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Sea urchin-like La-doped MnO_2 for electrocatalytic oxidation degradation of sulfonamide in water

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Abstract

A sea urchin-like La-doped $\alpha\text{-MnO}_2$ catalyst was successfully synthesized by a one-step hydrothermal method. The as-prepared material exhibits electrocatalytic activity for water oxidation, achieving an overpotential of 450 mV to reach a catalytic current density of 10 mA/cm^2 in 1.0 M KOH solution. The urchin morphology and open tunneling structure can fully expose the rich active sites and facilitate mass transfer during electrochemical oxidation process. Moreover, the catalyst is also applied for sulfonamide degradation due to the generation of strong oxidizing $\bullet\text{OH}$ species during the process of water oxidation. The indirect oxidation of sulfonamide by $\bullet\text{OH}$ species was confirmed through radical quenching and capture studies. The catalyst degraded sulfonamide antibiotics with up to 40% efficiency within 2 h. The introduction of the heteroatom La^{3+} into MnO_2 led to a redistribution of electrons around Mn, which altered the electron density of the metal sites, lowered the average valence state of Mn, facilitated the production of reactive Mn^{III} species, and optimized the exposure density of the active sites. Therefore, the sea urchin-like La-doped MnO_2 material shows potential for applications in electrochemical sustainability research.



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Keywords: Sulfanilamide, oxidation degradation, electrocatalysis, oxygen evolution reaction, manganese oxide

INTRODUCTION

Sulfonamides (SAs) are a common class of spectral antimicrobial drugs widely used in clinical medicine and veterinary health. However, their biotoxicity in aquatic environments has raised concerns^[1-4]. Their antibacterial properties can inhibit biodegradation, leading to pollution and the accumulation of this emerging contaminant in soil, surface water, groundwater, and drinking water^[5-7]. Moreover, sulfonamide antibiotics are readily transported in the environment due to their extensive use and strong hydrophilic and acid-base properties. As a result, even trace amounts in water bodies can be bioaccumulated through food chains, posing a serious threat to human health^[8]. Therefore, there is an urgent need to develop environmentally friendly, efficient, and cost-effective methods for the degradation and removal of sulfonamide antibiotics, which have become a major focus of research. Current approaches to managing antibiotic contamination include physical adsorption, biodegradation, and chemical degradation^[9,10]. Physical adsorption offers simple operation, low cost, and reproducibility. Common adsorbents include activated carbon, carbon nanotubes, graphene, and minerals and metal oxides such as montmorillonite and kaolinite. To enhance the performance of traditional adsorbents, modifications such as acidic, alkaline and oxidative treatment can be employed to optimize surface properties and pore structures, thereby improving adsorption capacity and selectivity^[11,12]. However, this method typically only transfers the antibiotic to a different phase without achieving actual degradation. It also carries the risk of secondary pollution upon adsorption saturation and is susceptible to interference from coexisting substances. Biological degradation relies on microbial metabolism, offering advantages such as environmental friendliness, low operating costs, and the potential for complete harmless disposal^[13,14]. Degrading bacteria are often sourced from contaminated environments or activated sludge in wastewater treatment systems. Degradation occurs either through direct metabolism of antibiotics or via co-metabolism during growth on substrates. However, microbial activity is limited by the antibiotics' antimicrobial properties and low environmental concentrations, resulting in generally low degradation efficiency, slow processes, and potential induction of drug-resistant bacteria and resistance genes. Chemical degradation, in contrast, relies on strong oxidative reactions to break down antibiotic molecules, offering high efficiency, rapid processing, suitability for high-concentration wastewater treatment, and improved wastewater biodegradability. Primary methods include advanced oxidation processes (AOPs) and electrochemical techniques. AOPs depend on the generation of highly reactive free radicals, whereas electrochemical methods involve both direct anodic oxidation and indirect oxidation via electrogenerated strong oxidants. Compared with traditional methods, AOPs have received increasing attention for their environmental friendliness^[15-18]. AOPs include the Fenton method, electrocatalytic oxidation, photocatalytic oxidation, ozone oxidation, and wet air oxidation. The electrochemical degradation method is considered one of the most promising AOPs, using electrical energy to drive further degradation and removal of antibiotics through electrochemical reactions. Initial research focused on the development of novel electrode materials to improve electro-Fenton efficiency. For example, Younis *et al.* fabricated oxygen-vacancy-rich NiFe-LDH/EG nanosheets, which utilized vacancies to catalyze the generation of hydroxyl radicals ($\cdot\text{OH}$) from H_2O_2 , achieving 98% mineralization of SAs within 80 min. This highlights the crucial role of material design in enhancing oxidative performance^[19]. Subsequent work shifted toward elucidating reaction mechanisms and innovating process configurations. Zeng *et al.* developed an Sb-SnO₂ titanium membrane from reduced TiO₂ nanotube arrays, revealing a synergistic mechanism between $\cdot\text{OH}$ oxidation and direct electron transfer. This system enhanced sulfamethoxazole (SMX) removal by 8.4-fold in flow-through mode, indicating strong potential for practical implementation^[20]. Recent advancements reflect two prominent trends: the exploration of non-metallic catalytic systems to avoid metal leaching and the pursuit of ultra-fast degradation kinetics. Peng *et al.* constructed defect-doped graphene/boron nitride heterojunctions that activate O₂ to generate $^1\text{O}_2$ via efficient electron transfer, offering new insights into metal-free catalytic mechanisms^[21]. Meanwhile, Zhang *et al.* designed a hydrophilic protein-like cobalt catalyst [AC-LDH@Co(OH)₂] with optimized metal sites

and mass transfer compatibility, achieving 80% antibiotic removal within 15 s using only 0.075 mM peroxymonosulfate (PMS), demonstrating exceptional efficiency and practical potential^[22]. These studies demonstrate that efficient degradation of SAs can be achieved through the rational design of electrocatalysts. Electrochemical oxidation produces strong oxidizing intermediates via water electrolysis, which directly oxidize and degrade SAs into CO₂, H₂O, and small organic acids. Thus, the efficiency of water decomposition largely determines the degradation efficiency of SAs. Electrocatalytic degradation efficiency is influenced by factors such as reaction temperature, pH^[23], current density, and electrode material. In recent years, inexpensive transition metal catalysts have attracted considerable attention as electrode materials for water decomposition^[24,25].

Inspired by the structure of Mn₄CaO₅ clusters in natural photosystem II (PS II), manganese-based catalysts have attracted considerable research interest^[26,27]. Manganese dioxide (MnO₂) is a promising electrocatalyst with great potential in electrocatalytic and environmental purification applications due to its strong oxidizing properties, high abundance, good acid resistance, low toxicity, low cost, and environmental adaptability^[28,29]. Strategies to optimize the activity of MnO₂ electrocatalysts primarily include increasing intrinsic surface activity, improving mass diffusion efficiency, and enhancing charge transfer ability^[30]. Considerable progress has been made in optimizing MnO₂ electrocatalyst activity through morphological control. MnO₂ nanostructures can be synthesized in diverse forms, including sea urchin-like, flower-like, tubular, plate-like, spherical, and wire-like architectures. Tailored morphologies significantly influence electrocatalytic performance by modulating surface area, charge transfer kinetics, and exposure of active sites. For example, Chen *et al.* synthesized a unique three-dimensional α -MnO₂ nanowire network (NWN) via a mild, surfactant-free hydrothermal method. The structure consists of interconnected nanowires extending continuously in all directions, enhancing both hydrophilicity and electrical conductivity, which is highly favorable for electrocatalytic applications^[31]. Further improvements have been achieved through heteroatom doping, a key strategy for enhancing oxygen evolution reaction (OER) activity. Doping modifies electronic structure, increases active site density, and optimizes reaction pathways^[32,33]. Heteroatom regulation is an efficient and precise approach for material design, encompassing both non-metallic and metallic doping. Non-metallic doping primarily modifies the surface chemistry of carbon-based materials through charge polarization and defect engineering^[34,35], whereas metallic doping introduces active metallic centers or induces lattice strain and oxygen vacancies, resulting in significant improvements in electronic properties^[36]. Rare earth metals exhibit exceptional capabilities in doping modifications due to their unique 4f electron configurations, variable oxidation states, and abundant energy level transitions^[37,38]. For instance, lanthanum, with its large ionic radius (~106.1 pm), can induce substantial lattice distortion and strain, while its high oxygen affinity contributes to modulation of surface oxygen chemistry.

Herein, sea urchin-like La-doped MnO₂ was prepared via a one-step simple hydrothermal method. By controlling the addition of H₂SO₄, uniform sea urchin-like La-doped MnO₂ was synthesized. The material exhibited electrocatalytic activity for water oxidation in 1.0 M KOH solution, achieving a catalytic current density of 10 mA/cm² at an overpotential of 450 mV. Additionally, the synthesized catalyst was applied for the electrochemical oxidation degradation of SA. Leveraging its optimized interfacial charge transfer and the generation of hydroxyl radicals ($\bullet$ OH), the sea urchin-like La-doped MnO₂ synergistically facilitates both direct and indirect oxidation processes, achieving a degradation efficiency of nearly 40% within 2 h. Therefore, the sea urchin-like La-doped MnO₂ shows promising potential for applications in electrochemical sustainability research.

EXPERIMENTAL

General materials

MnSO₄·H₂O (95.0%, Alfa), La(NO₃)₃·6H₂O (99.99%, Alfa), K₂S₂O₈ (98.0%, Alfa), H₂SO₄ (98%, Energy Chemical), sulfanilamide (SA) (≥ 98%, Merck), Na₂SO₄ (98%, Energy Chemical), *tert*-butanol (TBA) (99.5%, Energy Chemical), methanol (MeOH) (≥ 99.5, Energy Chemical), *p*-Benzoquinone (*p*-BQ) (95%, Energy Chemical), 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) (98%, Energy Chemical), and Nafion (5 wt%, DuPont) were used without further purification. Milli-Q water of 18 MΩ cm was used in all experiments unless otherwise stated.

Preparation of catalysts

The synthesis of the sea urchin-like MnO₂ (α -MnO₂): 2 mmol MnSO₄·H₂O, 2 mmol K₂S₂O₈ and 2 mL concentrated H₂SO₄ were mixed in 38 mL of water and stirred for 10 min to form a homogeneous solution at room temperature. Then, the solution was transferred into a Teflon-lined stainless-steel autoclave (100 mL) and heated at 110 °C for 2 h. Then, the autoclave was allowed to cool to room temperature naturally; the precipitates were collected by washing and centrifugation and dried at 60 °C in air.

The synthesis of the sea urchin-like La-doped MnO₂: The procedure was the same as above, except that an additional 0.1 mmol La(NO₃)₃·6H₂O was added to the reactant solution prior to the hydrothermal treatment.

Physical characterizations

The X-ray diffraction (XRD) patterns were collected using a Rigaku D/Max2550VB+/PC X-ray diffractometer operated with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 100 mA. The X-ray photoelectron spectroscopy (XPS) spectra were obtained on a Kratos AXIS ULTRA XPS analyzer using monochromatic Al K α ($h\nu = 1,486.6 \text{ eV}$). Scanning electron microscopy (SEM) images were obtained on a Hitachi SU8020 cold-emission field emission scanning electron microscope with an accelerating voltage of 5 kV. Energy-dispersive X-ray (EDX) analysis and elemental mapping were conducted using an AMETEK Materials Analysis EDX equipped on the transmission electron microscopy (TEM). The Ultraviolet-visible (UV-Vis) spectroscopy absorption spectra of SA were detected in the range of 200–600 nm using Shimadzu UV 3600. TEM images were taken from a FEI Tecnai G2 F2O field emission transmission electron microscope with an acceleration voltage of 200 kV. The contents of cations in the materials were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent 725ES, USA). Electron paramagnetic resonance (EPR) analysis was performed at room temperature using a Bruker E500. The X-ray absorption spectroscopy (XAS) measurements were performed using laboratory equipment (easyXAFS300+, easy XAFS LLC).

Electrocatalytic water oxidation

The electrochemistry was tested on CHI 660E electrochemical workstation with a three-electrode system using 1.0 M KOH as electrolyte under constant temperature of 25 °C. A standard three-electrode system, in which the Glass Carbon (GC, 0.07 cm²) loaded with catalyst was the working electrode, Ag/AgCl (3 M KCl) electrode was the reference electrode and the graphite rod was the counter electrode. Typically, the catalyst ink was prepared with 2 mg sample, 20 μ L of Nafion, and 0.5 mL of water-ethanol solution at a volume ratio of 2:1. The mixed solution was ultrasonically treated for 30 min. Then, 6 μ L of the catalyst ink was dropped on the effective working area of the GC and dried at room temperature. The potentials were determined with respect to the reversible hydrogen electrode (RHE) using $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + (0.197 + 0.059 \times \text{pH}) \text{ V}$. The potentials were also determined relative to the normal hydrogen electrode (NHE) using $E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V}$. Linear sweep voltammograms (LSVs) were recorded in 1.0 M KOH aqueous solution at a scan rate of 5 mV s⁻¹ with 100% iR compensation. Controlled potential electrolysis (CPE) was

recorded on carbon cloth (CC, 0.25 cm²) electrode without iR drop compensation. The electrochemistry active surface area (ECSA) was shown in the form of capacitances that obtained by cyclic voltammetry (CVs) in the non-Faradaic potential region. Electrochemical impedance spectroscopy (EIS) spectrum was performed with frequencies from 10⁻² Hz to 10⁶ Hz with an amplitude of 5 mV.

Electrochemical degradation of sulfonamide

The electrochemical degradation of SA was conducted using a CHI 660E electrochemical workstation at room temperature with a standard three-electrode configuration. The working electrode was a fluorine-doped tin oxide (FTO, 0.25 cm²) substrate drop-coated with the catalyst. An Ag/AgCl (3 M KCl) electrode served as the reference electrode, and a graphite rod was used as the counter electrode. A solution of 1.9 mg SA in 15 mL of 0.05 M Na₂SO₄ electrolyte was electrolyzed at an applied potential of 1.41 V (vs. RHE) for varying durations. The electrolyte was subsequently collected for UV-vis absorption analysis. The molar absorptivity was determined to be 2,934 L·mol⁻¹·cm⁻¹ through the calibration with standard solutions of known concentrations^[39].

RESULTS AND DISCUSSION

The XRD patterns show the phase information of the material. The XRD patterns of synthesized samples in [Figure 1A](#) indicate a pure phase of α -MnO₂ (JCPDS 44-0141), and the introduction of trace La ions did not change the physical phase structure of the catalysts. MnO₆ octahedral units of α -MnO₂ structure are connected in an edge-shared and vertex-shared forms, resulting in 2 × 2 and 1 × 1 tunnel structures at a space of 6.72 and 3.25 Å, respectively [[Figure 1B](#)]. During synthesis, K⁺ ions may be present in these tunnels as anti-balance cations^[40]. These open pore structures can provide abundant reaction sites and a large number of pathways for molecules, which enhance catalytic efficiency. The pore structure can be clearly seen from the high-resolution transmission electron microscopy (HR-TEM) image shown in [Supplementary Figure 1A](#)^[41]. The SEM images show that the MnO₂ exhibits a sea urchin spherical structure with a uniform scale and a diameter of about 1.4~1.5 μm from the particle size distribution graph [[Figure 1C](#)]. Sea urchin-like MnO₂ was synthesized by fine control of the amount of H₂SO₄ used in the hydrothermal process, where H₂SO₄ offers the acidic environment. [Supplementary Figure 1B-E](#) shows the morphologies of MnO₂ synthesized by adding different concentrations of H₂SO₄. An imperfect sea urchin-like morphology with blocky structures forms without H₂SO₄. As the concentration of H₂SO₄ gradually increases, the sea urchin-like morphology becomes fully developed and the particle size decreases to be more uniform. The amount of H₂SO₄ affects the morphology because the acidic environment enhances the stability and oxidizing properties of S₂O₈²⁻ ions, enabling efficient oxidation of Mn²⁺ ions. Under acidic hydrothermal conditions, K₂S₂O₈ functions primarily as a precursor for sulfate radical (SO₄^{•-}) generation. This enables the selective oxidation of Mn²⁺ to Mn⁴⁺, regulates the crystal structure and morphology of the resulting product, and suppresses side reactions, thereby enhancing the purity and crystallinity of MnO₂. The sea urchin morphology of MnO₂ was not disrupted by the introduction of trace amounts of La³⁺, but its size increased to 2~2.5 μm [[Figure 1D](#)]. The TEM image showed a hollow sea urchin morphology with the lattice fringes of 0.237 nm in the HR-TEM image, corresponding to the crystal plane (211) of MnO₂ [[Figure 1E and F](#)]. In [Supplementary Figure 2](#), the pure MnO₂ also showed a hollow sea urchin morphology, and the highly regular lattice fringes of 0.239 and 0.308 nm correspond to the crystal planes (211) and (310), respectively. The high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of the La-doped MnO₂ and the EDX elemental mapping images of Mn, O, K, and La are shown in [Figure 1G](#), indicating a uniformly distributed La element. In the La-doped MnO₂ sample with a starting Mn:La molar ratio of 1:0.05, the actual atomic ratio of Mn:La in the final sample is around 1:0.004 from EDX analysis [[Supplementary Figure 3](#)]. The ICP-OES test further revealed that the mass fractions of Mn, K, and La in the sample were 56.2%, 3.71%, and 0.038%, respectively [[Supplementary Figure 4](#)]. As shown in [Supplementary Figure 5](#), the Mn, O, and K elements are uniformly

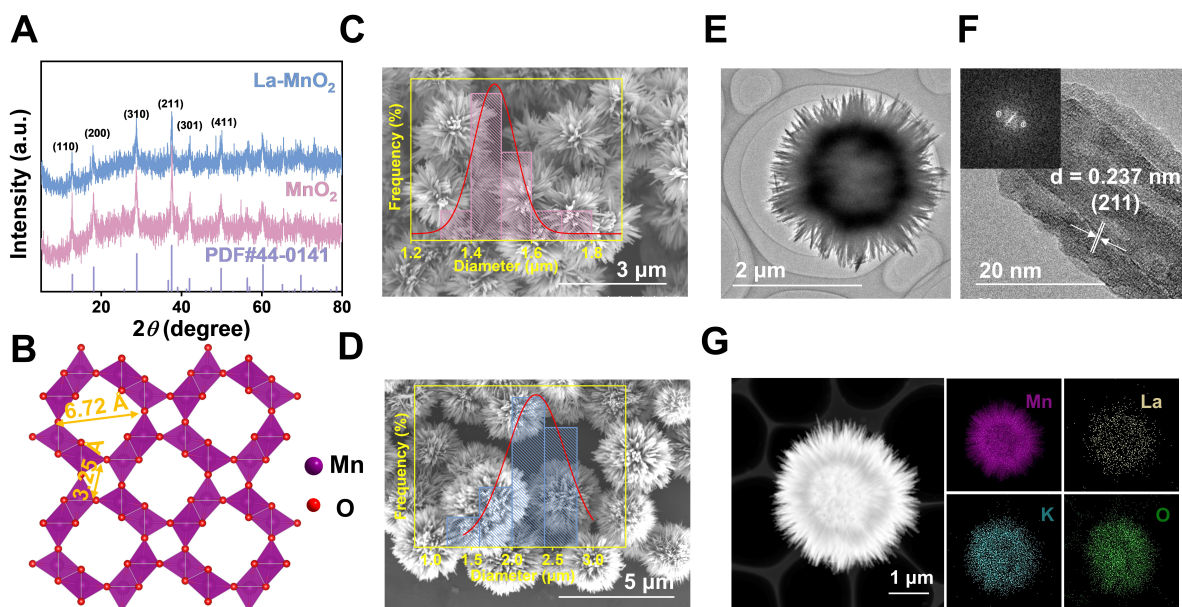


Figure 1. (A) The XRD patterns of La-doped MnO_2 and MnO_2 ; (B) The crystal structure of $\alpha\text{-MnO}_2$; The SEM images of (C) the sea urchin-like MnO_2 and (D) La-doped MnO_2 (The inset shows the particle size distributions); (E) The TEM and (F) HR-TEM images of La-doped MnO_2 (The inset shows the corresponding FFT pattern); (G) The HAADF-STEM image and the corresponding elemental mapping images of the La-doped MnO_2 . XRD: X-ray diffraction; SEM: scanning electron microscopy; TEM: transmission electron microscopy; HR-TEM: high-resolution transmission electron microscopy; HAADF-STEM: high-angle annular dark field scanning transmission electron microscopy; FFT: fourier filter transformation.

distributed in pure MnO_2 . The mass fractions of Mn and K in the pure MnO_2 were 56.9% and 3.80%, respectively, from the ICP-OES results. [Supplementary Figure 6A](#) shows that the introduction of La^{3+} into MnO_2 leads to a significant decrease in the K 2s signal in the XPS survey spectra.

After the OER test, the K 2s signal further weakens in MnO_2 , while the La 3d signal in La-doped MnO_2 gradually disappears [[Supplementary Figure 6B–D](#)], suggesting that La^{3+} may occupy sites similar to those of K^+ . This inference is further supported by the ICP-OES results, which show a reduction in K^+ content following La^{3+} incorporation. In summary, the La^{3+} likely occupies tunnel sites analogous to K^+ .

In order to further characterize the surface states of samples, the synthesized $\alpha\text{-MnO}_2$ samples were studied by XPS. The peaks at 834.8 eV correspond to La $3d_{5/2}$, along with one satellite feature at 838.1 eV^[42]. However, the splitting peak of La $3d_{3/2}$ around 850 eV is affected by the Mn LMM peak (852.69 eV), which prevents an accurate fit. This suggests the oxidation state of La^{3+} in La-doped MnO_2 [[Figure 2A](#)]. The high-resolution Mn 2p XPS spectrum shows that the peaks are located at about 653.8 and 641.9 eV for Mn $2p_{1/2}$ and Mn $2p_{3/2}$, respectively^[43]. Additionally, the Mn 2p peak of the synthesized La-doped MnO_2 catalyst was shifted by 0.14 eV in the low-energy direction [[Figure 2B](#)]. The Mn 2p peak shifts towards higher binding energy due to stronger electronegativity, resulting in an increase in the core electron binding energy, predicting higher valence manganese and vice versa. Specifically, the Mn 3s peak separation is caused by the electron exchange interaction upon photoelectron ejection, which is strong evidence for determining the valence of manganese. The ΔE_{3s} is about 4.77 eV for the synthesized La-doped MnO_2 catalyst. Compared to 4.65 eV for pure MnO_2 , an increase of nearly 0.12 eV is observed [[Figure 2C](#)]. The splitting value corresponds to Mn^{4+} from MnO_2 as discussed in literature^[44], and La doping of La leads to a decrease in the average valence state of Mn. To further analyze the local electronic structure and coordination environment of Mn atoms in La-doped MnO_2 and MnO_2 , XAS experiment was performed.

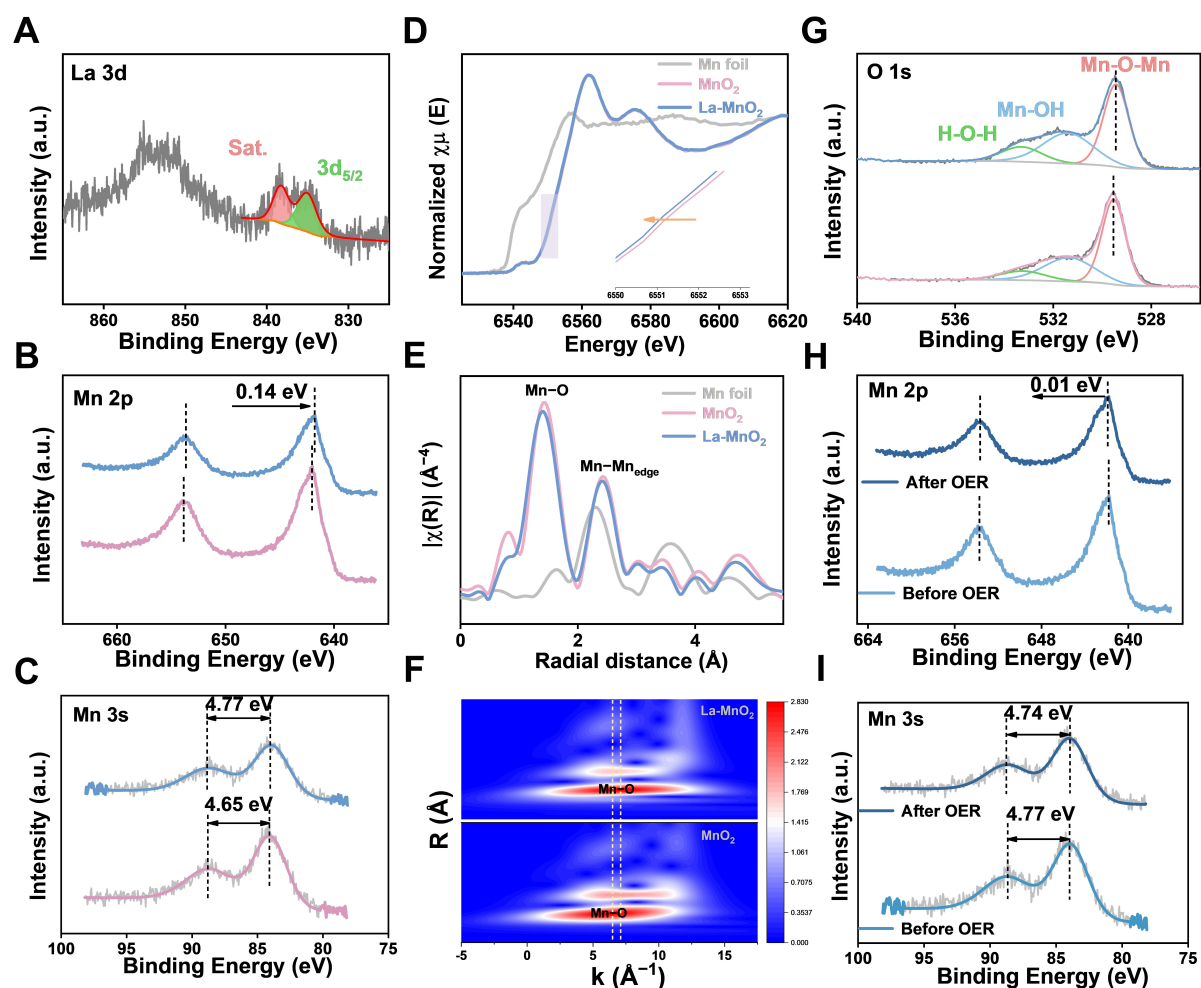


Figure 2. (A) The La 3d XPS spectrum of La-doped MnO_2 ; The XPS spectra comparison of Mn 2p (B), Mn 3s (C) for La-doped MnO_2 (blue) and pure MnO_2 (pink); (D) The XANES of Mn K-edge for La-doped MnO_2 , MnO_2 and Mn foil reference; (E) FT spectra of k^3 -weighted EXAFS spectra of Mn K-edge in La-doped MnO_2 , MnO_2 and Mn foil reference; (F) The WT of La-doped MnO_2 and MnO_2 ; (G) The O 1s XPS spectra of La-doped MnO_2 (blue) and pure MnO_2 (pink); (H) Mn 2p and (I) Mn 3s (I) spectra of La-doped MnO_2 before and after OER. XPS: X-ray photoelectron spectroscopy; XANES: X-ray absorption near-edge structure spectra; EXAFS: extended X-ray absorption fine structure spectroscopy; WT: wavelet transform; OER: oxygen evolution reaction.

Figure 2D shows the X-ray absorption near-edge structure spectra (XANES) of Mn K-edge in La-doped MnO_2 , MnO_2 , and standard Mn foil samples. The absorption edge of La-doped MnO_2 is left-shifted, indicating that the valence state of Mn decreases after the La^{3+} doping, which is consistent with the XPS results. The k^3 -weighted Fourier transforms of the extended X-ray absorption fine structure spectroscopy (FT-EXAFS) of La-doped MnO_2 and pure MnO_2 are shown in Figure 2E. The EXAFS data corresponds to two kinds of local structures in terms of the atomic distance: the first peak around 1.45 Å is typical for oxygen-coordinated Mn ions, and the second peak around 2.45 Å is assignable to di- μ -oxo bridged Mn ions (Mn-Mn_{edge}). The wavelet transform (WT) plots also confirm the change of Mn-O coordination in La-doped MnO_2 with a slightly higher intensity of the Mn-O bond (around $k = 7.0 \text{ Å}^{-1}$), which differs from the Mn-O bond observed in MnO_2 (around $k = 6.38 \text{ Å}^{-1}$) [Figure 2F]. Meanwhile, based on the analysis of the O 1s spectrum presented in Figure 2G, the binding energy positions for lattice oxygen, Mn-OH, and adsorbed H_2O are observed at around 529.5, 531.3, and 533.2 eV, respectively^[45]. Following La doping, the lattice oxygen position is shifted to a lower binding energy, which directly reflects the perturbation of the local structure of the material. Doping with heteroatoms may have important effects on catalytic properties.

Furthermore, the valence state of the catalysts after the OER was analyzed by XPS. It is noteworthy that after OER testing, Mn and O signals are evident; however, the XPS spectral signals of K and La are slightly attenuated [Supplementary Figure 6]. Subsequently, the electrolyte that had undergone 12 h stability test was analyzed using inductively coupled plasma mass spectrometry (ICP-MS). The test results confirmed the leaching of La with a concentration of 0.8436 ppb in the solution, corresponding to approximately 0.39% of the total La content [Supplementary Table 1]. It is speculated that the leaching may be caused by the weak bonding of La^{3+} in the tunnel sites. It was shown that La^{3+} and K^+ circulate in the tunnels of MnO_2 when a potential is applied. As shown in Supplementary Figure 7A-C, the valence of pure MnO_2 is reduced due to the enhanced dissolution of K^+ during the OER process, which promotes the formation of oxygen vacancies. This is because the presence of K^+ in $\alpha\text{-MnO}_2$ was originally intended to balance the negative charge resulting from the partial substitution of Mn^{3+} for Mn^{4+} . However, the results for La-doped MnO_2 are diametrically opposed [Figure 2H and I], with a slight increase in the Mn valence due to partial loss of La. Even though the solvation of La^{3+} and K^+ occurs simultaneously at high potentials, the presence of La^{3+} is rather favorable to the stability of the structure due to the greater ability of the highly electronegative La^{3+} to balance negative charges compared to K^+ . Therefore, the presence of La^{3+} has a positive effect on maintaining the stability of the catalyst's structure.

Electrocatalytic water decomposition and electrochemical oxidative degradation of SAs are two important electrochemical processes. The former is for hydrogen generation with clean energy and the latter is used to degrade organic pollutants to remediate the environment. Despite having different objectives, they both involve electron transfer and redox reactions that depend on the performance of the electrocatalyst. The catalysts are required to have high electrical conductivity, high specific surface area, abundant active sites, and good stability. The electrocatalytic water decomposition process also produces strongly oxidizing species, and the generation of such intermediates is equally applicable to the electrochemical oxidative degradation of SAs. Therefore, a typical three-electrode system was used to test OER activity of the sample with a scan rate of 5 mV s^{-1} in 1.0 M KOH , first. The overpotential of sea urchin-like La-doped MnO_2 is 450 mV at 10 mA/cm^2 [Figure 3A]. Such higher OER activity is also demonstrated by the turnover frequency (TOF) of O_2 molecules evolved per second per active site for the studied catalysts according to Supplementary Equations 1 and 2 in the Supplementary Materials. As shown in Supplementary Figure 8, a TOF of 0.0146 s^{-1} has been recorded for La-doped MnO_2 catalyst, which is about 3.5 times that of pure MnO_2 catalysts (0.00412 s^{-1}) at an overpotential of 470 mV . Meanwhile, the OER performance comparison of the sea urchin-like La-doped MnO_2 catalyst with other recently reported Mn oxide electrocatalysts is listed in Supplementary Table 2, which means it has acceptable ability to catalyze water oxidation. The OER performance of commercial RuO_2 was compared under alkaline conditions in Supplementary Figure 9. It can be clearly observed that the overpotential of the noble-metal RuO_2 is only 310 mV at 10 mA/cm^2 . Furthermore, the electrochemically active surface area (ECSA) was studied by CV at the non-Faradaic potential range with different scan rates [Supplementary Figure 10A and B]. The slope of the charging current (i_c) versus the scan rate (ν) represents the C_{dl} of La-doped MnO_2 and MnO_2 catalysts, which are 362.44 and $207.28 \text{ }\mu\text{F}$, respectively [Figure 3B]. The calculated ECSAs of La-doped MnO_2 and MnO_2 catalysts are 9.061 and 5.182 cm^2 , respectively, according to Supplementary Equation 3 in the Supplementary Materials. These results indicate that the introduction of La^{3+} is beneficial for increasing the active surface area of the catalyst and enriching the exposure of active sites. Considering the difference of ECSA of different materials, the water oxidation activity of these three materials was normalized by ECSA [Supplementary Figure 10C]. The La-doped MnO_2 sample has inherently much higher OER activity. In addition, the combined analysis of the Tafel slope [Figure 3C] and EIS plots [Figure 3D] provides a better understanding of the OER dynamics. The Tafel slopes of La-doped MnO_2 and MnO_2 were 71 and 87 mV dec^{-1} , respectively, indicating a decline in Tafel slope by doping and affirming the role of introducing La^{3+} in hastening OER kinetics. Since the electrode processes are controlled by both charge transfer and

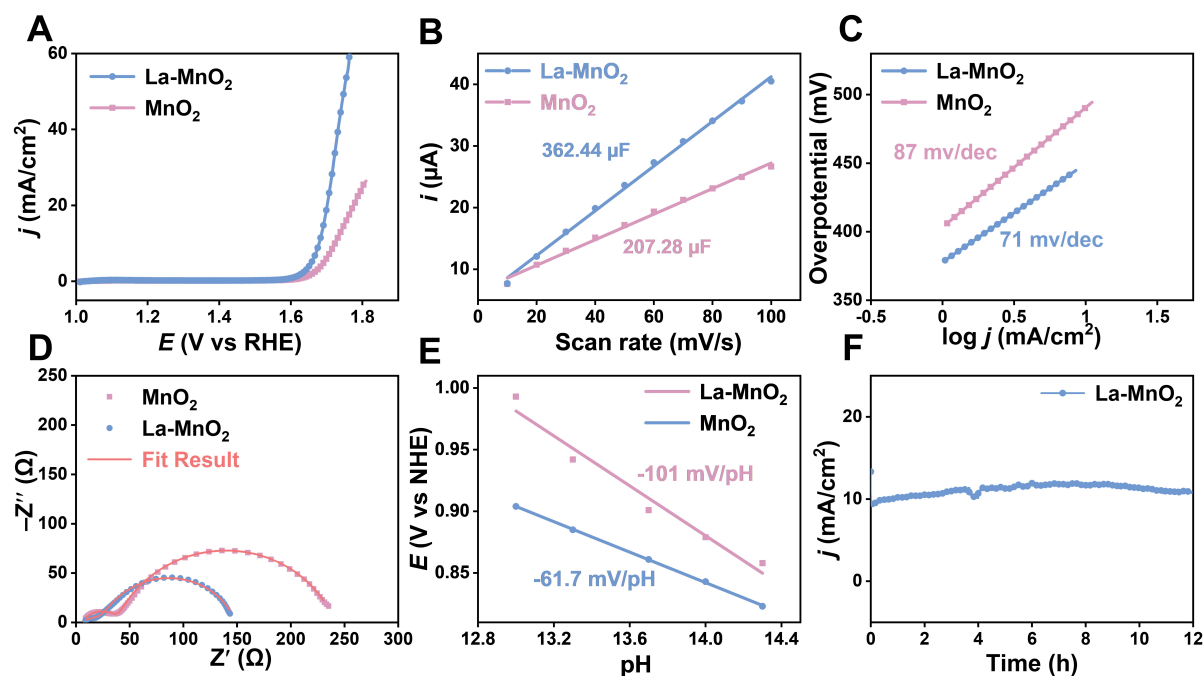


Figure 3. (A) OER LSV polarization curves, (B) the anodic charging currents at 1.34 V (vs. RHE) plotted against the scan rates, (C) the Tafel plots, (D) the Nyquist plots with fitting, and (E) the potentials against the pH values of the electrolytes at 4 mA/cm² of La-doped MnO₂ and MnO₂; (F) The CPE of the La-doped MnO₂ electrocatalyst at 1.75 V (vs. RHE) without iR compensation. OER: Oxygen evolution reaction; RHE: reversible hydrogen electrode; CPE: controlled potential electrolysis.

diffusion processes at the planar electrode, the high-frequency region is controlled by the kinetic processes of the electrode reaction and the low-frequency region is controlled by the diffusion of the reactants or products of the electrode reaction^[46,47]. In EIS plots, the Nyquist plot is composed of two semicircles throughout the frequency region, and a simplified circuit model is utilized to fit the Nyquist plot [Supplementary Figure 11]. Then, the charge transfer resistance R_{total} ($R_1 + R_2$) of La-doped MnO₂ and MnO₂ catalysts is estimated to be ~145.8 and ~235.4 Ω , indicating a sequential decrease in R_{total} and further implying enhanced electrochemical transfer kinetics from La-doping. The required potential of the electrocatalysts at a current density of 4 mA/cm² also shows a pH-dependent behavior, with slopes of -101 and 67 mV pH⁻¹ for La-doped MnO₂ and pure MnO₂ [Supplementary Figure 12 and Figure 3E]. It shows the process of proton-coupled electron transfer (PCET). OER typically involves four consecutive PCET steps, each of which is accompanied by the generation and conversion of oxygenated intermediates. For example, the conversion from H₂O to O₂ generates a series of oxygen-containing intermediates (M-OH, M=O, and M-OOH)^[48,49], and the PCET mechanism also generates highly reactive oxygen-containing free radicals ($\bullet$ OH) through the synergistic action of proton transfer and electron transfer. These radicals play a key role in the degradation of organic pollutants and biomass conversion.

Long-term stability testing was conducted on La-doped MnO₂ at a potential of 1.75 V (without iR compensation) [Figure 3F]. The results of the CPE tests show that the La-doped MnO₂ maintains excellent catalytic activity with a current density of around 10 mA/cm² over a period of 12 h, which highlights its remarkable electrochemical stability in alkaline environments. The CPE of the pure MnO₂ is also shown in Supplementary Figure 13. Initial fluctuations are a natural manifestation of the system's transition from a non-equilibrium state to a quasi-steady/steady state. Initial fluctuations in electrocatalytic stability tests typically stem from transient processes: (1) electrode surface activation, involving reconstruction, dissolution/redeposition, or chemical state evolution of metastable fresh surfaces toward electrochemical

equilibrium; (2) interfacial establishment, characterized by incomplete electrolyte wetting and evolving diffusion layers that affect the reaction area and mass transport; and (3) adsorbate accumulation, where dynamic coverage equilibria of intermediates or impurities influence catalytic activity and surface properties. Further observation of SEM images after OER testing showcased no significant change in the overall morphology of La-doped MnO_2 and MnO_2 catalysts, which retained their fine sea urchin-like morphology with a uniform particle size distribution, thus affirming their structural stability [Supplementary Figure 14]. As shown in Supplementary Figure 15, La-doped MnO_2 and MnO_2 catalysts retain the phase structure of α - MnO_2 after OER. Therefore, the introduction of La^{3+} not only enriches the exposure of active sites, optimizes the electron density of metal-centered Mn, enhances the electrical conductivity of the catalysts, and promotes charge transfer in the OER process, but also has a positive impact on the stability of the catalyst structure.

After clarifying the electrochemical activity of the α - MnO_2 material, it was applied to SA degradation experiments. SAs are a class of medicines with p-aminobenzene sulfonamide structure, as shown in Supplementary Figure 16. Electrocatalytic oxidation of SA occurs simultaneously in two ways: direct and indirect oxidation processes. Direct oxidation uses electron transfer at the electrode to protonate sulfanilamide; and indirect oxidation uses electrocatalytic water oxidation to produce a strongly oxidizing intermediate product to oxidize SA to produce CO_2 , H_2O , and small molecule acid [see Supplementary Equations 4 and 5]^[50]. It has the advantages of simple operation, wide application, high oxidation ability, environmental friendliness, low secondary waste generation and oxidant-free feature compared with other traditional technologies^[51]. Thus, in this work, the prepared sea urchin-like La-doped MnO_2 and pure MnO_2 were used for electrochemical degradation of SA, respectively. The catalyst was loaded on FTO conductive glass and the degradation experiment was carried out with 0.05 M Na_2SO_4 electrolyte. The UV-vis absorption increased with increasing sulfanilamide concentration and was plotted against the standard curve [Supplementary Figure 17A and B]. The initial concentration was 0.034 mmol/L for SA and the electrolytic voltage was 2.1 V. Then, SA degradation occurs at different times of electrolysis. The primary reaction of SA degradation by electrocatalytic oxidation is a process in which direct and indirect oxidation work together. A part of SA is directly oxidized on the anode surface by electron transfer to generate primary products, while the other part of SA is oxidized indirectly with $\cdot\text{OH}$ produced by the electrolysis system. The two primary products continue to be oxidized by $\cdot\text{OH}$ to produce maleic acid and fumaric acid. Thus, the same potential applied to the blank FTO electrode was used to observe the degradation of SA at first to clarify the degradation of the electrode surface [Figure 4A]. The blank FTO electrode also showed degradation of SA, with 15% degradation efficiency of SA within two h. Then, the La-doped MnO_2 and pure MnO_2 catalysts were drop-coated on the surface of the FTO electrode, and the degradation of SA was dramatically enhanced. The change of UV-vis absorption of SA after 2 h electrocatalytic oxidation degradation showed marked difference compared with the starting solution [Figure 4B and C]. The results proved that sea urchin-like La-doped MnO_2 has excellent ability to electrochemically degrade SA. At the same time, the catalyst was removed, and a control study was conducted by observing the UV-vis absorption without potential applied under static conditions, which showed that the SA concentration was essentially unchanged to exclude the effect of SA volatilization [Supplementary Figure 18]. The kinetic curves of electrocatalytic degradation and the degradation efficiency of SA under the catalyst were shown in Figure 4D and E. The efficiency of the catalytic degradation of SA was calculated according to Supplementary Equation 6 in the Supplementary Materials. The SA degradation efficiency was nearly 40% after 2 h for sea urchin-like La-doped MnO_2 . Therefore, the Langmuir-Hinshelwood kinetic model was used to describe the electrocatalytic degradation of SA. Their electrocatalytic degradation conformed to the pseudo-first-order kinetic equation, with degradation rate constants of 0.00637 and 0.0043 min^{-1} for La- MnO_2 and MnO_2 electrocatalytic degradation, respectively [Figure 4F].

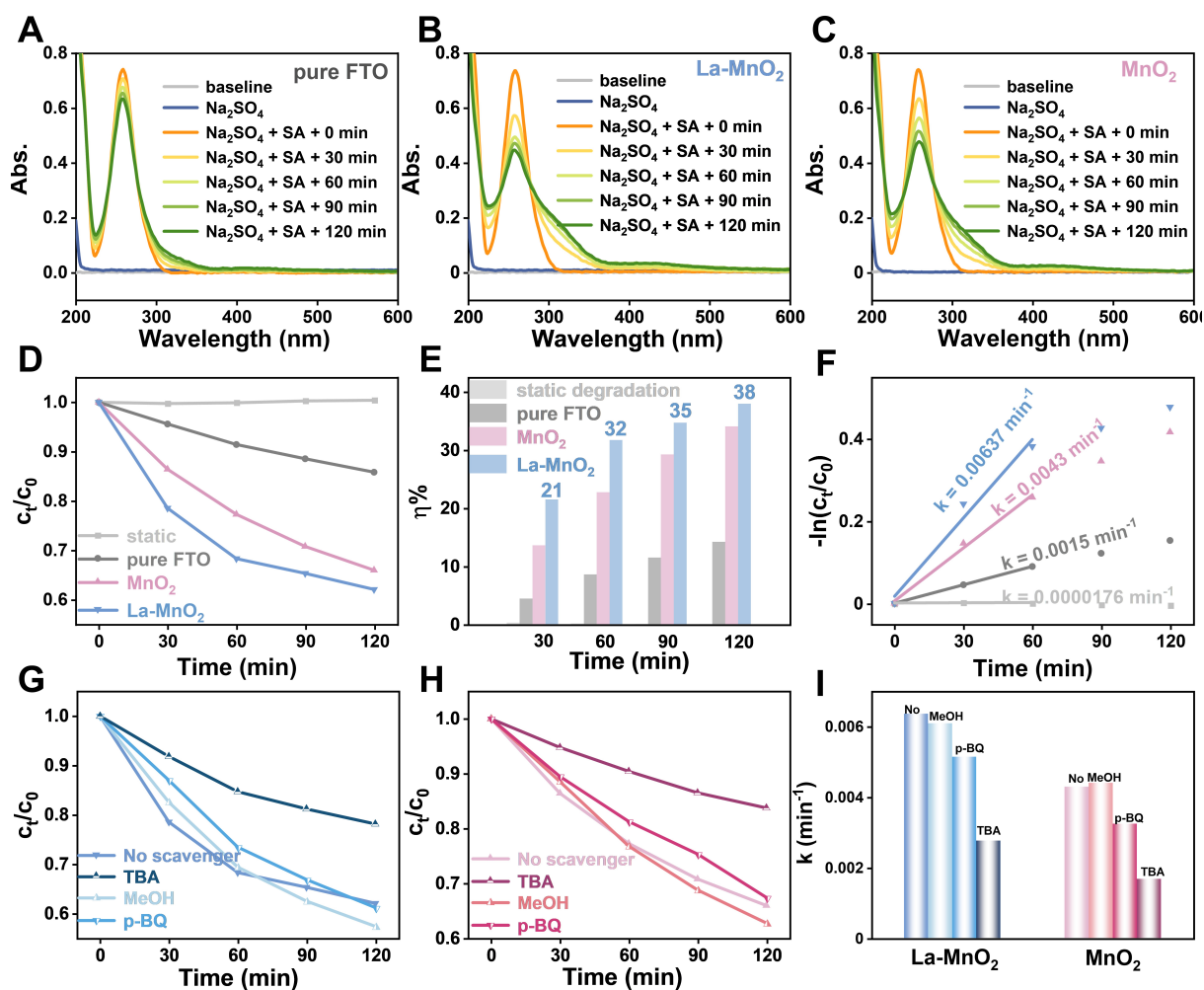


Figure 4. Electrochemical degradation of SA by the sea urchin-like La-doped MnO₂ and MnO₂ catalysts. The UV-vis absorption spectra of mixed solution of Na₂SO₄ and SA during electrolysis by (A) pure FTO, (B) La-doped MnO₂ and (C) MnO₂ catalysts at 2.1 V for different times; (D) The comparison of electrochemical degradation efficiency and static degradation efficiency of SA; (E) Degradation efficiency of SA by La-doped MnO₂ and MnO₂ catalysts at different times; (F) The electrocatalytic degradation kinetics of SA. The comparison of the electrochemical degradation efficiency of SA using (G) La-doped MnO₂ and (H) MnO₂ in the presence of TBA, MeOH, or p-BQ; (I) The comparison of the electrocatalytic degradation kinetics of SA with TBA, MeOH, and p-BQ. SAs: Sulfonamides; FTO: fluorine-doped tin oxide; UV-vis: ultraviolet-visible; TBA: *tert*-butanol; p-BQ: *p*-Benzoquinone; MeOH: methanol.

Scavenger quenching tests were conducted to evaluate the contribution of reactive oxygen species (ROS) to SA degradation^[52]. To quench the •OH, SO₄^{•-}, and O₂^{•-} radicals, 1 mL of 100 mM TBA, methanol (MeOH), or p-BQ was added, respectively [Supplementary Figure 19A-F]. When MeOH and p-BQ were introduced as scavengers for SO₄^{•-} and O₂^{•-}, respectively, the SA degradation efficiencies in both cases were comparable to those observed without the introduction of scavengers. Furthermore, the electrocatalytic degradation rate constants of La-doped MnO₂ and MnO₂ were 0.0061 and 0.0044 min⁻¹, respectively, in the presence of MeOH, and were 0.00515 and 0.00346 min⁻¹, respectively, in the presence of p-BQ [Supplementary Figure 19G and H]. These results rule out the possibility that ROS such as SO₄^{•-} and O₂^{•-} are produced during SA degradation. In contrast, after adding TBA, a scavenger of •OH radicals, the degradation efficiency of La-doped MnO₂ and MnO₂ significantly decreased as shown in Figure 4G and H. The electrocatalytic degradation rate constants of La-doped MnO₂ and MnO₂ were reduced to 0.00294 and 0.00168 min⁻¹, respectively [Figure 4I]. •OH served as the dominant active species in SA degradation by both La-doped MnO₂ and MnO₂, corresponding to the indirect oxidation pathway. Under conditions where La-doped

MnO₂ exhibits much higher SA degradation efficiency, its indirect oxidation contribution is 57%, compared to 60% for MnO₂ with lower degradation efficiency. The La-doped MnO₂ generates more highly reactive •OH radicals during degradation. The superior performance of La-doped MnO₂ is also attributed to its enhanced adsorption capacity toward SA and improved interfacial electron transfer efficiency, both of which facilitate the direct oxidation process. Based on the above analysis, the •OH is the ROS generated for SA degradation in this system. Thus, the active species were then characterized through EPR tests. The identification of •OH within the La-doped MnO₂ and MnO₂ systems was achieved by introducing DMPO, which successfully captured these radicals, resulting in a pronounced radical characteristic peak with a 1:2:2:1 ratio [Supplementary Figure 20A and B]^[53]. The SA degradation efficiency of the noble metal RuO₂ is also presented in Supplementary Figure 21. Its performance is inferior to that of inexpensive manganese-based materials. This is because RuO₂ oxidizes water into O₂ with exceptional efficiency, rapidly consuming species that would otherwise generate •OH or other. Reactions occurring on the surface of RuO₂ tend to favor the oxygen evolution pathway rather than the generation of highly oxidizing free radicals or the direct oxidation of organic molecules. In contrast, MnO₂ nanostructures with lower OER activity typically exhibit surfaces rich in hydroxyl groups and variable valence states. These characteristics may enhance the adsorption of SA molecules, increase local concentrations of substrates, and thereby improve reaction efficiency. Moreover, the SEM and XRD results for both materials after SA degradation are shown in Supplementary Figures 22 and 23. The sea urchin morphology and crystal structure are clearly preserved, proving their stability during the degradation process. Thus, the sea urchin-like La-doped MnO₂ electrocatalyst has potential applications in the field of electrocatalytic water oxidation and SA degradation.

CONCLUSIONS

In summary, the La-doped MnO₂ catalyst was successfully synthesized by a one-step hydrothermal method. It has sea urchin-like morphology with rich, open tunnel structures, providing abundant reaction sites and a large number of pathways for molecules to enhance catalytic efficiency. The introduction of La³⁺ not only enhances the electrical conductivity of the catalyst, and promotes charge transfer during the OER process, but also positively influences the structural stability of the catalyst. Therefore, the prepared sea urchin-like La-doped MnO₂ catalyst exhibits good electrocatalytic activity in OER, requiring an overpotential of 450 mV to reach a current density of 10 mA/cm². Additionally, this material shows improved degradation efficiency for sulfonamide antibiotics compared to pure MnO₂. La incorporation enhances SA adsorption and generates highly reactive •OH species, thereby optimizing both direct and indirect oxidation pathways, achieving up to 40% degradation within 2 h. Therefore, the sea urchin-like La-doped MnO₂ material holds promising potential for applications in electrochemical oxidation reactions.

DECLARATIONS

Authors' contributions

Supervised and designed the research: Xu, X.; Wang, W.; Zhang, W.; Cao, R.

Participated in catalyst synthesis and characterization: Liu, X.

Co-wrote the paper: Wu, X.; Chen, M.; Li, S.

All authors revised the manuscript and have given approval to the final version of the manuscript.

Availability of data and materials

All detailed materials and methods supporting the results of this study are included in the article and Supplementary Materials. Further inquiries can be directed to the corresponding author(s).

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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