Enhanced electron transfer using NiCo₂O₄@C hollow nanocages with an electronshuttle effect for efficient tetracycline degradation

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Abstract: Spinel oxides are recognized as promising Fenton-like catalysts for the degradation of antibiotics. However, the catalytic performance is restrained by the poor electron transfer rate (ETR). Herein, hollow NiCo₂O₄@C nanocages are rationally designed and prepared to accelerate ETR in peroxymonosulfate (PMS) activation for tetracycline (TC) degradation. Enhanced ETR of the NiCo₂O₄@C/PMS system is due to three aspects: (1) The hollow nanocage facilitates the diffusion and adsorption of TC, improving the ion transfer at a macroscopic level; (2) Electron reconfiguration in octahedral sites of NiCo₂O₄ increases the ratio of Co²⁺, resulting in highly efficient PMS activation; (3) In-situ generated carbon acts as "electron shuttles", improving the electrical conductivity of catalysts at a microscopic level. As a result, the NiCo₂O₄@C demonstrates rapid ETR, leading to a high-efficiency activation of PMS. The NiCo₂O₄@C/PMS system exhibits exceptional TC degradation efficiency and reusability. Non-radical pathway, including ¹O₂ and direct electron transfer, dominates

the system. This work offers a feasible strategy for enhancing electron transfer in the Fenton-like system.

Keywords: Spinel oxide; Electron shuttle; Electron transfer; Tetracycline; Peroxymonosulfate

1. Introduction

The excessive usage of antibiotics including tetracycline (TC) [1] and improper wastewater treatment lead to emerging pollution and threat to human health [2,3]. Thus, it is urgent to develop innovative approaches to tackle this issue. Heterogeneous Fenton-like catalysis based on peroxymonosulfate (PMS) is considered one of the most effective techniques [4,5] with high oxidation capacity and minimized catalyst loss for the removal of organic pollutants. However, the slow electron transfer rate (ETR) limits the efficiency of PMS activation and antibiotic removal [6,7]. Therefore, the key to improving the efficiency of a Fenton-like system relies on the higher ETR.

At a macroscopic level, ETR can be improved by improving the ion transfer process, including diffusion and adsorption of PMS and antibiotics. Various strategies have been exploited. For example, Liu et al. [8] assembled Co₃O₄ in a carbon nanotube to create a nanoconfined structure, which can enrich contaminants and mitigate the mass transfer resistance. At a microscopic level, the electrical conductivity of catalysts is crucial for improving ETR. For metal-based catalysts, especially, higher electronic conductivity means a faster redox cycle among multivalent metals [9], resulting in higher PMS activation efficiency. Based on these thoughts, novel Fenton-like catalysts could be rationally designed.

Spinel oxides, which consist of metal-oxygen octahedron and tetrahedron structures, have been widely applied in pollutant degradation [10,11]. Compared to monometallic

spinel oxides, bimetallic spinel oxides have higher intrinsic activity and stability owing to the synergy of different metals. Moreover, electron reconfiguration between different metals in spinel oxides has been widely observed in electrocatalysis [12,13]. Li et al. reported [14] that Ni dopants facilitate the formation of oxygen vacancies and enhance electron transfer from Ni²⁺ to Co³⁺. It is reasonable to assume that such electron interactions may also promote PMS activation. However, the poor electrical conductivity of spinel oxides hinders the ETR, leading to insufficient PMS activation and instability of catalysts. In this case, carbonaceous materials such as biomass carbon, graphite, and carbon nitride are good candidates for improving ETR and stabilizing spinel oxides [15–17]. Carbonaceous materials typically exhibit high electrical conductivity due to the abundance of free electrons that can move among delocalized π bonds formed by sp²-hybridized carbon atoms. These free electrons in carbon can make it serve as "electron shuttles", mediating electron transfer in the Fenton-like system [18]. Therefore, combining spinel oxides with carbon is a rational strategy for efficient Fenton-like degradation of antibiotics.

Conventional modification needs extra carbon sources as support, which may exhibit a weaker anchoring effect for spinel oxides. Metal-organic frameworks (MOFs) are considered ideal precursors for preparing metal oxides [19–21]. The metals coordinated to organic ligands are arranged uniformly, preventing the agglomeration of metal oxides during calcination. Besides, organic ligands can serve as carbon sources, generating carbon in situ. These in-situ generated carbon has a more robust interaction with metal oxides than external carbon support which leads to higher ETR. Moreover, MOFs usually possess a unique structure that can be exploited to create a nanoconfined structure for enrichment of antibiotics. In this work, we utilized zeolitic imidazolate framework-67 (ZIF-67) as a template to prepare NiCo₂O₄@C hollow nanocages with in-situ generated carbon to enhance the ETR of the Fenton-like system. The rapid ETR of NiCo₂O₄@C was attributed to the electron reconfiguration and electron-shuttle effect. Initially, we examined the unique nanocage structure and the composition of the catalysts to confirm the successful preparation of NiCo₂O₄@C. The chemical state of NiCo₂O₄@C was further elucidated. Next, the catalytic performance of NiCo₂O₄@C hollow nanocages was assessed by activating PMS to degrade TC. Later, the contribution of radical and non-radical pathways was examined using various techniques, including chemical probe methods and electrochemical measurements. With the assistance of theoretical calculations, the toxicity of degradation intermediates was reasonably assessed.

2. Experimental section

2.1. Chemicals

 $Co(NO_3)_2 \cdot 6H_2O$, tetracycline (TC, $C_{22}H_{24}N_2O_8$) and furfural alcohol (FFA, $C_5H_6O_2$) were purchased from Aladdin. Ni(NO₃)₂ · 6H₂O, 2-methylimidazole (2-MeIm, C₄H₆N₂), oxytetracycline (OTC, $C_{22}H_{24}O_9N_2$), chlortetracycline hydrochloride (CTC, $C_{22}H_{23}CIN_2O_8 \cdot HCl$), benzoic acid (BA, C₆H₅COOH) and nitrobenzene (NB, C₆H₅NO₂) were purchased from Macklin. Peroxymonosulfate (PMS, KHSO₅ · 0.5KHSO₄ · 0.5K₂SO₄) was purchased from Sigma Aldrich.

2.2. Catalyst preparation

In a typical synthesis of ZIF-67 [22], 2.9 g $Co(NO_3)_2 \cdot 6H_2O$ and 3.3 g 2-MeIm were separately dissolved in 100 mL of methanol. The former was added dropwise into the latter under stirring, and the final suspension was kept for 24 h. The purple suspension was then rinsed with methanol, centrifuged, and dried in a vacuum at 60 °C for 12 h. ZIF-derived NiCo₂O₄@C hollow nanocages were prepared through ion exchange and calcination procedures (Fig. 1). In detail, as-prepared ZIF-67 and Ni(NO₃)₂·6H₂O at a mass ratio of 1:2 were mixed in 100 mL of absolute ethanol and stirred vigorously for 30 min, in which Ni²⁺ was partially substituted for Co²⁺ in the ZIF-67 framework by ion exchange. The etched ZIF-67, denoted as NiCo-ZIF, was afterward collected by filtration. It was rinsed with ethanol and dried in a vacuum. Later, the powder was placed in a combustion boat and carbonized at 600 °C under an Ar atmosphere with a heating rate of 1 °C min⁻¹ for 2 h. The carbonized materials were then calcined again in the air at 350 °C with the same ramp rate for 2 h to obtain NiCo₂O₄@C. In addition, ZIF-derived Co₃O₄ and NiCo₂O₄ were prepared by directly calcinating ZIF-67 and NiCo-ZIF in the air at 350 °C, respectively.



Fig. 1. Synthesis routine of ZIF-derived Co₃O₄, NiCo₂O₄ and NiCo₂O₄@C.

2.3. Characterization

X-ray diffraction (XRD, Rigaku Ultima IV) was used to investigate the composite of catalysts. Scanning electron microscopy (SEM, ZEISS Sigma 500) and transmission electron microscope (TEM, FEI Talos-F200S) were used to observe the morphologies. An automatic surface area and porosity analyzer (BET, Micromeritics TriStar 3000) were employed to analyze the specific surface area. Raman spectrometer (Renishaw inVia) was employed with 532 nm HeNe lasers. Fourier transform infrared spectroscopy (FT-IR, Nicolet iS50) was employed. Electron paramagnetic resonance (EPR) was performed on Bruker A300-10-12. The surface element valence state of catalysts was examined with K-Alpha X-ray Photoelectron Spectrometer (XPS). Electrical conductivity was measured by a four-probe resistance ratio tester (FT-8100A). The leaching level of metals was examined by inductively coupled plasma-optical emission spectrometry (ICP-OES, PerkinElmer Optima 5300DV).

2.4. Electrochemical measurements

Electrochemical methods were performed on a CHI761E electrochemical workstation. The working electrode was prepared in this way: 5 mg of catalysts were dispersed in 5% Nafion ethanol solution under sonication for 10 min. 100 μ L of the suspension was added dropwise on an FTO glass and dried at room temperature. A conventional three-electrode system was adopted. Pt wire was used as the counter electrode and Ag/AgCl was employed as the reference electrode. The electrolyte was 1 M Na₂SO₄. Linear sweep voltammetry (LSV) was assessed at 5 mV s⁻¹. Chronoamperometry measurements were carried out under 0.4 V vs Ag/AgCl.

2.5. Experiment procedures

TC degradation experiments were performed at room temperature in 50 mL of 10 mg L^{-1} TC solution. 5 mg catalysts were dispersed in the solution with ultrasonication followed by magnetic stirring for 60 min to achieve adsorption-desorption equilibrium, then 0.8 mM PMS was injected to initiate the degradation reaction. 0.5 mL of samples were withdrawn at specific intervals within 20 min, which were immediately mixed with 0.5 mL of methanol to terminate the reaction.

The concentration of collected samples were determined by high-performance liquid chromatography (HPLC, Shimadzu LC-20A). A Shimadzu-C18 column (4.6 \times 250 mm, 5 μ m) was deployed to elute target pollutants. Detection conditions were listed in Table S1. Degradation intermediates were analyzed by liquid chromatography-mass spectroscopy (LC-MS, Thermos Scientific Ultimate 3000 HPLC). The mobile phase comprised 0.1% formic acid water solution and 0.1% acetic acid acetonitrile solution at 0.3 mL min⁻¹ under gradient elution mode.

2.6. Steady-state concentration of reactive oxygen species

The steady-state concentrations of reactive oxygen species (ROS) were measured and calculated with the chemical probe method reported in [23]. Specifically, BA, NB and FFA were used as chemical probes (0.1 mM for BA, 0.2 mM for NB and FFA) to capture different ROS. The change in probe concentrations was detected with HPLC (Table S1) and can be expressed in Eqs. 1-3:

$$-ln\frac{[\text{BA}]}{[\text{BA}]_0} = \left(k_{\text{BA},\text{OH}} \left[\cdot \text{ OH}\right]_{ss} + k_{\text{BA},\text{SO}_4^-} \left[\cdot \text{ SO}_4^-\right]_{ss}\right)t = k_{\text{obs},\text{BA}}t$$
(1)

$$-ln\frac{[\text{NB}]}{[\text{NB}]_{0}} = \left(k_{\text{NB,}\cdot\text{OH}} \left[\cdot \text{OH}\right]_{ss} + k_{\text{NB,}\cdot\text{SO}_{4}^{-}} \left[\cdot \text{SO}_{4}^{-}\right]_{ss}\right)t = k_{\text{obs,NB}}t$$
(2)
$$-ln\frac{[\text{FFA}]}{[\text{FFA}]_{0}} = \left(k_{\text{FFA,}\cdot\text{OH}} \left[\cdot \text{OH}\right]_{ss} + k_{\text{FFA,}\cdot\text{SO}_{4}^{-}} \left[\cdot \text{SO}_{4}^{-}\right]_{ss} + k_{\text{FFA,}^{-1}\text{O}_{2}} \left[\cdot \text{O}_{2}\right]_{ss}\right)t$$
$$= k_{\text{obs,NB}}t$$
(3)

In the equations, $k_{probe,ROS}$ represents the second-order reaction rate constants between probes and ROS (M⁻¹ s⁻¹, Table S2), while $k_{obs,probe}$ represent the observed pseudo-first-order reaction rate constants (s⁻¹). The steady-state concentration ([ROS]_{ss}) can be obtained by calculating Eqs. 1-3.

2.7. Computational methods

The Fukui function based on Density Function Theory (DFT) calculation was calculated to predict the active sites of possible attack sites on TC molecule[24], which is defined as follows Eq. 4:

$$f(r) = \left[\frac{\partial \mu}{\partial \nu(r)}\right]_{N} = \left[\frac{\partial \rho(\mathbf{r})}{\partial N}\right]_{\nu(r)}$$
(4)

where $\rho(r)$ is the electron density at a point r in space, N is the electron number in the current system, the constant term v in the partial derivative is external potential. In the condensed version of Fukui function, atomic population number is utilized to represent the amount of electron density distribution around an atom[25]. The condensed Fukui function (f) is calculated using Eqs. 5-7:

Nucleophilic attack:
$$f_A^+ = q_N^A - q_{N+1}^A$$
 (5)

Electrophilic attack:
$$f_{\rm A}^- = q_{\rm N-1}^{\rm A} - q_{\rm N}^{\rm A}$$
 (6)

Radical attack:
$$f_{A}^{0} = (q_{N-1}^{A} - q_{N+1}^{A})/2$$
 (7)

Similarly, condensed dual descriptor (Δf) can be written using Eq. 8:

$$\Delta f_{\rm A} = f_{\rm A}^{+} - f_{\rm A}^{-} = 2q_{\rm N}^{\rm A} - q_{\rm N+1}^{\rm A} - q_{\rm N-1}^{\rm A} \tag{8}$$

where q^A is the atomic charge of atom A at the corresponding state. In this study, Hirshfeld charge was employed to investigate reactive sites. Toxicity Estimation Software Tool (TEST) was utilized to investigate the toxicity of intermediates in the process of TC degradation.

3. Results and discussion

3.1 Catalyst characterization

After synthesis, SEM and TEM were used to investigate the morphology of asprepared Co₃O₄, NiCo₂O₄ and NiCo₂O₄@C. As shown in Fig. 2a, the original ZIF-67 exhibited a solid dodecahedron shape with a size of about 1 µm. After calcination, the size of Co₃O₄, NiCo₂O₄ and NiCo₂O₄@C decreased to varying extents (Figs. 2b-d), and TEM images (Figs. 2e-f) of NiCo₂O₄@C indicated the formation of a hollow nanocage structure. The smaller size and hollow structure increased the specific surface area of the NiCo₂O₄@C, exposing more reactive centers for TC degradation. Interestingly, the shrinkage behaviors differed among different catalysts. While Co₃O₄ and NiCo₂O₄@C inherited the dodecahedral shape of ZIF-67, NiCo₂O₄ transformed into a cube. It could be speculated that pre-carbonization helped maintain the dodecahedral framework, preventing excessive shrinkage and collapse during calcination. Another essential factor that could lead to structure collapse is the ramping rate. As shown in Fig. S1, when the calcination of NiCo₂O₄@C was performed at a heating rate of 2 °C min⁻¹ and 5 °C min⁻¹, more intense shrinkage resulted in severe deformation and collapse, potentially reducing effective reactive sites. These findings confirmed the successful construction of the unique hollow nanocage structure of NiCo₂O₄@C.

To preliminarily reveal the composition of NiCo₂O₄@C hollow nanocages, HRTEM (Fig. 2g) was used to identify the crystal phases. The lattice fringe spacing of 0.203 nm and 0.245 nm corresponded to (400) and (311) planes of NiCo₂O₄, respectively. SAED patterns (Fig. 2h) also showed lattice spacing of 0.245 nm, 0.203 nm and 0.144 nm, corresponding to the (311), (400) and (440) planes of NiCo₂O₄. Furthermore, elemental mapping in Fig. 2i suggested that Ni, Co, O and C were uniformly distributed on the nanocages, albeit the content of C was lower than the others. The results confirmed the intense combination of in-situ carbon and NiCo₂O₄.



Fig. 2. SEM images of (a) ZIF-67, (b) Co₃O₄, (c) NiCo₂O₄ and (d) NiCo₂O₄@C. (e-f) TEM images, (g) HRTEM, (h) SAED, and (i) elemental mapping of NiCo₂O₄@C hollow nanocages.

XRD was employed to confirm the composition of different catalysts further. As shown in Fig. 3a, the diffraction peaks of Co₃O₄ could be indexed to cubic Co₃O₄ (PDF #74-2120), and the peaks of NiCo₂O₄ and NiCo₂O₄@C matched cubic NiCo₂O₄ (PDF #02-1074), which coincides with the results of HRTEM. Notably, the signal peaks of NiCo₂O₄@C were broader and weaker than those of Co₃O₄ and NiCo₂O₄, suggesting a smaller crystal size in NiCo₂O₄@C. Raman spectroscopy was further employed to verify the existence of carbon. In Fig. 3b, the peaks at 1346 cm⁻¹ and 1600 cm⁻¹ were ascribed to the D band and G band of carbon, respectively, indicating the existence of both sp³ and sp² hybridized carbon. Raman spectra of three catalysts (Fig. S2) all showed peaks at 190, 474, 516 and 681 cm⁻¹, corresponding to the vibration mode of F^{1}_{2g} , E_{g} , F^{2}_{2g} and A_{1g} in spinel oxides, respectively. Besides, FT-IR (Fig. S3) also

confirmed the formation of spinel structure in all prepared catalysts. These results suggested the successful preparation of spinel oxides with in-situ generated carbon. Specific surface area was measured by the BET method (Fig. 3c and Table S3). The BET isotherms of all the catalysts were identified as type IV, indicative of a mesoporous structure. Moreover, the pore size distribution in Fig. 3d indicates that Ni etching and carbonization significantly reduced the mesopore diameter from approximately 22.2 nm to 10 nm. The BET specific surface area of Co₃O₄, NiCo₂O₄ and NiCo₂O₄@C were 53.89, 75.77 and 62.9 m² g⁻¹, respectively. Above all, NiCo₂O₄@C hollow nanocages were successfully fabricated.



Fig. 3. (a) XRD patterns, (b) Raman spectra of NiCo₂O₄@C, (c) N₂ adsorptiondesorption isotherms, and (d) pore diameter distribution of Co₃O₄, NiCo₂O₄ and NiCo₂O₄@C.

To unveil the inherent catalytic activity of NiCo₂O₄@C, the surface element valence state of the catalysts was investigated by XPS. Fig. 4a shows Co 2p spectra of Co₃O₄, NiCo₂O₄ and NiCo₂O₄@C. Peaks at 779.96 eV and 795.26 eV were attributed to Co³⁺ 2p_{3/2} and Co³⁺ 2p_{1/2}, and peaks at 781.36 eV and 797.09 eV belonged to Co²⁺ 2p_{3/2} and Co²⁺ 2p_{1/2}, respectively. The ratios of Co²⁺/Co³⁺ in Co₃O₄, NiCo₂O₄ and NiCo₂O₄@C were 0.87, 1.11 and 1.28, respectively. Namely, the content of Co²⁺ exceeded Co³⁺ in NiCo₂O₄ and NiCo₂O₄@C and was higher than that in Co₃O₄. Therefore, the increasing Co²⁺ species in NiCo₂O₄ and NiCo₂O₄@C could accelerate PMS activation and TC degradation efficiency. The electron transfer between Ni²⁺ and Co³⁺ accounted for the increase in Co²⁺ content. Since the redox potential of Ni³⁺/Ni²⁺ and Co³⁺/Co²⁺ were 3.7 V and 1.5 V [26,27], the reduced Co³⁺ by Ni²⁺ was thermodynamically available. Ni 2p spectra in Fig. 4b confirmed the apparent existence of Ni³⁺ (856.16 eV). Overwhelmingly, it was reported that Ni²⁺ tends to occupy the octahedral site in spinel oxide [28]. Thus, the edge-sharing interaction between Co³⁺Oet and Ni²⁺Oet was more reasonable (Fig. 4c).



Fig. 4. (a) Co 2p, (b) Ni 2p XPS spectra, and (c) representative illustration of electron configuration between octahedral Co and Ni. (d) Oxygen species distribution of Co₃O₄, NiCo₂O₄ and NiCo₂O₄@C.

Calculated by O 1s spectra (Fig. S4), the distribution of lattice oxygen (Lattice O), adsorbed hydroxyl group (Surface-OH), and adsorbed H₂O (Surface-H₂O) (Fig. 4d) clearly showed that the content of Surface-OH increased by more than 10% in NiCo₂O₄ and NiCo₂O₄@C compared to Co₃O₄, while that of lattice oxygen decreased by a similar amount. The increasing adsorbed hydroxyl groups on the surface decreased the activation barrier for water dissociation, and thus catalysts became more hydrophilic [29]. NiCo₂O₄ (18.6°) and NiCo₂O₄@C (11.2°) exhibited lower contact angles than Co₃O₄ (36.8°) in sessile drop analysis, indicating that the catalysts' hydrophilicity was enhanced (Fig. S5). The higher hydrophilicity benefited the adsorption of TC since it is hydrophilic [30], which consequently improved the efficiency of TC degradation.

3.2 Catalytic performance

TC adsorption experiments were firstly conducted to compare the adsorption capacity of different catalysts. As depicted in Fig. S6, NiCo₂O₄@C hollow nanocages could adsorb about 20% of TC within 60 min, 4 and 2 times higher than Co₃O₄ and NiCo₂O₄, respectively. These results confirmed the enhanced hydrophilicity had improved the adsorption of TC. On the other hand, despite NiCo₂O₄ having a larger surface area than NiCo₂O₄@C, the presence of carbon, which is electron-rich, enables higher adsorption capacity due to the strong electrostatic adsorption of TC.

The degradation performance of NiCo₂O₄@C was investigated using 10 mg L⁻¹ TC as the target pollutant. As shown in Fig. 5a, pure PMS degraded 18% of TC due to self-activation. In the Co₃O₄, NiCo₂O₄, and NiCo₂O₄@C systems, TC degradation efficiencies attained 85.2%, 93.0% and 98.1% within 20 min, respectively. The

corresponding kinetic rate constants were calculated to be 0.0905, 0.1249 and 0.1829 min⁻¹ (Fig. 5b). Although both NiCo₂O₄ and NiCo₂O₄@C systems removed more than 90% of TC, the kinetic constant of the latter was 1.46 times faster. This can be attributed to the extraordinary TC adsorption capabilities of NiCo₂O₄@C, which facilitated the removal of pollutants by shortening the distance between TC and ROS. Metal leaching in the NiCo₂O₄ and NiCo₂O₄@C systems was detected using ICP-OES to evaluate catalyst stability. As shown in Fig. 5c, Co and Ni leaching were significantly inhibited in the NiCo₂O₄@C systems. In particular, the leaching level of Ni decreased from 20.09 mg L⁻¹ to 4.18 mg L⁻¹. These results revealed that carbon in NiCo₂O₄@C could stabilize the spinel oxides. Additionally, XRD and XPS spectra of NiCo₂O₄@C before and after reactions (Figs. S7-S8) showed minor changes in crystal phases or in chemical states of Ni and Co, implying excellent stability. An equal amount of leaching Ni and Co ions in the NiCo₂O₄@C system were added directly to activate PMS for TC degradation. As shown in Fig. 5a, negligible catalytic performance could be observed in the Ni²⁺ and Co²⁺ system compared to the PMS alone system, excluding the impact of homogenous activation of PMS by Co and Ni ions. The capability of NiCo₂O₄@C was further evaluated for the degradation of other tetracycline antibiotics, including chlortetracycline (CTC) and oxytetracycline (OTC). Fig. 5d exhibited 74.8% and 83.5% removal efficiencies for CTC and OTC, respectively, demonstrating satisfactory capability for degrading other tetracycline antibiotics. Fig. 5e and Table S4 compared the TC degradation performance of the optimal NiCo₂O₄@C/PMS system in this study with previously reported catalyst/PMS systems [31-38] based on kinetic rate, catalyst dosage, and PMS/TC ratio. The results above demonstrated that the NiCo2O4@C hollow nanocages possess excellent catalytic activity and stability.



Fig. 5. (a) TC removal in different reaction systems and (b) corresponding kinetic constant. (c) Co and Ni leaching concentration in the NiCo₂O₄/PMS and NiCo₂O₄@C/PMS systems. (d) TC, OTC, and CTC removal efficiencies in the NiCo₂O₄@C/PMS systems. (e) A comparison of TC degradation performance of the NiCo₂O₄@C/PMS system and other catalyst/PMS systems [31–38]. Experimental conditions: [catalyst] = 0.1 g L⁻¹, [TC] = 10 mg L⁻¹, [PMS] = 0.8 mM, initial pH = 7.0, T = 298 K.

Commonly existing anions and cations in the water matrix, as well as pH, can impact the degradation of organic pollutants. Therefore, we conducted various environmental impact factor tests to evaluate the anti-interference capability of the NiCo₂O₄@C/PMS system. In Fig. S9a, Na⁺, K⁺, Mg²⁺ and Ca²⁺ harmed TC degradation, while the inhibition effect was more evident with monovalent cations. Fig. S9b displayed the influence of anions (Cl⁻, NO₃⁻, SO₄²⁻ and CO₃²⁻). While Cl⁻, NO₃⁻, and SO₄² limited the rate constant of TC degradation, CO₃²⁻ enhanced the performance of TC degradation, resulting in the removal of more than 90% of TC within 5 min. It has been reported that dissolved carbonates can enhance catalytic activity by producing \cdot CO₃⁻ radicals and serving as electron mediators for the redox cycle of metals [39]. Moreover, the effect of pH on TC degradation was also studied. Fig. S9c suggested that the optimal pH was 7, while about 80% of TC could still be removed under acidic or basic conditions. These results confirmed the exceptional ecological resistance of the NiCo₂O₄@C/PMS system.



Fig. 6. (a) Schematic illustration of the simulated continuous flow system. (b) TC degradation performance and metal leaching detection in the continuous flow system. Experimental conditions: Catalyst loading = 50 mg, $[TC] = 10 \text{ mg } \text{L}^{-1}$, [PMS] = 0.8 mM, flow rate = 5 mL min⁻¹, initial pH = 7.0, T = 298 K.

To evaluate the reusability and potential application in continuous operating conditions, a constant flow system was built to monitor the catalytic performance of NiCo₂O₄@C hollow nanocages (Fig. 6a). 50 mg catalysts were loaded on the PTFE membrane by vacuum filtration, and the TC degradation process was run for 300 min. As shown in Fig. 6b, TC removal efficiency sustained more than 90% during continuous operation. Moreover, the leaching of Ni and Co decreased while maintaining excellent performance, suggesting good reusability and less metal leaching pollution to the environment. In general, the NiCo₂O₄@C/PMS system exhibited superior catalytic performance in TC degradation.

3.3 Mechanisms

3.3.1 Determination of ROS

Scavenging experiments were first conducted to quantitatively determine the contribution of different ROS for TC removal in the NiCo₂O₄@C/PMS system. The commonly seen ROS in PMS activation included \cdot OH, \cdot SO₄⁻, \cdot O₂⁻ and $^{1}O_{2}$. Therefore, methanol (MeOH), tert-butanol (TBA), furfuryl alcohol (FFA) and p-benzoquinone (p-BQ) were used to scavenge various ROS and identify the dominant species. As shown in Fig. 7a, p-BQ quenching test revealed the negligible effect of \cdot O₂⁻, while the FFA quenching test suggested the vital participation of $^{1}O_{2}$. MeOH and TBA only showed slight inhibition of TC degradation, indicating the minor role of \cdot OH and \cdot SO₄⁻ in the reaction system. EPR was utilized to detect the existence of ROS directly with DMPO and TEMP as spin-trapping reagents (Figs. 7b-d). Septet signals of DMPOX were seen in the NiCo₂O₄@C/PMS system, which may be due to the direct oxidation of DMPO by PMS [40]. No signals of DMPO- \cdot O₂⁻ were detected, and robust triple peaks of TEMP- $^{1}O_{2}$ were detected. These results suggested that $^{1}O_{2}$ was the main ROS.



Fig. 7. (a) Quenching experiments of TC degradation and (b) corresponding kinetic rates in the NiCo₂O₄@C/PMS system. (c) Calculated contributions of different ROS in

the NiCo₂O₄@C/PMS system. EPR spectra captured by (d-e) DMPO and (f) TEMP. Experimental conditions: [MeOH] = [TBA] = 100 mM, [FFA] = [p-BQ] = 10 mM, [catalyst] = 0.1 g L⁻¹, [TC] = 10 mg L⁻¹, [PMS] = 0.8 mM, initial pH = 7.0, T = 298 K.

Chemical probes, including benzoic acid (BA), nitrobenzene (NB) and FFA, were employed to further quantify the steady-state concentration of different ROS (Fig. 8). Calculation results showed that the steady-state concentration of ${}^{1}O_{2}$ (2.13 × 10⁻¹¹ M) was significantly larger than that of \cdot OH (9.40 × 10⁻¹⁴ M) and \cdot SO₄⁻ (1.22 × 10⁻¹⁴ M), which was consistent with the quenching experiments. However, the addition of FFA only inhibited 22% of TC removal efficiency, indicating the essential participation of direct electron transfer reaction pathway.



Fig. 8. (a) The degradation of chemical probes in the NiCo₂O₄@C/PMS system and (b) corresponding pseudo-first-order rate constant. (c) Steady-state concentration of \cdot OH, \cdot SO₄⁻, and ¹O₂.

3.3.2. Electron-shuttle effect of in-situ carbon

The electrical conductivity of catalysts was measured via the four-point probe method. As shown in Fig. 9a, the conductivity of Co₃O₄, NiCo₂O₄ and NiCo₂O₄@C were determined to be 16.79, 30.99, and 201.82 S m⁻¹. Compared with Co₃O₄, the substitution of Ni for Co in NiCo₂O₄ facilitated the electron transfer and exhibited a synergistic effect between Ni and Co for PMS activation. Moreover, a surge of conductivity appeared in the NiCo₂O₄@C due to the existence of in-situ carbon. LSV curves further confirmed the apparent increase of the ETR in NiCo₂O₄@C. In-situ carbon with abundant free electrons serves as the "electron shuttles", mediating the electron transfer between NiCo2O4 and PMS as well as the redox cycle between Co and Ni, which enhanced the activity and stability of NiCo2O4@C hollow nanocages. Moreover, chronoamperometry measurements were conducted to confirm the direct electron transfer reaction pathway (Fig. 9b). Compared to the other two catalysts, the injection of PMS and TC caused distinct current jumps for the NiCo2O4@C, demonstrating efficient electron transfer between NiCo₂O₄@C and PMS. The result also confirmed the essential contribution of direct electron transfer pathway in the NiCo₂O₄@C/PMS system (Fig. 9c) [41,42]. The above discussion collectively demonstrated that the notable activity of the NiCo₂O₄@C/PMS system was due to the enhanced ETR, which resulted from the combined effects of the nanocage confinement, Ni-Co synergy, and the electron-shuttle effect.



Fig. 9. (a) Conductivity and LSV curves, and (b) i-t curves of Co₃O₄, NiCo₂O₄ and NiCo₂O₄@C under 0.4 V vs Ag/AgCl with 1 M Na₂SO₄ as the electrolyte. (c) Proposed degradation mechanism.

3.4 Degradation intermediates and toxicity

To identify possible degradation intermediates, DFT calculations were utilized to predicted attack sites on TC (Table S5). Fukui index predicted the radical and non-radical attack sites on TC. Fig. 10a suggested that the most positive part of f^0 function was mainly on C3, O22 and O23, related to the major carbonyl group, which suggests radical attack tended to happen on these sites. The most positive part of f function (Fig. 10b) was mainly on C16, C20, O22, O26 and O27, related to the hydroxyl group and amino group on TC, indicating electrophilic attack may happen on these sites. Possible attack sites on TC were demonstrated in Fig. 10c. Noticeably, the number of f function values higher than 0.04 was more than that of f^0 and f^+ (Fig. 10d), suggesting that electrophilic attack was more likely to happen on TC.



Fig. 10. Visualization of (a) f^0 and (b) f Fukui functions of TC. (c) Attack sites on TC molecule. (d) f^0 , f^+ and f Fukui function value distribution.

TC and its degradation intermediates were analyzed using LC-MS (Fig. S10), and the possible degradation pathway was proposed in Fig. 11a. With the dehydration and hydroxylation processes, TC (m/z = 445) could be transformed into P2 (m/z = 427) and P5 (m/z = 459). Through serial ring opening procedures, P2 was further degraded into P3 (m/z = 346) and P4 (m/z = 247). Due to removing the N-methyl substituent, P5 transformed into P6 (m/z = 374), which was further converted to P7 (m/z = 337) through dehydration and the ring opening reactions. Multiple hydrogenation and N-dealkylation reaction converted P5 to P8 (m/z = 365) and P10 (m/z = 362). Continuous ring opening reactions formed P9 (m/z = 337) and P11 (m/z = 274). Toxicity of TC and intermediates was predicted with TEST. As shown in Figs. 11b-c and Table S6, LC₅₀ (Lethal Concentration, 50%) of TC to fathead minnow and daphnia magna were 0.90 and 8.73 mg L⁻¹, respectively, identified as the toxicant. After the degradation process, although the toxicity of P2, P3, and P11 was higher than that of the original TC molecules, LC₅₀ of most intermediates increased significantly, suggesting the general abatement of toxicity. These results confirm that the degradation process could reduce biological toxicity of antibiotics.



Fig. 11. (a) Possible degradation pathways. Acute toxicity LC₅₀ of (b) fathead minnow and (c) daphnia magna.

4. Conclusions

In this work, we have enhanced the electron transfer rate of the Fenton-like system via preparing ZIF-derived NiCo₂O₄@C hollow nanocages with in-situ generated carbon. The optimal NiCo₂O₄@C/PMS system exhibited a notable removal efficiency of 98.1% for 10 mg L⁻¹ TC within 20 min. Detailed characterization and experiments have demonstrated that the hollow nanocage structure promoted TC adsorption through confinement effect. The synergy between Ni and Co increased the ratio of Co^{2+} , resulting in more efficient PMS activation. In-situ carbon with abundant free electrons largely increased the electrical conductivity of NiCo₂O₄@C to 201.82 S m⁻¹, serving as electron shuttles to facilitate PMS activation and stabilize NiCo₂O₄@C/PMS system.

DFT calculations and toxicity evaluation indicated that the degradation intermediates exhibited reduced toxicity, effectively mitigating the environmental impact caused by antibiotics. Overall, the rationally designed hollow spinel oxides provide a distinctive approach to enhancing the efficiency of Fenton-like systems for antibiotic removal.

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