Persulfate-based advanced oxidation processes mediated by high valent Mn species

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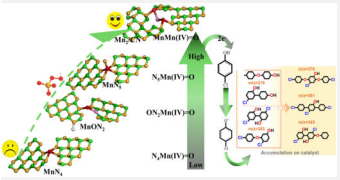

In peroxymonosulfate (PMS)-based advanced oxidation processes (AOPs), stable and efficient functional materials are the crucial. Single-atom catalysts (SACs) are broadly recognized as the most efficient active sites, but diatomic catalyst and SACs with a coordination number higher than four are rarely explored. We experimentally demonstrate here that five-nitrogen-coordinated Mn (MnN_5) and diatomic Mn (Mn_2/CN) more effectively activate PMS than MnN_4 sites. The high activity of MnN_5 was discerned to be due to the formation of higher-spin-state Mn^{IV}−o, which enable efficient two-electron transfer from organics to Mn sites. The interaction between the coordination of Mn DACs and their electronic structures may provide a more optimized structure, which is beneficial for the adsorption and desorption of substrates to reach appropriate states and improve intrinsic activity. Overall, this work aims to develop efficient manganese catalysts at the molecular level for PMS-based AOPs.

Introduction

Heterogeneous peroxymonosulfate (PMS)-based advanced oxidation processes (AOPs) are powerful remediation technologies to treat recalcitrant organic contaminants in water. 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 higher steady-state concentrations, 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 , and this decreases the utilization efficiency of the oxidant. Therefore, it is important to develop transition metal-based heterogeneous catalysts that activate persulfate by efficiently generating HVMO species with high reactivity.

We experimentally and theoretically investigated the five-nitrogen coordinated Mn configuration (MnN_5) and diatomic Mn (Mn_2/CN) in PMS activation via the Mn−HVMO pathway. We synthesized MnN_5/CN and Mn_2/CN to demonstrate the importance of high coordination numbers and electronic structure for efficient PMS activation. This work provides information for the design of next-generation catalysts.

Material and Methods

Materials. Dicyandiamide (DCD), manganese(III) acetylacetonate ($Mn(acac)_3$), ammonium chloride (NH_4Cl), PMS, and were purchased from Sigma-Aldrich Chemical Co., Ltd. Manganese(II) chloride ($MnCl_2$), oxalic acid, and 2,2,-bipyridine were obtained from Sinopharm Chemical Reragent Co., Ltd.

Synthesis of g-C_3N_4. The DCD was heated to 550 °C with a rate of 2.5 °C/min and kept for 4 h in a muffle furnace.

Synthesis of $Mn_2(bpy)_2(\mu\text{-ox})$. The copper-dimer precursor $Mn_2(bpy)_2(\mu\text{-ox})$ was first prepared by a complexation reaction of manganese chloride ($MnCl_2$), 2,2,-bipyridine and oxalic acid.

Synthesis of Mn SACs. For the synthesis of MnN_5, NH_4Cl was selected to control the coordination environment of Mn single-atom sites on g-C_3N_4. Typically, g-C_3N_4 and $Mn(acac)_3$ were mixed with NH_4Cl 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. MnN_4 was synthesized by a similar procedure but without the addition of NH_4Cl.

Synthesis of Mn_2/CN. The only difference between MnN_5 and Mn_2/CN is that the precursor $Mn_2(bpy)_2(\mu\text{-ox})$ is chosen.

Results and Discussion

Atomic structures of the dimeric manganese moieties were resolved by using aberration correction high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging (Fig. 1a). The collected STEM images exhibit a large number of adjacent, paired bright dots (labeled with red circles, <0.35 nm in size for each dot) distributed on a substrate of lower contrasts. These small bright dots can be attributed to atomically dispersed Cu considering their much higher Z contrast than C_3N_4. Line-profile scanning for 33 pairs of such bright dots give an average distance of 2.7 (±0.07 Å) (Fig. 1b). This is much shorter than the value (5.2 Å) for the two manganese atoms within $Mn_2(bpy)_2(\mu\text{-ox})$, again confirming the reconstruction

and condensation of the manganese-dimer moieties as a result of the removal of organic ligands in the synthesis.

In the in situ Raman spectra of PMS (Fig. 1c), the simultaneous appearance of a new Raman peak at 751 cm^{-1} could be assigned to the stretching vibration of Mn^{IV}−oxo structures, suggesting that PMS molecules chemically bound to Mn_2/CN sites dissociated and transformed into Mn^{IV}−oxo species[2]. Similar phenomena were also observed in the MnN_5/PMS system, indicating that PMS activation pathways over the two catalysts were similar. Furthermore, the Mn^{IV}−oxo stretching frequency (751 cm^{-1}), persisting under ambient conditions, disappeared immediately after the addition of 4-CP, implying that Mn^{IV}−oxo species have a strong oxidation capacity to induce a rapid electron transfer from 4-CP to Mn^{IV}−oxo.

We then conducted density functional theory (DFT) calculations to explore PMS adsorption and activation over Mn SACs. On the surface of two catalysts, PMS is chemically bound to the Mn sites by one peroxyl oxygen in a terminal end-on mode with large adsorption energies. The longer O−O bond on MnN_5 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 bounded oxygen of MnN_5 than that of MnN_4. Thus, we estimated that a Mn SAC with five-nitrogen coordination is an efficient catalyst for PMS activation, which is consistent with the experimental results.

The enhanced reactivity of Mn^{IV}−o was corroborated by in situ open-circuit potential (OCP) tests via recording OCP values of Mn SAC and DAC electrodes with the increase of PMS dosages. The Mn_2/CN and MnN_5 electrode had the highest positive OCP value in the MnN_4, suggesting that the Mn^{IV}−o species of Mn_2/CN and MnN_5 have the highest oxidative capacity. We normalized the positive potential difference (ΔE) values by the unit moles of catalysts to obtain a parameter ($\Delta E_{per\text{-}site}$). A linear positive correlation between $\Delta E_{per\text{-}site}$ and $k_{per\text{-}site\text{-}4\text{-}CP}$ ($R^2 \geqslant 0.75$) was obtained. The slope of the correlation curve, representing the increased tendency of the organic degradation rate at the same increase of $\Delta E_{per\text{-}site}$ for Mn SACs and DACs, is an indicator of the intrinsic reactivity of Mn^{IV}-O species generated in PMS activation. The slope value in the Mn_2/CN /PMS system was 3.55, significantly higher than that of Mn SAC (0.43), further proving the significantly enhanced intrinsic reactivity of Mn^{IV}−o species in the Mn_2/CN (Fig. 1d)[3]. The k_{SA} value of Mn_2/NC (0.151 min^{-1} g m^{-2})and MnN_5 (0.022 min^{-1} g m^{-2}) were highest, and higher than that of g-C_3N_4 (0.0002 min^{-1} g m^{-2}) and MnN_4 (0.006 min^{-1} g m^{-2}), respectively. The intrinsic catalytic performance of Mn_2/NC and MnN_5 were superior to that of many reported Mn-based catalysts and Cu/Fe SACs (Fig. 1e).

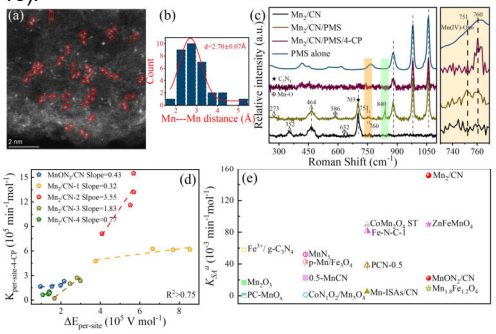

Figure 1. (a) Representative HAADF-STEM images of Mn_2/CN. (b) Statistical distribution of the Mn-Mn distance. (c) In situ Raman spectra. (d) Relationship between specific potential changes (ΔE_{SSA}) and k_{SA} for 4-CP degradation. (e) Comparison of the kinetics of organic pollutants degradation in the reported heterogeneous PMS-based AOPs.

Conclusions

Mn DACs and five-nitrogen coordinated Mn SACs are efficient catalyst for the treatment of wastewater contaminated by recalcitrant organic compounds and for groundwater remediation by PMS-based AOPs. This work addresses the fundamental knowledge gap in promoting PMS activation in coordination chemistry and emphasizes the key reason why Mn_2/CN and MnN_5 forms highly active Mn^{IV}-o species. Specifically, during PMS activation, Mn(II) sites on the catalysts are spontaneously oxidized into reactive Mn^{IV}−o species, whose reactivity strongly depends on the coordination number of nitrogen atoms and the electronic structure of Mn. These mechanistic insights suggest that the activity of SAC in HVMO mediated PMS activation depends not only on the coordination number that controls the reactivity of HVMO species, but also on the electronic regulation between metal atoms. Overall, this work provides a strategy for developing DACs and SACs with high nitrogen coordination numbers, which can enhance PMS-based AOPs for developing next-generation environmental catalysts and enhancing HVMO-mediated PMS based AOPs.

Acknowledgments

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References

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