generate high-spin \(\text{N}_5\text{Mn(IV)}\) and O species with a stronger oxidation capacity, resulting in the faster 2e⁻-oxidation of organic pollutants (Figure 6b). In conclusion, Mn(IV) and O species formed on the Mn SAC surface could serve as electron acceptors, leading to the PR of 4-CP and generating no residual byproducts that could be released to the aqueous environment. Thus, this Mn(IV) and O-mediated heterogeneous PMS activation system has the potential to remove phenolic pollutants and recover polymerized organic residues from water.

**Environmental Implications.** Five-nitrogen coordinated Mn SACs have been overlooked for efficient persulfate activation during the treatment of wastewater contaminated by recalcitrant organic compounds and for groundwater remediation. This work addresses a fundamental knowledge gap in coordination chemistry to boost PMS activation and highlights the critical role of five-nitrogen coordinated Mn SACs to form highly reactive Mn(IV)-oxo species that significantly enhance such AOPs. Specifically, during PMS activation, Mn(II) sites on the catalysts are spontaneously oxidized into reactive Mn(IV)-oxo species, whose reactivity strongly depends on the coordination number of nitrogen atoms. Compared to MnN₅, MnN₅ enables more efficient PMS activation to generate \(\text{N}_5\text{Mn(IV)}\) and O species with higher reactivity, which is facilitated by the higher spin state of Mn(IV)-oxo species under five-nitrogen coordinated conditions. Accordingly, the rapid two-electron transfer from target organics to the generated \(\text{N}_5\text{Mn(IV)}\)-oxo species promotes oxidative oxidation with high PMS activation efficiency. These mechanistic insights indicate that the activity of SACs in HVMO-mediated PMS activation depends greatly on the coordination numbers, which control the reactivity of HVMO species. Overall, this work provides a strategy to develop SACs with high nitrogen coordination numbers, which enhance PMS-based AOPs and encourages exploration of other transitional metals with high nitrogen coordination numbers to develop next-generation environmental catalysts that enhance HVMO-mediated PMS-based AOPs.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c08836.

Characterization; degradation of 4-CP and its reaction kinetics in different PMS activation systems; adsorption of 4-CP; comparison of the \(k_{SA}\) of different organics; cycle tests; correlation between \(k_{SA}\) and N, C, and O species; identification and quantifying the contribution of ROS; preparation of pre-oxidized Mn SACs (i.e., MnN₅-R0) and their oxidation of 4-CP; PMS decomposition; comparison of \(k_{SA,PMS}\) values and their relationship with \(k_{SA,4-CP}\) values; DFT results; electrochemical measurement; and identification of degradation intermediates of 4-CP (PDF)

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**Notes**
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REFERENCES


(41) Wang, Y.; Sun, H.; Ang, H. M.; Tadé, M. O.; Wang, S. Facile synthesis of hierarchically structured magnetic MnO2/ZnFe2O4 hybrid materials and their performance in heterogeneous activation of peroxymonosulfate. ACS Appl. Mater. Interfaces 2014, 6, 19914−19923.


(51) Yin, G. Understanding the oxidative relationships of the metal oxo, hydroxo, and hydroperoxide intermediates with manganese(IV) complexes having bridged cyclams: correlation of the physicochemical properties with reactivity. Acc. Chem. Res. 2013, 46, 483−492.

(52) Huang, Y.; Zou, J.; Lin, J.; Yang, H.; Wang, M.; Li, J.; Cao, W.; Yuan, B.; Ma, J. ABTS as both activator and electron shuttle to activate persulfate for diclofenac degradation: Formation and contributions of ABTS•−, SO4•−, and OH•. Environ. Sci. Technol. 2022, 202438.


