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A highly active and durable bimetallic CoMnO_x catalyst supported on carbon nanofibers for peroxymonosulfate activation toward water treatment

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A bimetallic CoMnO_x catalyst supported on carbon nanofibers has been constructed for peroxymonosulfate (PMS) activation.

In contemporary water treatment technologies, the effective and targeted elimination of hazardous contaminants is substantially challenging.¹ In recent years, peroxymonosulfate (PMS)-activated oxidation systems have emerged as a prominent research focus in advanced oxidation processes (AOPs), demonstrating remarkable potential for environmental remediation.^{2,3} Reactive oxygen species (ROS), including free radicals like hydroxyl radicals ($\cdot\text{OH}$) and sulfate radicals ($\text{SO}_4^{\cdot-}$), as well as non-radical species, can be generated from PMS molecules with an asymmetric structure.⁴ In comparison to radical-based ROS, $^1\text{O}_2$ has emerged as a particularly attractive oxidant in AOPs due to its inherent benefits, including prolonged longevity, broad pH tolerance, robust electrophilicity, and exceptional target specificity.⁵

Defect engineering has proved to be a promising strategy to promote the catalytic efficiency in Fenton-like reactions. Upon oxygen vacancy formation, electrons adjacent to the defect sites undergo delocalization. This critical electronic restructuring process not only significantly enhances surface activation but also concurrently improves the charge transfer capability and electrical conductivity. Consequently, transition metal oxides enriched with oxygen vacancies exhibit exceptional PMS activation efficiency in Fenton-like systems.⁶ In a typical example, Zhu *et al.* introduced oxygen vacancies on commercial MnO_2 surfaces under ambient atmospheric conditions. The resulting defect-rich MnO_2 exhibited enhanced catalytic performance in PMS activation, achieving complete mineralization of tetrabromobisphenol (TBBPA) with a remarkable pseudo-first-order rate constant of 0.21 min^{-1} , a notable 22-fold enhancement compared to pristine MnO_2 .⁷ Although the metal oxide-activated persulfate system exhibited advantageous characteristics such as mild reaction conditions, cost-effectiveness, and

high efficiency,⁸ they often suffer from the obstacles of agglomeration of the active components, which leads to diminished catalytic efficacy and durability. The integration of carbon-based materials holds promise for bolstering the electron transfer capacity of metal oxide components and establishing robust covalent bonds between carbon carriers and metal elements, ultimately enhancing the stability of catalysts.⁹

Inspired by the preceding discussions, we propose an innovative defect engineering strategy that synergistically integrates bimetallic oxide architecture with oxygen vacancy modulation, yielding a CNFs@CoMnO_x-500 catalyst featuring exceptional PMS activation efficiency. The study also delved into the examination of various influential factors, including catalyst and PMS dosage, pH of the solution, co-existing anions, and natural organic matter, among others. Concurrently, the generated ROS species are identified through quenching experiments and electron paramagnetic resonance (EPR) spectroscopy analysis. The findings demonstrate the effectiveness of the CNFs@CoMnO_x catalyst for rhodamine (RhB) degradation *via* non-radical pathways, specifically $^1\text{O}_2$ species.

The synthesis procedure and structural evolution of the CNFs@CoMnO_x-500 composite are illustrated in Fig. 1, which involves a co-deposition strategy followed by controlled thermal annealing at 500 °C under an inert atmosphere. During the initial deposition process, a critical redox reaction occurs between KMnO_4 and carbon that leads to the deposition of MnO_2 nanosheets onto the CNFs ($4\text{MnO}_4^- + 3\text{C} + \text{H}_2\text{O} \rightarrow 4\text{MnO}_2 +$

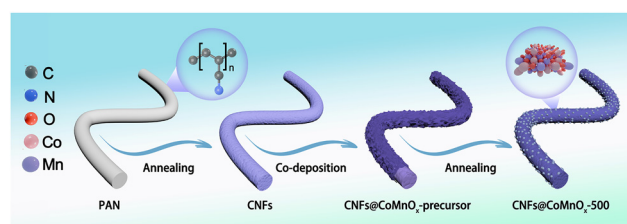


Fig. 1 Schematic diagram for the synthetic process of CNFs@CoMnO_x-500 nanofibers.

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evolution of the obtained CNFs@CoMnO_x-500. The Mn-O stretching vibration in CNFs@MnO_x-500 appears at 656 cm⁻¹, while in the CNFs@CoMnO_x-precursor and CNFs@CoMnO_x-500 samples, this band exhibits a marked shift, suggesting the incorporation of Co species into the lattice (Fig. S9).¹² HRTEM analysis further reveals well-defined lattice fringes with measured interplanar spacings of 0.25 nm and 0.22 nm, corresponding to the (111) and (200) crystallographic planes of CNFs@CoMnO_x-500, respectively (Fig. 2e and f). Energy-dispersive X-ray (EDX) spectroscopy confirms the coexistence of Co, Mn, O, C, and N elements in the CNFs@CoMnO_x-500 sample (Fig. S10), while the elemental mapping demonstrates their spatially homogeneous distribution across the nanostructure (Fig. 2g). EPR analysis reveals that the CNFs@CoMnO_x-precursor sample exhibits a characteristic signal at $g = 2.003$ (Fig. S11a), which is typically associated with unpaired electrons trapped at oxygen vacancies.¹³ Complementary XPS deconvolution of the O 1s spectra resolves three distinct contributions, including lattice oxygen (O_{lat}) at 530.2 eV, oxygen vacancies at 531.3 eV, and surface-adsorbed hydroxyl species from H₂O (O_{H₂O}) at 532.2 eV (Fig. S11b).¹⁴ Comparative quantification reveals that both CNFs@CoMnO_x-400 (29.7%) and CNFs@CoMnO_x-500 (28.4%) exhibit significantly elevated oxygen vacancy fractions relative to CNFs@CoMnO_x-600 (21.6%). It can be concluded that the oxygen vacancy concentration decreases in the following order: CNFs@CoMnO_x-400 \approx CNFs@CoMnO_x-500 > CNFs@CoMnO_x-600. The chemical valence states of various crystalline materials were further investigated by Co 2p and Mn 2p XPS spectra. As illustrated in Fig. S12a, the Mn 2p spectrum exhibits two primary spin-orbit components of Mn 2p_{1/2} at 653.4 eV and Mn 2p_{3/2} at 642.1 eV, respectively. High-resolution fitting of the Mn 2p_{3/2} identifies three distinct oxidation states of Mn²⁺ (641.1 eV), Mn³⁺ (642.5 eV), and Mn⁴⁺ (644.1 eV).¹⁵ The Co 2p exhibits characteristic peaks at 782.2 eV (Co²⁺ 2p_{3/2}) and 796.9 eV (Co²⁺ 2p_{1/2}), with additional features at 780.5 eV (Co³⁺ 2p_{3/2}) and 795.6 eV (Co³⁺ 2p_{1/2}), complemented by satellite peaks at 787.5 eV and 801.9 eV (Fig. S12b).¹⁶ It can be seen that as the temperature increases, the oxidation states of Co and Mn decrease.

We systematically investigated the PMS activation capability of CNFs@CoMnO_x-500 through RhB degradation, a typical model reaction for AOPs. Control experiments demonstrate negligible RhB degradation (below 5%) with CNFs@CoMnO_x-500 alone and <10% with PMS only (Fig. 3a). Strikingly, the first-order kinetic constant (k , min⁻¹) for RhB degradation is substantially enhanced in the CNFs@CoMnO_x-precursor/PMS system, reaching a value of 0.249 min⁻¹ (Fig. 3b, c and Fig. S13). The favorable catalytic performance of the CNFs@CoMnO_x-precursor sample can be attributed to its oxygen vacancies. Notably, after the annealing treatment, the k value of the obtained CNFs@CoMnO_x-500 increases to 0.659 min⁻¹. This performance underscores the synergistic interplay between the bimetallic solid solution architecture and oxygen vacancy in modulating redox-active sites. For comparative analysis, the catalytic performances in the monometallic counterparts of CNFs@CoO_x-500 and CNFs@MnO_x-500 are suboptimal, achieving merely 42.0% and 28.7% RhB degradation, respectively (Fig. 3a).

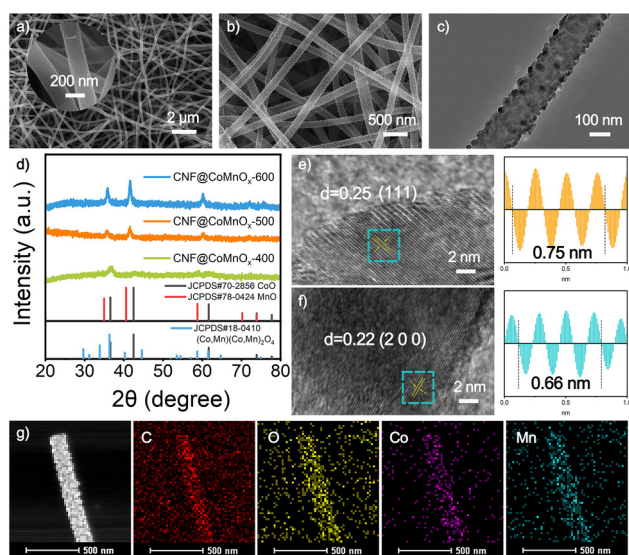


Fig. 2 (a) FESEM image of CNFs@CoMnO_x-precursor nanofibers. (b) and (c) FESEM and TEM image; (d) XRD patterns; (e) and (f) HRTEM image; (g) HAADF-STEM and EDX mappings of CNFs@CoMnO_x-500.

The DMPO–PMS system exhibits characteristic 1:2:2:1 quadruplet signals, corresponding to DMPO–•OH adducts (Fig. 4b). Remarkably, the introduction of CNFs@CoMnO_x-500 into the DMPO–PMS system markedly attenuates these signals to near-background levels. In contrast, a prominent 1:1:1 triplet signal emerges in the TEMP–PMS system and an enhancement after the addition of the CNFs@CoMnO_x-500 catalyst, providing unequivocal evidence of ¹O₂ generation (Fig. 4c). Control experiments reveal diminished ¹O₂ signals in the catalyst-only system, demonstrating that ¹O₂ serves as the predominant reactive species governing RhB degradation in the CNFs@CoMnO_x-500/PMS system.

XPS analysis is used to elucidate the catalytic mechanism of the CNFs@CoMnO_x-500/PMS system. As illustrated in Fig. S24a, quantitative deconvolution reveals a discernible decrease in the Co²⁺ contribution from 39.4% to 37.2%, accompanied by a proportional increase in Co³⁺ content from 60.6% to 62.8% after the catalytic degradation reaction. This redox evolution indicates electron transfer from Co²⁺ to PMS during activation, with subsequent regeneration of Co²⁺ *via* reduction of Co³⁺ by HSO₅[−] and the SO₄^{2−} intermediate, thereby generating reactive SO₅^{•−} and OH[•] species.²⁷ For Mn species, quantitative XPS analysis reveals a notable valence state redistribution, indicating an Mn-mediated electron redistribution process (Fig. S24b). Parallel characterization from XPS and EPR spectroscopy demonstrates a marked reduction in oxygen vacancy content from 28.4% to 19.7% after the catalytic degradation reaction (Fig. S24c and S25), confirming the pivotal role of these structural defects in electron transfer mechanisms during redox cycling. Additionally, oxygen vacancies operate as PMS adsorption sites, facilitating electron transfer to surface-bound PMS, which increases the production of ROS.²⁸

The degradation mechanism of RhB is systematically elucidated by high-performance liquid chromatography mass spectrometer (HPLC-MS) measurement.²⁹ The primary degradation pathway initiates with sequential *N*-deethylation, consistent with the established literature,³⁰ wherein RhB (*m/z* = 443) undergoes stepwise ethyl group elimination to yield P1 (*m/z* = 415) and P2 (*m/z* = 331) (Fig. S26 and S27). Subsequently, cleavage induces chromophore destruction *via* dehydroxylation of the product to produce P3, P4 and P5. Progressive fragmentation of these aromatic intermediates through bond scission and oxidation ultimately produces low-molecular-weight aliphatic compounds (P6–P8).

In this study, an oxygen vacancy-enriched CNFs@CoMnO_x-500 catalyst is strategically prepared *via* a co-precipitation protocol coupled with an annealing process. The catalyst exhibits exceptional PMS activation capability, achieving an impressive over 99% RhB degradation within 13 min. Mechanistic studies identify ¹O₂ as the dominant ROS, with the oxygen vacancy-abundant interface facilitating PMS adsorption and electron shuttling. This work establishes a paradigm for designing multifunctional composite catalysts, offering critical guidelines for optimizing AOPs.

Siyu Ren: investigation, data curation and drafting the manuscript. Yue Zhang: investigation. Linfeng Zhang:

investigation. Xiaofeng Lu: funding acquisition, resources, review and editing and supervision.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: detailed experimental procedures, supplementary figures, and tables. See DOI: <https://doi.org/10.1039/d5cc06807j>.

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