

Article

Laser-Induced Nitrogen-Doped Graphene Composite Iron–Cobalt Hydroxide for Methylene Blue Degradation via Electrocatalytic Activation of Peroxymonosulfate

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Abstract: With the acceleration of industrialization, the removal of refractory organic dyes from water and how to promote its practical application remains a challenge. Herein, we synthesized an FeCo-LDH/LI-NDG composite electrode material by a simple laser-induced technique on polyimide films, which could electrocatalytically activate peroxymonosulfate (PMS) to completely degrade MB in about 6 min. The reaction rate constant (k_{obs}) was 0.461 min^{-1} . It was faster than most of the currently reported electrocatalysts. The reaction system demonstrated good interference resistance and catalytic effectiveness in the pH range of 3 to 9. According to the chemical quenching and electron paramagnetic resonance (EPR) experiments, the non-radical pathway of $^1\text{O}_2$ and the radical pathways of $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ were involved in the reaction synergistically, with $^1\text{O}_2$ playing the dominant role. $^1\text{O}_2$ was produced through the dual pathway of PMS electron loss at the anode and $\text{O}_2^{\cdot-}$ intermediate transformation at the cathode. The two activation methods of electro-activation and catalytic activation of PMS had synergistic effects to achieve high efficiency in the whole process of production, reaction and recovery, providing new ideas to advance practical applications.

Keywords: laser induced; peroxymonosulfate; methylene blue; non-radical; dual pathway



Citation: Chen, L.; Liao, J.; Li, C.; Xu, Y.; Ge, C.; Xu, W.; He, X.; Liu, W. Laser-Induced Nitrogen-Doped Graphene Composite Iron–Cobalt Hydroxide for Methylene Blue Degradation via Electrocatalytic Activation of Peroxymonosulfate. *Catalysts* **2023**, *13*, 922. <https://doi.org/10.3390/catal13060922>

Academic Editor: Roberto Fiorenza

Received: 27 April 2023

Revised: 16 May 2023

Accepted: 21 May 2023

Published: 23 May 2023



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1. Introduction

Advanced oxidation processes (AOPs) are extensively applied to treat refractory organic pollutants in wastewater due to their high efficiency [1,2]. Electro-Fenton and persulfate-based Fenton-like methods are of interest. The electro-Fenton method has a narrow pH range, usually only for acidic conditions (pH = 2.8–3.5) [3–5], that brings high requirements for equipment, such as the need for corrosion resistance. In contrast, persulfate-based advanced oxidation processes (PS-AOPs) not only possess sulfate radicals with a longer lifetime than hydroxyl radicals but also have a broader pH applicability range [6]. The persulfate (PS) itself is weakly oxidized and needs to be activated to produce reactive oxygen species (ROS), and most of the catalysts used in the system suffer from difficult recovery and high losses. Based on this, the combination of PS-AOPs with electro-activation has the advantage of the synergistic degradation of pollutants.

In recent studies, Zhang et al. prepared a novel iron metal–organic framework (Fe-MOF) heterogeneous catalyst dispersed in reaction solution. Integrating electrochemical (EC) with PS approaches, it was used to degrade the electroplated metal complex Cu-EDTA [7]. Qi et al. prepared an in situ sulfur-doped activated carbon particle (ACS) as a heterogeneous catalyst and used the combination of electrocatalytic activation of PS

to achieve 100% phenol degradation [8]. In these studies, the heterogeneous catalysts added to the solution co-activated PS under the action of an electric field. However, the heterogeneous catalysts still have to be recycled and may incur a loss of recovery mass. Therefore, loading catalysts on electrodes to form composite electrode materials is beneficial for solving this problem and promoting practical applications.

Graphene is a sp^2 hybrid carbon with excellent electrical conductivity and charge mobility [9] and is widely used in capacitors, solar cells and electrochemical sensors [10–12]. Graphene is a promising and highly regarded conductive material. However, its traditional preparation methods such as chemical vapor deposition and chemical reduction are complicated and the preparation conditions are harsh, which limits its practical applications. In 2014, Lin et al. discovered that graphene can be fabricated on polyimide films using a CO_2 infrared laser [13]. Compared with graphene synthesized by conventional methods, graphene prepared by laser-induced techniques can achieve electrical conductivity of $5\text{--}25\text{ S}\cdot\text{cm}^{-1}$ without high temperature and complex preparation processes [14]. Therefore, the simple laser-induced method can be chosen to produce graphene (LI-NDG) as an electrode substrate material, which is beneficial for further applications. Most importantly, the selection of the reactive substances loaded on the electrode substrate is very critical. The transition metals Fe and Co are promising catalytic materials for PS activation [15], and the redox cycle between Fe and Co can improve the catalytic activity [16,17]. Gong et al. prepared FeCo-layered double hydroxides (FeCo-LDH) in situ on nickel foam (NF) that had good oxygen evolution reaction (OER) and urea oxidation reaction (UOR) capabilities, durability and fast electron transfer [18]. Jiang et al. fabricated FeCo LDH@NiCoP/NF nanowire arrays with outstanding performance. The prepared FeCo LDH@NiCoP/NF electrocatalysts exhibited excellent OER activity [19]. Shao et al. obtained by an electrostatic assembly process a hybrid CoAl-LDHs nanosheets/ $Ti_3C_2T_x$ MXenes photocatalyst that exhibited good visible light photocatalytic activity [20]. The bimetallic hydroxides showed high catalytic activity in electrocatalysis and photocatalysis [21]. In contrast, the bimetallic hydroxide composite graphene electrode materials with high activity produced based on laser-induced technology are less studied for application in PS-AOPs and their synergistic reaction mechanism is not clear.

In this study, we prepared laser-induced nitrogen-doped graphene composite FeCo layered double hydroxide (FeCo-LDH/LI-NDG) electrode materials by a simple and efficient laser-induced technique [13] and electrodeposition method [22] that were used as cathodes and anodes for the degradation of methylene blue (MB) by electro-activated synergistic catalytic activation of peroxydisulfate (PDS). The main work was as follows: (1) FeCo-LDH/LI-NDG was characterized to confirm its morphology, phase and chemical state; (2) The capability of FeCo-LDH/LI-NDG for electrocatalytically activating PDS to degrade MB was studied; (3) The interference resistance, recyclability and stability of FeCo-LDH/LI-NDG were explored; (4) The reactive oxygen species in the FeCo-LDH/LI-NDG/EC/PDS system and reaction mechanism were confirmed; (5) The degradation intermediates of MB were identified and evaluated for biological toxicity.

2. Results and Discussion

2.1. Characterizations

To confirm the surface appearance of LI-NDG and FeCo-LDH/LI-NDG, scanning electron microscopy (SEM) was performed. The SEM image of LI-NDG presents a 3D porous layered graphene material in Figure 1a, which was produced by a laser-induced technique with irregular five-membered rings and seven-membered rings. The prepared graphene was in a high-energy state due to the transient heating and cooling of the laser and had more abundant defective sites relative to the conventional graphene, providing more sites for the next material modification [14]. The abundant porous structure of graphene also provided a larger specific surface area to support the composites and supplied the possibility to fully contact the contaminant medium to accelerate the reaction. The SEM images of FeCo-LDH/LI-NDG are shown in Figure 1b,c. The thin lamellar structure of

FeCo-LDH grew on LI-NDG and dispersed on the graphene surface, thus obtaining a larger exposure space and facilitating the acquisition of more active sites for PMS activation. The irregular shape of FeCo-LDH flakes was due to the addition of Fe, which led to a decrease in the crystallinity of LDH, and the presence of iron inhibits the crystallization of LDH [23].

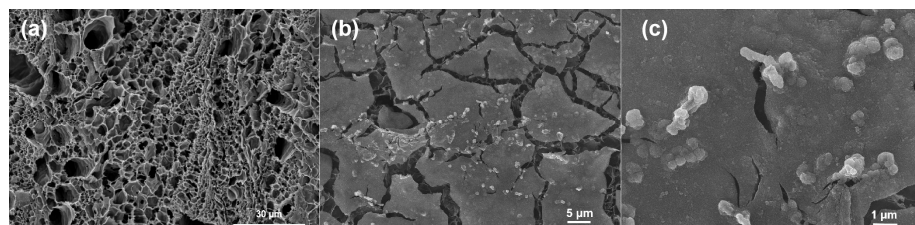


Figure 1. (a) SEM images of LI-NDG. (b,c) SEM images of FeCo-LDH/LI-NDG.

It can be observed from the XRD patterns of LI-NDG (Figure 2a) that the distinctive diffraction peaks were located at 26° and 44° , respectively, and represented the (002) and (101) crystal facets of graphene. In addition, the characteristic diffraction peaks at 23.6° , 34.1° , 38.7° , 59.1° and 60.7° , corresponding to the (006), (012), (015), (110) and (113) crystal facets of FeCo-LDH were found from the XRD patterns of FeCo-LDH/LI-NDG (JCPDS NO. 50-0235) [18,24]. This also confirmed the existence of FeCo-LDH, but the presence of iron inhibited the crystallinity of the material and thus the characteristic diffraction peaks are not significant, which is in agreement with the SEM analysis.

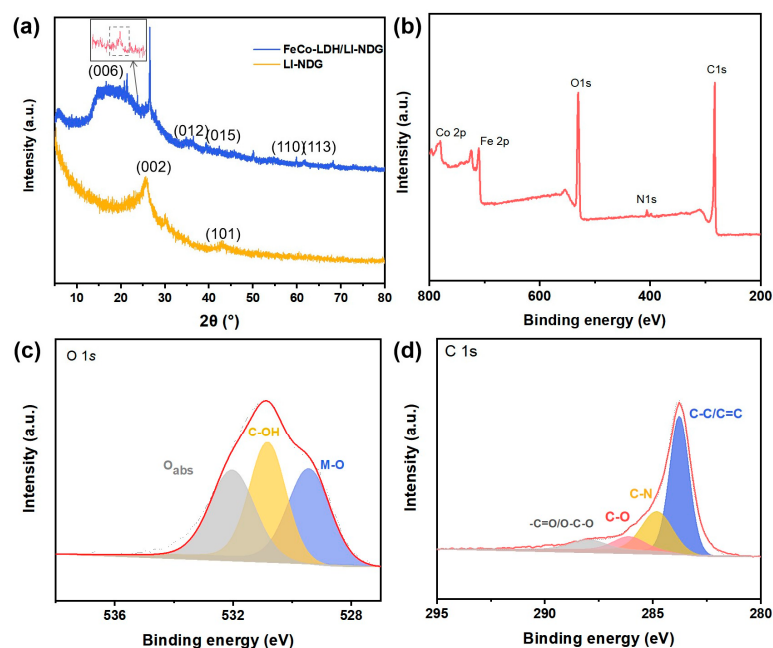


Figure 2. (a) XRD patterns of LI-NDG and FeCo-LDH/LI-NDG. (b) XPS survey of FeCo-LDH/LI-NDG. (c) O 1s and (d) C 1s XPS spectra of FeCo-LDH/LI-NDG.

XPS tests were conducted to confirm the surface elemental composition and elemental valence of FeCo-LDH/LI-NDG. The results of XPS tests (Figure 2b–d) show that C, N, O, Fe and Co elements were present in FeCo-LDH/LI-NDG. According to the XPS survey (Figure 2b), the proportions of C, N, O, Fe and Co elements were 60.84 at%, 2.96 at%, 27.66 at%, 5.95 at% and 2.66 at%, respectively. Apparently, oxygen elements accounted for a large proportion without carbon elements. It can also prove the formation of metal hydroxides and introduce a high amount of oxygen-containing functional groups to the composite. Moreover, the O 1s spectra may be fitted to three peaks at 529.43 eV, 530.82 eV and 532.02 eV, standing for metal–oxygen bonds (M–O), hydroxide (–OH) and surface-

adsorbed oxygen (O_{abs}) (Figure 2c) [25]. The presence of M-O helped to confirm the existence of FeCo-LDH. According to Figure 2d, the C 1s spectrum may be separated into four peaks that correspond to C-C/C=C, C-N, C-O and -C=O/O-C-O [26]. The N 1s spectrum could be divided into three peaks corresponding to pyridine nitrogen, pyrrole nitrogen and graphite nitrogen (Figure S1a). The Fe 2p spectra could be divided to six peaks at 710.21 eV, 723.41 eV, 718.11 eV, 712.62 eV, 726.21 eV and 732.11 eV; the first three peaks corresponded to Fe^{2+} and the last three peaks corresponded to Fe^{3+} (Figure S1b) [27]. The Co 2p spectra of FeCo-LDH/LI-NDG showed six peaks at 780.19 eV, 796.09 eV, 786.43 eV, 782.15 eV, 797.90 eV and 802.53 eV (Figure S1c); the peaks at 780.19 eV, 796.09 eV and 786.43 eV represented Co^{3+} , whereas the peaks at 782.15 eV, 797.90 eV and 802.53 eV represented Co^{2+} [28]. This demonstrated the presence of Co^{2+} and Co^{3+} in FeCo-LDH/LI-NDG. Therefore, the characterization results mutually confirmed the successful synthesis of FeCo-LDH/LI-NDG.

2.2. Catalytic Activity

2.2.1. Electrochemical Performance

To analyze the electrochemical activity and the flow of charge at the contact of FeCo-LDH/LI-NDG, cyclic voltammetry (CV) tests were conducted in Na_2SO_4 and Na_2SO_4 /PMS solutions (Figure 3a and Figure S2). From Figure 3a, the oxidation and reduction currents were observed in Na_2SO_4 solution on FeCo-LDH/LI-NDG. At scan rates of 50 mV/s and 100 mV/s, the prominent oxidation peaks were clearly observed and the peak potentials were around 0 V, whereas the reduction peaks had peak potentials around 0.2 V. Notably, the CV tests were performed after the addition of PMS (Figure 3b), and significant reduction peaks were seen at different scanning speeds with peak potentials around 0.05 V. The reduction ability was correlated with the electrochemical activity and the electron transport capacity of the active site during the reduction reaction [8]. This implied that PMS was readily reduced on FeCo-LDH/LI-NDG and activated during the electrochemical process, indicating the good electrochemical activity and ability of FeCo-LDH/LI-NDG to reduce PMS [29].

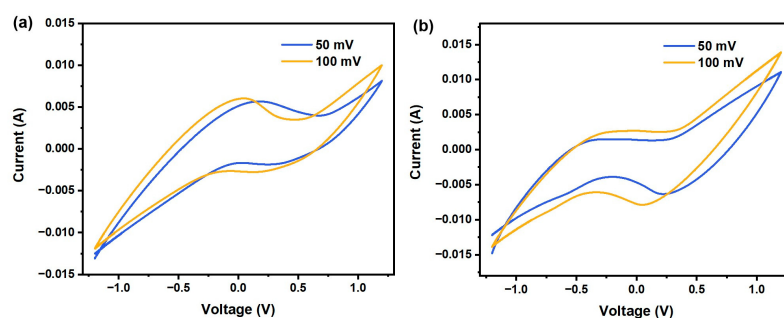


Figure 3. (a) CV curves of FeCo-LDH/LI-NDG; (b) CV curves of FeCo-LDH/LI-NDG + PMS.

2.2.2. Catalytic Performance

Firstly, the adsorption–desorption equilibrium reaction was performed 15 min before all the degradation reactions. The adsorption capacity of these electrode materials was negligibly small. Secondly, the catalytic degradation capacities of the different catalytic systems were compared under the optimal reaction conditions as shown in Figure 4a. It can be observed that with PMS injection only, there was little change in its catalytic systems within 10 min, which also meant that the catalytic reactions occurring in the system were very weak. Similarly, when LI-NDG was used as the electrode with the applied voltage and the addition of PMS, the degradation efficiency within 10 min was still negligible. However, after the electrode was compounded with FeCo-LDH, the reaction system's degradation efficiency with the addition of PMS was enhanced, with a 55.5% degradation rate at 6 min and an 82.7% degradation rate at 10 min. The reaction rate constant k_{obs} was 0.168 min^{-1} (Figure 4b). The FeCo-LDH compounded on the electrode surface had a high activation

ability for PMS. More importantly, the catalytic degradation performance of the FeCo-LDH/LI-NDG/EC/PMS system was greatly improved after the introduction of the electric activation method. The degradation efficiency was 62.5% higher than that of the FeCo-LDH/LI-NDG/PMS system within 2 min, and the contaminant was completely degraded in 10 min. The reaction rate constant k_{obs} was more than two times faster. Meanwhile, the capacity of FeCo-LDH/LI-NDG was contrasted with that of similar electrocatalysts reported recently. The degradation efficiency was greatly improved compared with the electrocatalytic system without powder catalyst, as shown in Table S1. Compared with the electrocatalytic system containing powder catalyst, the degradation efficiency and reaction rate were also improved. Moreover, the catalyst recovery was more convenient, and the loss rate was low. This demonstrated the superior catalytic activity of the FeCo-LDH/LI-NDG/EC/PMS system as well. The advantages of the two activation methods over the single activation method of PMS were complementary to each other. We investigated the mineralization degree of the FeCo-LDH/LI-NDG/EC/PMS system by TOC experiments. MB was completely degraded into small molecules within 10 min and the mineralization was only 10.4%. However, the mineralization of MB could reach 91% after 5 h of reaction.

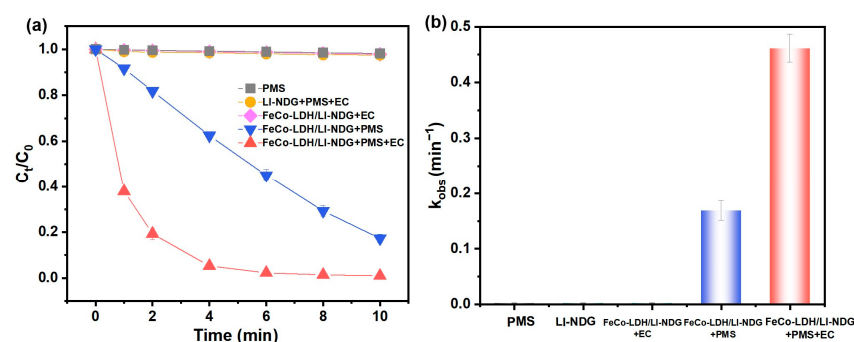


Figure 4. (a) Comparison of degradation efficiency and (b) reaction rate constant of different catalytic systems. Conditions: Applied voltage = 2 V; Electrode area = $2 \times 2 \text{ cm}^2$; [PMS] = 0.5 mM; [MB] = 20 mg/L.

2.2.3. The Effect of Reaction Parameters

The exploration of the preparation parameters of the FeCo-LDH/LI-NDG composite electrode materials was the basis for confirming their optimal conditions in practical applications. Firstly, the size of electrode area is an important influencing factor. FeCo-LDH/LI-NDG composites with different electrode areas were used for degradation kinetics testing (Figure 5a). The electrode areas were set at $1 \times 2 \text{ cm}^2$, $2 \times 2 \text{ cm}^2$ and $2 \times 3 \text{ cm}^2$. A total of 84.3% of MB was degraded in 6 min and 96.4% in 10 min using the $1 \times 2 \text{ cm}^2$ electrode. The $2 \times 2 \text{ cm}^2$ and $2 \times 3 \text{ cm}^2$ composite electrodes were able to achieve 100% degradation efficiency within 6 min. The degradation process of MB was in accordance with the pseudo-first-order kinetic model. Comparing the reaction rate constants k_{obs} of the above, we can find that the $2 \times 3 \text{ cm}^2$ electrode possessed a larger rate constant of 0.576 min^{-1} . However, combined with the calculation of the unit reaction rate constant, we found that the unit reaction rate gradually declined as the electrode area increased. For this reason, it can be considered that $2 \times 2 \text{ cm}^2$ electrode area was a more suitable preparation parameter. The electrodeposition time also affected the final degradation efficiency. The longer the electrodeposition time, the more the loading of FeCo-LDH on the electrode surface will be. Thus, the appropriate loading was a factor to be considered. From Figure 5b, the pure LI-NDG electrode with the deposition time of 0 s was almost inactive and could not activate PMS to degrade MB. The composite electrode loaded with FeCo-LDH had a significantly higher degradation efficiency. Even with the electrodeposition time of 400 s, 88% degradation efficiency was achieved in 10 min. With the increase in deposition time, the degradation efficiency reached 100% within 6 min. Combined with k_{obs} , the longer the deposition time, the larger the reaction rate constant. These values were 0.191 min^{-1} , 0.461 min^{-1} and 1.296 min^{-1} for deposition times of 400 s, 900 s and 1200 s, respectively.

However, the increase in deposition time may bring about an increase in cost in practical application and also the risk of metal leaching. In summary, the electrode area of $2 \times 2 \text{ cm}^2$ and the electrodeposition time of 900 s were chosen as the optimal preparation parameters.

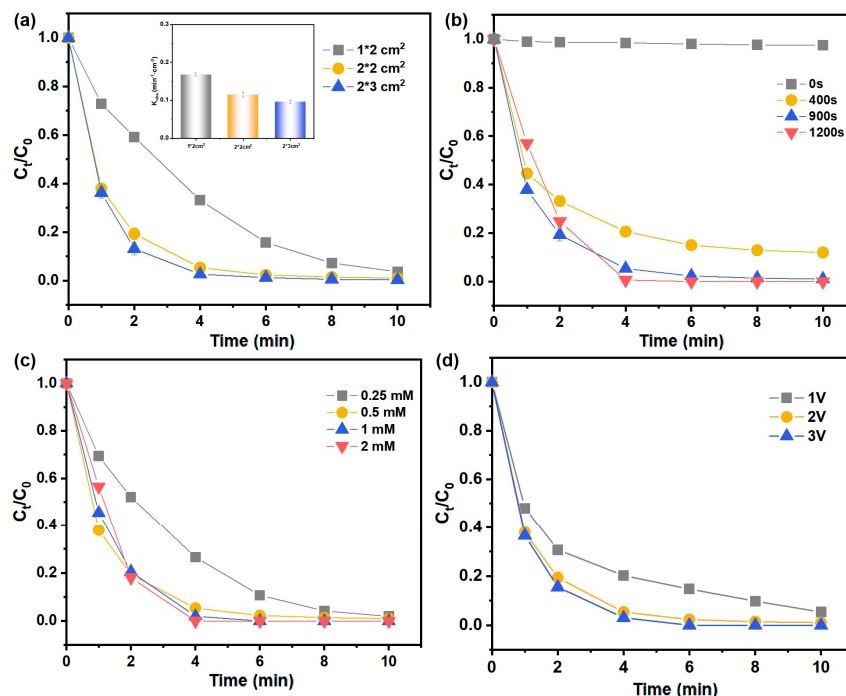


Figure 5. The degradation efficiency of MB in the FeCo-LDH/LI-NDG/EC/PMS system with different reaction parameters: (a) Various electrode areas; (b) Various electrodeposition times; (c) Various PMS dosages; (d) Various applied voltages. Conditions: Applied voltage = 2 V; Electrode area = $2 \times 2 \text{ cm}^2$; [PMS] = 0.5 mM; [MB] = 20 mg/L.

To investigate the degradation effect of the FeCo-LDH/LI-NDG/EC/PMS system on MB under different reaction parameters, related tests were conducted at different PMS dosages and different applied voltages. The reaction system degraded 89.3% of pollutants at 6 min and 98.1% at 10 min when a PMS dosage of 0.25 mM was applied (Figure 5c). However, the degradation rate was 100% within 6 min at a PMS dosage of 0.5 mM. It can be proved that as the amount of PMS increased, more active species were involved in the reaction and thus the degradation rate was increased. Correspondingly, the k_{obs} became larger (from 0.404 min^{-1} to 0.461 min^{-1}) and reached 0.986 min^{-1} at 1 mM PMS dosing. However, the excess PMS could not continue to enhance the degradation rate but led to a slower reaction rate, probably attributed to the self-quenching reaction of the excess PMS [30]. In addition, different applied voltages (1–3 V) were set to study the degradation efficiency changes in the system (Figure 5d). When we set the applied voltage to 1 V, the degradation efficiency was 85.4% in 6 min and 94.7% in 10 min, with a k_{obs} of 0.26 min^{-1} . After increasing the applied voltage to 2 V, the degradation efficiency was increased to 100% in 6 min and the k_{obs} was increased to 0.461 min^{-1} . k_{obs} was further increased to 0.868 min^{-1} after increasing the applied voltage to 3 V. This may be due to the increase in applied voltage, which increased the current density and thus the capacity of electro-activation co-catalytic activation of PMS [7]. However, the applied voltage should not be too large, otherwise it may bring other side reactions to affect the system. Consequently, 0.5 mM PMS and a 2 V applied voltage as the basic parameters of the reaction were optimal, considering the degradation effect and the economic cost in practical applications.

The pH is another important influencing factor for the catalytic degradation reaction. Before the reaction began, the pH of the starting MB solution was adjusted with 1 M H_2SO_4 and 1 M NaOH. It is clear that the FeCo-LDH/LI-NDG/EC/PMS system exhibited great cat-

alytic performance in the pH range from 3 to 9 (Figure 6a). The reaction system was slightly inhibited when the solution's initial pH was changed to 3. Under acidic conditions, H^+ readily undergoes quenching reactions with $SO_4^{\cdot-}$ and $\cdot OH$ radicals (Equations (1) and (2)), thus inhibiting the degradation reaction [31]. Apparently, the inhibition in the system was minimal, and the final degradation rate of the system under acidic conditions still reached 95.5%, which laterally confirmed that the $SO_4^{\cdot-}$ and $\cdot OH$ radicals were not the dominant reactive species in the FeCo-LDH/LI-NDG/EC/PMS system. In contrast, the reaction system achieved complete degradation of MB in both neutral and weakly basic environments, showing the excellent catalytic performance.

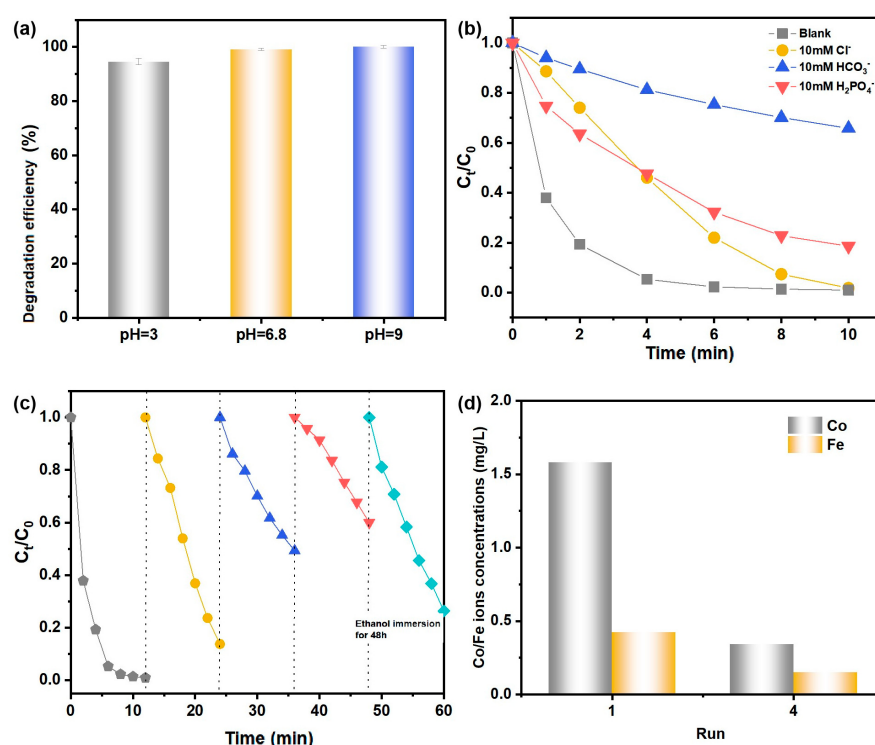


Figure 6. Effects of (a) initial pH and (b) inorganic anions for FeCo-LDH/LI-NDG/EC/PMS. (c) Reatability and (d) metal leaching of FeCo-LDH/LI-NDG. Reaction conditions: [MB] = [RhB] = [MO] = 20 mg/L; [PMS] = 0.5 mM; Applied voltage = 2 V; Electrode area = $2 \times 2 \text{ cm}^2$.

2.2.4. Interference Resistance and Universality

Usually, a certain number of inorganic anions are present in the actual wastewater, and the presence of anions may affect the catalytic performance by competing for the active species [32,33]. Thus, inorganic anions such as 10 mM HCO_3^- , Cl^- and $H_2PO_4^-$ were introduced into the FeCo-LDH/LI-NDG/EC/PMS system (Figure 6b). When Cl^- was present, the efficiency of MB's degradation decreased. However, the system was still able to achieve 100% degradation rate within 10 min. The degradation rate of the system was slowed down and slightly inhibited by the introduction of $H_2PO_4^-$ [33], which may be due to the reaction of $H_2PO_4^-$ with the free radicals in the system (Equations (3) and (4)). The system was still able to achieve nearly 80% MB removal within 10 min. However, in the presence of the anion HCO_3^- , the reaction system was obviously inhibited, which may be as a result of the quenching reaction of HCO_3^- with the ROS in the system [34]. The reason may be due to the reaction of HCO_3^- with the free radicals (Equations (5) and (6)) or

may be due to the consumption of singlet oxygen by HCO_3^- , which weakens the catalytic reaction [35].



To confirm the universality of the FeCo-LDH/LI-NDG/EC/PMS system, related tests were conducted with different contaminants (Figure S3a) and different aqueous media (Figure S3b). Obviously, the reaction rate of the system became faster when changing the target pollutants to rhodamine b (RhB) and complete degradation was achieved within 1 min. When using methyl orange (MO) as the contaminant, the system was also able to completely degrade within 6 min. This also indicated that the FeCo-LDH/LI-NDG/EC/PMS system had a good degradation effect on organic dyes. In addition, catalytic performance tests were carried out using river water and seawater instead of deionized water. In the actual water, the system was slightly inhibited, probably because the complex inorganic ions and components in the seawater and river water affected the catalytic performance of the system [32]. However, the overall degradation efficiency of MB was about 70%, which still indicated catalytic degradation performance.

2.2.5. Reusability and Stability

Reusability and metal ion leaching are also the important parameters affecting practical applications. In the practical applications, the FeCo-LDH/LI-NDG composite electrode material exhibited superior recycling advantages. Compared with powder catalysts and homogeneous catalysts, the recovered FeCo-LDH/LI-NDG electrode material had almost no quality loss. It can be recycled and washed and then dried before entering the next cycle. As shown in Figure 6c, the system was able to achieve a degradation rate close to 90% when entering the second cycle of testing. However, the performance decreased after entering the third cycle. This may be due to the fact that the organic dyes have their intermediate products covering the active sites on the electrode surface during the degradation process [28,36]. The small area of the electrode itself also made the number of sites that can be exposed to full contact significantly reduced, which led to a decrease in catalytic performance. Therefore, we used the ethanol immersion to clean the dye from the electrode surface. It can be observed that after the treatment the system reached about 80% MB degradation, which also implied the recovery of FeCo-LDH/LI-NDG active sites. Moreover, we examined the leaching concentration of Fe/Co ions in the reaction solution (Figure 6d). When sampled and tested after the first cycle, the concentration of Fe ions was 1.58 mg/L and the concentration of Co ions was 0.42 mg/L. This may be due to the Fe/Co ions floating on the surface of the electrode into the reaction solution. However, after the fourth cycle, the concentrations of Fe ions and Co ions were 0.34 mg/L and 0.15 mg/L, respectively. These results complied with the environmental quality standards for surface water (GB 3838-2002) [37].

2.3. Activation Mechanism

2.3.1. Reactive Oxygen Species

To identify the reactive oxygen species in the FeCo-LDH/LI-NDG/EC/PMS system, chemical quenching experiments were first performed in our work (Figure 7a). Typically, we utilized MeOH and TBA to quench $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ [38]. After the addition of 500 mM MeOH, the reaction rate was slowed down, and the degradation efficiency was 60% in 4 min and 91% in 10 min, indicating that the system was slightly restrained. The addition of 500 mM TBA also had an impact on the system's catalytic performance; however, it was less significant than the quenching impact of methanol. It indicated the presence of

a small amount of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ in the system. Additionally, the inhibition was more pronounced upon the addition of 10 mM p-benzoquinone (p-BQ) to the system [39], which also illustrated that a certain concentration of $\text{O}_2^{\cdot-}$ was generated. Moreover, the system was substantially inhibited by the addition of 10 mM singlet oxygen quencher (TEMP), which almost completely prevented the reaction. This reflected that $^1\text{O}_2$ was the dominant active species in the FeCo-LDH/LI-NDG/EC/PMS system.

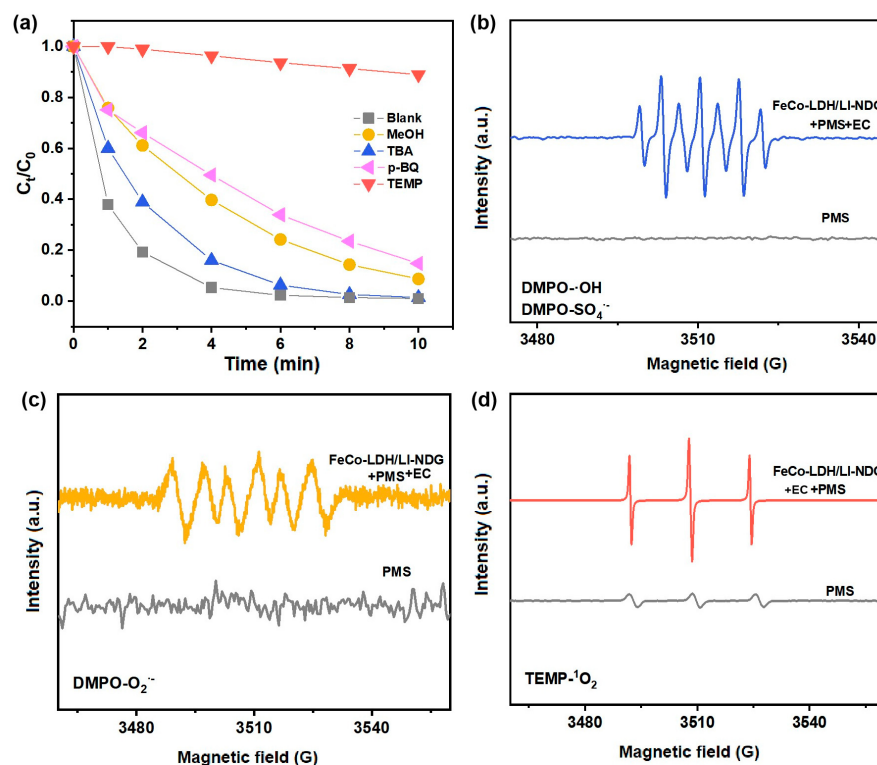


Figure 7. Identification of active species of (a) various chemical quenching agents and EPR tests for (b) $\cdot\text{OH}/\text{SO}_4^{\cdot-}$; (c) $\text{O}_2^{\cdot-}$; (d) $^1\text{O}_2$ in the FeCo-LDH/LI-NDG/EC/PMS system; Conditions: Applied voltage = 2 V; Electrode area = $2 \times 2 \text{ cm}^2$; [MB] = 20 mg/L; [PMS] = 0.5 mM; [MeOH] = [TBA] = 250 mM; [DMPO] = [TEMP] = 10 mM.

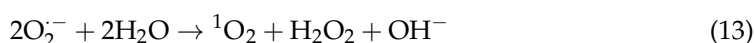
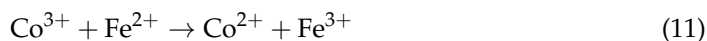
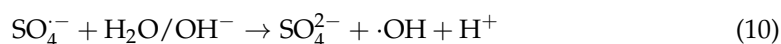
To validate the outcomes of the chemical quenching trials, we conducted electron paramagnetic resonance (EPR) measurements (Figure 7b–d). As can be observed in Figure 7b,c, we employed 10 mM DMPO as a trapping agent. We detected $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$ and $\text{O}_2^{\cdot-}$ signals in the FeCo-LDH/LI-NDG/EC/PMS system, indicating that $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$ and $\text{O}_2^{\cdot-}$ were present in the FeCo-LDH/LI-NDG/EC/PMS reaction system. EPR tests were conducted to confirm the $^1\text{O}_2$ in the FeCo-LDH/LI-NDG/EC/PMS system (Figure 7d). We used 10 mM TEMP to quench $^1\text{O}_2$. In the pure PMS system, a weak signal was observed. This may be related to past reports of PMS self-decomposition [40]. Notably, a stronger TEMP- $^1\text{O}_2$ signal was detected in the FeCo-LDH/LI-NDG/EC/PMS system. A stronger signal meant a higher concentration of $^1\text{O}_2$ in the system. In summary, both the EPR results and the chemical quenching experiments confirmed the presence of $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ as well as $^1\text{O}_2$ in the FeCo-LDH/LI-NDG/EC/PMS system. We can conclude that in the FeCo-LDH/LI-NDG/EC/PMS system, the radical pathways of $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ and the non-radical pathway $^1\text{O}_2$ synergistically participated in the reaction, whereas $^1\text{O}_2$ was the dominant active species.

2.3.2. Feasible Activation Mechanism

According to the experiments related to the identification of the active species, the radical pathways of $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ and the non-radical pathway of $^1\text{O}_2$ were

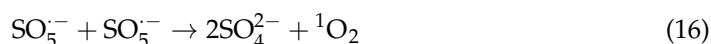
synergistically involved in the FeCo-LDH/LI-NDG/EC/PMS reaction system and $^1\text{O}_2$ was the dominant reactive oxygen species. XPS and XRD analysis of fresh and spent FeCo-LDH/LI-NDG and electrochemical tests were carried out to analyze the mechanism and pathways of these ROS generation.

The XRD tests of FeCo-LDH/LI-NDG after four uses were conducted and compared with fresh FeCo-LDH/LI-NDG (Figure 8a). It can be found that the crystal structure of fresh and used FeCo-LDH/LI-NDG did not change significantly, which also indicated that FeCo-LDH/LI-NDG maintained the structural stability after recycling. In addition, the FeCo-LDH/LI-NDG electrode material reused four times was compared with the fresh FeCo-LDH/LI-NDG by XPS tests. According to the XPS survey of fresh and used FeCo-LDH/LI-NDG, the proportion of N, O, Fe and Co elements decreased in the used FeCo-LDH/LI-NDG (Figure 8b). Combined with the O 1s spectrum analysis (Figure S4a), the proportion of metal–oxygen (M–O) bonds decreased from 33.08% to 30.92% and the proportion of C–OH bonds decreased from 35.37% to 34.06% after use, whereas the proportion of surface adsorbed oxygen O_{abs} increased. This may be due to the participation of FeCo-LDH and C–OH in the catalytic reaction leading to a decrease in oxygen content (Equations (7)–(10)) [41]. The spectrum of N 1s (Figure S4b) shows a decrease in the proportion of graphitic nitrogen and an increase in the proportion of pyrrole nitrogen and pyridine nitrogen. It illustrates the possible involvement of graphitic nitrogen in the reaction. More importantly, according to the spectra of Fe 2p and Co 2p (Figure S4c,d), it was observed that the proportion of Fe (II) decreased from 52.56% to 48.67% and the proportion of Fe (III) increased from 47.44% to 51.33% after use. The percentage of Co (II) decreased from 54.62% to 44.19% and the percentage of Co (III) increased from 45.38% to 55.81% after use. Combined with chemical quenching experiments and EPR experiments, Co(II)-LDH may generate $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ radicals through activation of PMS (Equations (7)–(9)). The redox cycle of Fe (II) and Co (III) occurred (Equation (11)) [26]. Since the main reactive species of the system was $^1\text{O}_2$, $\text{O}_2^{\cdot-}$ was further reacted to produce $^1\text{O}_2$ (Equations (12)–(14)) [42–44]. According to past reports [45], the weakly positively charged Co atom was likely to be the active center of the catalytic reaction, capable of adsorbing and activating PMS.



In order to verify the electron transfer pathway of the reaction system and the formation pathway of $^1\text{O}_2$, LSV tests were performed (Figure 8c). After the PMS was added to the reaction system, we noticed an increase in the current. This indicated that electron transfer occurred, where electrons flowed from PMS to FeCo-LDH/LI-NDG and electron loss occurred from PMS [46]. It also implied that there was another $^1\text{O}_2$ formation pathway for PMS electron loss in the FeCo-LDH/LI-NDG/EC/PMS system. Past reports have mentioned that catalysts with weakly positive charges can convert PMS into $\text{SO}_5^{\cdot-}$ by extracting its electrons and $\text{SO}_5^{\cdot-}$ itself reacted with each other to form $^1\text{O}_2$ (Equations (15) and (16)) [47]. The Co atom was the active center with a weak positive charge, which had the conditions

to form this pathway [45]. In addition, combined with the OCPT curves (Figure 8d), we found that the potential increased from negative to positive throughout the reaction process after the addition of PMS. This implied that the current increased and then decreased, which also proved the existence of dual $^1\text{O}_2$ production pathways in the reaction process. Therefore, we believe that the process of $^1\text{O}_2$ generation was to produce $^1\text{O}_2$ by the electron loss reaction of PMS and then through $\text{O}_2^{\cdot-}$ to produce another pathway of $^1\text{O}_2$.



In general, the Co atoms of the FeCo-LDH/LI-NDG surface may be the active center of the catalytic reaction and the PMS molecules adsorbed onto the Co atoms and turned on the activation reaction. On the one hand, the weakly positively charged Co atoms of the anode made PMS produce weak radical $\text{SO}_5^{\cdot-}$ by extracting electrons from PMS. On the other hand, the Co(II)-LDH of the cathode activated PMS to produce $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$, which further reacted to produce $^1\text{O}_2$. These two pathways worked together to make the FeCo-LDH/LI-NDG/EC/PMS reaction system effective by attacking organic pollutants mainly through $^1\text{O}_2$.

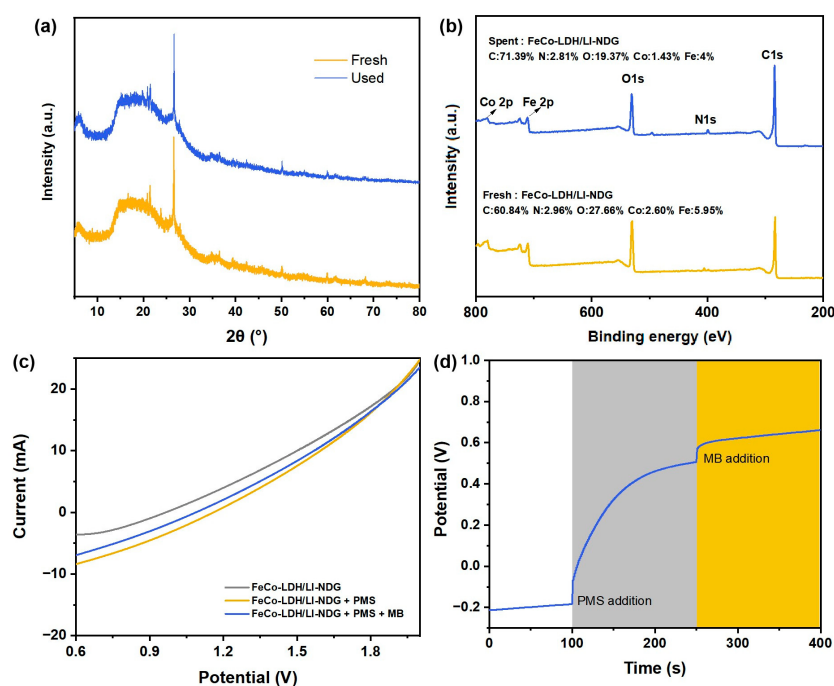


Figure 8. (a) XRD patterns and (b) XPS survey of the spent and fresh FeCo-LDH/LI-NDG. (c) LSV curves and (d) OCPT curves under different conditions.

2.4. Degradation Intermediate Product Identification and Analysis

To confirm the degradation pathway of MB in the FeCo-LDH/LI-NDG/EC/PMS reaction system, the degradation intermediates were detected by liquid chromatography–mass spectrometry (LC-MS). The m/z of methylene blue was 284 [48]. Sixteen degradation intermediates of MB were also detected with m/z values of 318, 263, 298, 270, 256, 242, 218, 173, 195, 182, 167, 112, 155, 136, 142 and 118 (Figure 9). We summarized four possible degradation pathways for MB in the FeCo-LDH/LI-NDG/EC/PMS reaction system. Firstly, the methyl group on MB may be attacked by $^1\text{O}_2$ to form the intermediate P3, which was later demethylated to form P4, P5 and P6 [49]. Secondly, $^1\text{O}_2$ may attack functional groups and electron-rich sites. These sites were susceptible to oxidation, and the S atom on MB was oxidatively added to produce P1. In addition, it may cleave the C-C bond to form the

product P9, which later decomposed to P10 and P11 or to form the monocyclic products P7 and P8. It may also cleave C-N to form P2, and these intermediates can then decompose to P12, P13, P14, P15, P16 and inorganic substances. Moreover, to assess the biological toxicity of MB and its breakdown products, we employed ECOSAR software (Figure 10). The globally harmonized system of classification and labeling of chemicals (GHS) was used to classify the toxicity grade [50]. It can be seen from the figure that the treatment did not introduce more serious ecological toxicity because the catalytic effect of FeCo-LDH/LI-NDG significantly reduced the biological toxicity of MB and most intermediates.

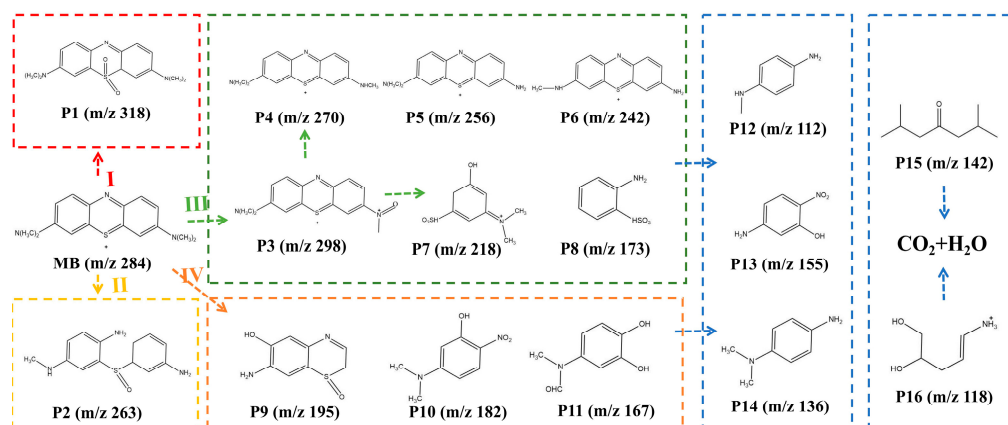


Figure 9. MB degradation pathways in the FeCo-LDH/LI-NDG/EC/PMS system.

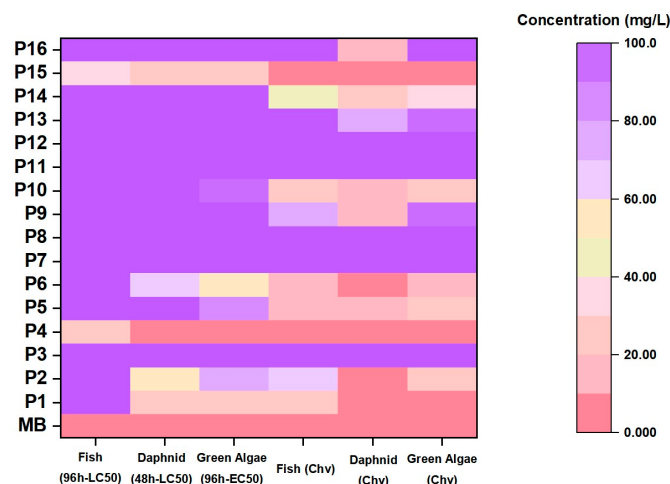


Figure 10. The ecotoxicity prediction of MB and its degradation intermediates in FeCo-LDH/LI-NDG/EC/PMS system.

3. Materials and Methods

3.1. Materials

Supplementary Materials Text S1 describes the chemicals that were utilized in the studies.

3.2. Methods

3.2.1. Synthesis of the Precursor FeCo-LDH/LI-NDG

We used a simple laser-induced technique combined with an electrodeposition method to prepare catalyst composite electrode materials [13,22]. Laser-induced nitrogen-doped graphene (LI-NDG) was synthesized as an electrode substrate material using the laser-induced technique, which was performed on polyimide (PI) films through a 10.6 μm CO_2 infrared laser. The samples were then rinsed three times in ethanol and deionized water before being dried overnight. With LI-NDG, Pt and Ag/AgCl serving as the working electrode, counter electrode, and reference electrode, respectively, the electrodeposition

process was conducted utilizing a three-electrode system. A 0.1 M mixed solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was utilized as the deposition solution. The working electrode was immersed in the electrolytic cell and a constant current was used for electrodeposition. After deposition, the electrode was washed and dried overnight to obtain FeCo-LDH/LI-NDG electrode material. The preparation process is shown in Figure 11.

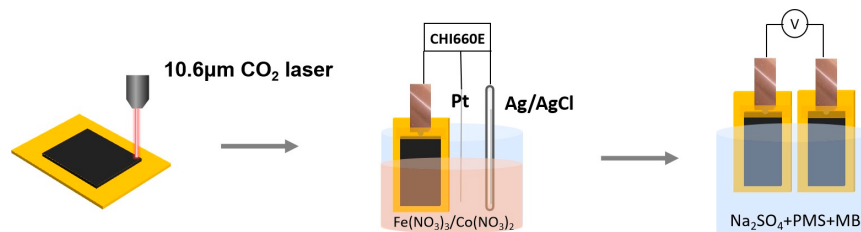


Figure 11. The preparation procedure of FeCo-LDH/LI-NDG.

3.2.2. Catalytic Degradation Experiments

Methylene blue (MB) served as the goal contaminant in our work. FeCo-LDH/LI-NDG was used for both cathode and anode; the electrode area was $2 \times 2 \text{ cm}^2$. The electrolytic solution was 80 mL of a 0.1 M Na_2SO_4 solution and 20 mg/L MB with continuous stirring on a magnetic stirrer for 15 min. The sample was made to be at adsorption–desorption equilibrium. These two electrodes were connected to an electrochemical workstation (CHI660E, Shanghai Chenhua Instruments Co., Shanghai, China), the applied constant voltage was set and the required amount of PMS was added. Then, we sampled at certain time intervals and measured the absorbance of the sample solutions at 664 nm by UV spectrophotometer (UV1800, Shanghai Aonan Scientific Instruments Co., Shanghai, China). The whole procedure was carried out in the dark. Experiments with different initial pH values were adjusted with 1 M H_2SO_4 and 1 M NaOH solutions. All experiments were conducted three times. The Supplementary Materials Text S2 contains the characterization's specifics.

3.2.3. Electrochemical Tests

The electrochemical properties were tested using the electrochemical workstation (CHI660E). As the working electrode, counter electrode and reference electrode, FeCo-LDH/LI-NDG, Pt and Ag/AgCl, respectively, were utilized. To explore the redox performance of the reaction system, cyclic voltammetry (CV) tests were carried out with 0.1 M Na_2SO_4 electrolyte solution in the voltage range -1.2 V to 1.2 V at different scan rates. In addition, LSV and OCPT were applied to study the electron transfer pathways of the catalytic degradation system. The LSV curves of different reaction systems were tested in the voltage range from 0.6 V to 2 V at 50 mV/s scanning speeds, respectively. The OCPT curves were tested after adding PMS and MB, respectively.

4. Conclusions

In this study, FeCo-LDH/LI-NDG composite electrodes were efficiently produced by laser-induced technology combined with the electrodeposition technique. The FeCo-LDH/LI-NDG/EC/PMS system acquired rapid and complete degradation of MB within 6 min, which was faster than most of the currently reported similar electro-catalysts. According to active species identification experiments, $^1\text{O}_2$ played a dominant role in the MB degradation. It demonstrated good catalytic performance in the pH range from 3 to 9 and had anti-interference ability. The related experimental analysis confirmed that the radical pathways of $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ and the non-radical pathway of $^1\text{O}_2$ participated in the reaction synergistically and $^1\text{O}_2$ was the dominant reactive oxygen species. The formation of $^1\text{O}_2$ through the dual pathways of PMS electron loss at the anode and $\text{O}_2^{\cdot-}$ intermediate conversion at the cathode promoted the rapid degradation of organic pollutants. In summary, this study combined two PMS activation methods, which could not only achieve high efficiency in the whole process of production, reaction and

recovery but also supplement the new perspective of the dual pathway coexistence of $^1\text{O}_2$ in the non-radical pathway for the PMS activation mechanism.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13060922/s1>, Text S1: Chemicals and materials; Text S2: Characterization; Table S1: Recently reported catalytic performance of comparable electrocatalysts; Figure S1: (a) N 1s, (b) Fe 2p and (c) Co 2p XPS spectra of FeCo-LDH/LI-NDG; Figure S2: (a) CV curves for 10 consecutive scans of FeCo-LDH/LI-NDG; (a) CV curves for 10 consecutive scans of FeCo-LDH/LI-NDG + PMS; Figure S3: The degradation efficiency of MB in FeCo-LDH/LI-NDG/EC/PMS system with different conditions: (a) various contaminants; (b) various water bodies; Figure S4: (a) O1s, (b) N1s, (c) Fe 2p and (d) Co 2p XPS spectra of spent and fresh FeCo-LDH/LI-NDG. References [7,8,51–53] are cited in the supplementary materials.

Author Contributions: Conceptualization, L.C. and J.L.; methodology, L.C.; form analysis, L.C.; investigation, L.C., C.L. and W.X.; resources, J.L. and X.H.; data curation, L.C., Y.X., C.L. and W.L.; writing—original draft preparation, L.C.; writing—review and editing, J.L. and C.G.; visualization, L.C., Y.X. and X.H.; supervision, J.L. and C.G.; project administration, J.L.; funding acquisition, J.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the Haikou Science and Technology Planning Project (No. 2021003), Scientific Research Project of Hainan Higher Education Institutions (No. Hnky2023-9) and Hainan University Research Start-up Fund (No. kyqd(zr)22185).

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

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