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Perovskite LaMnO_3 Composite Graphene Carbon Nitride $\text{g-C}_3\text{N}_4$ Improves the Photocatalytic Performance of Tetracycline Degradation

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Abstract: With the extensive use and improper treatment of antibiotics, antibiotic pollution in aquaculture wastewater has become increasingly severe. Tetracycline antibiotics have become one of the most commonly used fishery antibiotics. In this study, a Z-scheme heterostructure $\text{LaMnO}_3/\text{g-C}_3\text{N}_4$ was constructed by the sol–gel method as a photocatalyst to degrade tetracycline, and the influence of anions on the degradation effect was investigated. The $\text{LaMnO}_3/\text{g-C}_3\text{N}_4$ hybrid was successfully constructed by scanning electron microscope, Fourier transform infrared spectrum, and X-ray diffraction. The results of degradation experiments demonstrated that the maximum tetracycline degradation efficiency of $\text{LaMnO}_3/\text{g-C}_3\text{N}_4$ -10 (LMO/CN-10) was 80%, the removal rate of TC decreased from 71% to 48% when the concentration of chloride ions increased from 0 mM to 10 mM, and the removal rate of TC decreased from 75% to 28% when the concentration of carbonate ions increased from 0 mM to 10 mM. This enhanced photocatalytic activity was attributed to the formation of a Z-scheme structure that promoted the separation of photoinduced electron holes while maintaining its own strong redox ability. Finally, the photocatalytic mechanism was designed based on the free radical trapping experiment, electrochemical impedance, and photoluminescence spectra, providing an opportunity for the construction of a new photocatalyst for the treatment of aquaculture tailwater in the future.

Keywords: photocatalysis; $\text{LaMnO}_3/\text{g-C}_3\text{N}_4$; visible light; z-scheme mechanism



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1. Introduction

The excellent ecological environment of aquaculture waters is the premise to maintain the sustainable development of aquaculture. In recent years, domestic breeding density keeps increasing to raise production and income, resulting in the accumulation of residual bait and excrement in water and the continuous deterioration of the aquaculture environment. Antibiotics have been widely used in aquaculture to prevent and treat fish diseases [1]. However, antibiotic pollution in aquaculture wastewater has become increasingly severe with the massive use and improper treatment of antibiotics, and it is urgent to tackle this problem [2]. Tetracycline antibiotics (TC) have become one of the commonly used fishery antibiotics owing to their low price and broad-spectrum antibacterial properties. High tetracycline content in aquacultural tailwater influences the growth and development of fish and indirectly affects human health [3]. Additionally, tetracycline remains in the soil along with aquaculture tailwater, resulting in the loss of soil fertility [4]. Therefore, methods for treatment of tetracycline in aquaculture tailwater are urgently needed. At present, the main treatment methods for TC wastewater comprise physical [5–7], biological [7–9], and chemical methods [10–13].

Photocatalysis technology has been applied in many fields, such as environmental, catalysis, and energy due to the advantages of having high efficiency and offering environmental protection, being clean and pollution-free, with sustainable utilization [14]. Photocatalytic hydrogen production is the process of converting solar energy into hydrogen energy through semiconductor materials to realize the collection and utilization of hydrogen [15]. There are many applications, such as decontamination of organic pollutants, inactivation of toxic bacteria, and carbon dioxide reduction. Aslam prepared a CeO_2 photocatalyst to degrade phenol pollutants [16]. The analysis of the degradation process and degradation products demonstrated that the photocatalyst played a significant role in the degradation process and did not cause secondary pollution to the environment. Tzeng studied the mechanism of bacterial damage under a visible-light-driven photo-inactivation system [17] and demonstrated that the as-synthesized nitrogen-schroter co-modified TiO_2 (N-Schroter- TiO_2) photocatalytic nanocomposite is highly effective in deactivating pathogenic *C. albicans* under visible-light irradiation [18]. However, photocatalysis technology has encountered drawbacks, such as issues with the stability of the catalysts, separation difficulties of catalysts themselves, and a low removal efficiency.

In recent years, the synthesis of carbon materials and semiconductor photocatalysts has gradually become a research hotspot of modified photocatalysts. Carbon materials mainly consist of biochar, graphene, and carbon nanotubes [19]. Graphene carbon nitride ($\text{g-C}_3\text{N}_4$) is a highly efficient photocatalyst that reacts under visible light. Furthermore, $\text{g-C}_3\text{N}_4$, as a non-metallic polymer material, has become one of the recent research hotspots in the field of photocatalysis.

Perovskite is a class of crystalline ceramic oxides with the molecular formula ABO_3 , where A and B represent the rare earth element or alkali metal element ion and the transition metal element ion, respectively [20]. It occupies the cubic densely packed octahedral body center with six oxygen complexes. Lanthanide perovskite-type oxides are an essential branch of perovskite oxides. The rare earth element lanthanum (La) occupies a site of perovskite and has the characteristics of stability and easy coordination. B-site is a transition metal cation, comprising Fe, Co, Ni, Cr, Ti, Mn, and Al [21]. Lanthanide perovskite oxides have been further investigated in the field of photocatalysis. Hu successfully prepared Ag-modified LaMnO_3 -graphene composite photocatalytic materials by the sol-gel method [22]. Chen prepared a series of ABO_3 perovskites ($\text{A} = \text{La}, \text{Ce}, \text{Sm}$). The photocatalytic degradation of volatile styrene by different perovskites was studied [23]. Perovskite-structured catalysts LaMO_3 ($\text{M} = \text{Co}, \text{Fe}$) were successfully synthesized, and an attempt was made to catalyze hydrogen peroxide (H_2O_2) for the degradation of Direct Blue 86 (DB86) [24]. Ibarra-Rodriguez prepared LaMO_3 ($\text{M} = \text{Co}, \text{Ni}$ and Fe) doped photocatalysts by sol-gel and solid phase reaction methods and found that LaMO_3 series perovskite oxides prepared by the sol-gel method had a greater specific surface area and photocatalytic hydrogen production efficiency [25]. $\text{La}_2\text{MnTiO}_6$, a double perovskite photocatalytic material prepared by Shirazi using the sol-gel method, exhibited high cyclic stability in the process of acid blue degradation by visible light [26]. Previous reports demonstrated that the construction of heterojunction is an advisable approach to designing high-efficient photocatalysts. Among the heterojunction photocatalysts, the Z-scheme photocatalytic system has outstanding ability to inhibit the recombination of photogenerated electron-hole pairs [27]. A novel Z-scheme heterojunction magnetic $\text{ZnFe}_2\text{O}_4/\text{BiO-Bi}_2\text{MoO}_6$ photocatalyst synthesized by Wang for tetracycline degradation and the results showed the maximum degradation rate for TC via 30%- $\text{ZnFe}_2\text{O}_4/\text{BiO-Bi}_2\text{MoO}_6$ reached 86.32% after 60 min reaction [28]. According to previous studies, many of these Z-scheme heterogeneous catalysts have been synthesized for tetracycline degradation, such as $\text{Fe-g-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ [29], $\text{g-C}_3\text{N}_4/\text{FeWO}_4$ [30], crystalline carbon nitride/ $\delta\text{-Bi}_2\text{O}_3$ [31], and $\text{BiOI}/\text{Ag@AgI}$ [32].

In summary, LaMnO_3 and $\text{g-C}_3\text{N}_4$ themselves have certain photocatalytic properties, and $\text{g-C}_3\text{N}_4$ loading in perovskite can effectively improve its photocatalytic properties according to the previous literature reports. Therefore, in this study, CN was loaded to improve the limited photocatalytic performance of LaMnO_3 . The synthesized composite

$\text{LaMnO}_3/\text{g-C}_3\text{N}_4$ was used to degrade tetracycline in aquaculture tailwater, and the effect of anion concentration in actual tailwater on degradation performance was studied. Finally, the photocatalytic degradation mechanism was also studied. The results provide some basic research for the future construction of a new photocatalytic system in environmental remediation and energy protection.

2. Materials and Methods

2.1. Materials

Lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), citric acid monohydrate, melamine, tetracycline, Sodium carbonate (Na_2CO_3), Sodium chloride (NaCl), p-benzoquinone (BQ), tert-butanol (TBA), triethanolamine (TEOH), and 2, 2, 6, 6-tetramethyl-4-piperidone (TEMP) were purchased from Sinopharm Group Chemical Reagents Co., LTD. None of the reagents were further purified. Distilled water was employed in all experiments.

2.2. Preparation of Photocatalyst

2.2.1. Preparation of $\text{g-C}_3\text{N}_4$

Melamine was kept in a crucible and heated to 550°C in a muffle furnace for 4 h in a semi-closed system at a heating rate of $10^\circ\text{C min}^{-1}$ under air conditions. The product was washed several times with distilled water and absolute ethanol, dried at 80°C for 12 h, and named CN.

2.2.2. Preparation of LaMnO_3

LaMnO_3 nanoparticles were prepared by the sol-gel method. Specifically, 10 mmol of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and 20 mmol of citric acid monohydrate were weighed and dissolved in 50 mL of deionized water, respectively. Thus, the molar ratio of hair metal ions to citric acid in the solution was 1:1. The solution was heated in a water bath at 80°C for 2 h until it became a dry gel precursor. Afterward, the gel was dried in an oven at 110°C for 8 h, and the dried precursor was ground into powder and put into an alumina crucible. Under air conditions, the dried precursor was calcined in a muffle furnace at 700°C at a heating rate of 20°C/min for 4 h, and the sample was taken out after being cooled to room temperature. After being washed with anhydrous ethanol and deionized water several times, the LaMnO_3 sample was finally oven dried at 80°C for 12 h, and named LMO.

2.2.3. Preparation of $\text{LaMnO}_3/\text{g-C}_3\text{N}_4$

Additionally, 0.57 g of LaMnO_3 sample and 0.03 g of $\text{g-C}_3\text{N}_4$ sample were dispersed into 30 mL of deionized water, and the mixture was subjected to ultrasound. The frequency of ultrasonic cleaning machine (SB-800 DTD) is 99 kHz, and the time was 15 min. Then, the LaMnO_3 suspension was slowly added to $\text{g-C}_3\text{N}_4$ suspension and stirred for 5 h under magnetic agitation. The resulting suspension was heated at 110°C until the water in the suspension was removed. The obtained solid product was dried at 110°C for 6 h, and the dried sample was calcined at constant temperature for 1 h in a muffle furnace at the heating rate of 20°C/min to 400°C . The product was $\text{LaMnO}_3/\text{g-C}_3\text{N}_4$ (5 wt%), denoted as LMO/CN-5. The samples were named LMO/CN-10, LMO/CN-15, and LMO/CN-20, respectively, following the mass fraction of $\text{g-C}_3\text{N}_4$ in the total mass of the prepared complex.

2.3. Characterization of Catalyst

The morphology and element distribution of the catalyst were determined by a field emission scanning electron microscope (SEM) (ZEISS Gemini 300) and an energy dispersive spectrometer (EDS) (ZEISS Gemini 300). Transmission electron microscopy (TEM) (jeol2100f) was employed to detect the crystal structure microregion of the sample. The particle size, shape, and particle size distribution of the sample were visually detected. The phase composition and crystal structure of the samples were analyzed by an X-ray diffrac-

tometer (XRD) (Rigaku Ultimate IV Japan). Cu K α radiation was adopted at 40 kV, 40 mA, $2\theta = 20$ – 80 degree, and the scanning rate was $10^\circ \text{ min}^{-1}$. X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha) was utilized to analyze the valence state and the relative content of each element on the surface. Furthermore, the absorption performance of solid materials was explored using solid diffuse reflection spectroscopy (UV-vis DRS) (Shimadzu UV-3600i Plus). A Hitachi UV-3010 spectrophotometer was operated with an acquisition speed of $40 \text{ nm} \cdot \text{min}^{-1}$ and a wavelength range of 200–800 nm. All the samples were measured with BaSO₄ as the reference. The Fourier transform infrared (FT-IR) (Thermo Scientific Nicolet iS20) spectrum was a Nicolet 6700 spectrometer, and the KBr particle range was 4000 – 400 cm^{-1} . The photoluminescence (PL) (Edinburgh FLS1000) spectra of the samples were obtained by a Varian Cary Eclipse spectrometer with an excitation wavelength of 325 nm. The specific surface area, pore volume, and pore size distribution of the catalyst were determined by the low-temperature liquid N₂ desorption method. The specific surface area of the catalyst was calculated using the Brunauer–Emmett–Teller (BET) (Mike 2460) method. Additionally, the pore volume and pore size distribution in the catalyst were calculated by the Barrett–Joyner–Halenda (BJH) (Mike 2460) method.

2.4. Performance Tests of Photocatalysts

A 300 W xenon arc lamp was adopted as the visible light source, and a 400 nm cut-off filter was used in this study. In the photocatalytic measurement, a suspension of the photocatalyst and TC solution was placed in a 25 mL cylindrical adaptation reactor with a water recycling facility. Before irradiation, the reaction suspension was ultrasonic for 15 min and stirred in a dark environment for 30 min to guarantee the equilibrium of adsorption and desorption. In the photocatalytic test, a 3 mL suspension was taken at a given time interval and then centrifuged at 1000 rpm for 10 min to remove the photocatalyst. The concentration of the remaining TC was measured by an ultraviolet spectrophotometer at 368 nm. The photocatalytic reaction device is displayed in Figure 1.

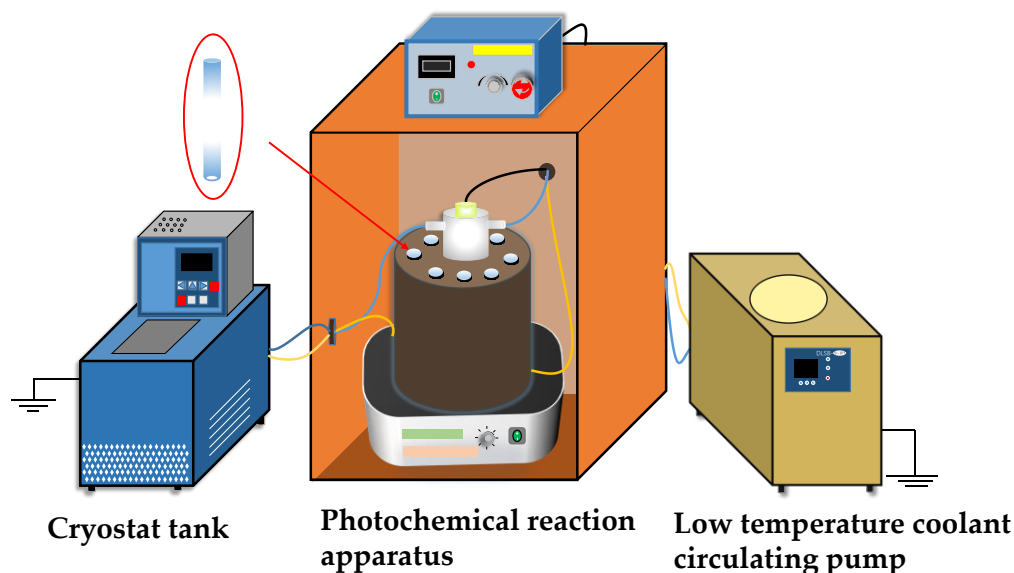


Figure 1. The photocatalytic reaction device.

The degradation rate of TC was calculated by

$$X(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 (mg/L) and C_t (mg/L) denote the initial concentration of TC and residual concentration of TC at time t , respectively.

2.5. Mechanism of Photocatalytic Degradation

Free radical capture experiments were conducted on the active species produced during the photocatalytic experiment to determine the photocatalytic degradation mechanism. In this experiment, BXU034 photochemical reaction instrument was employed for photochemical experiment. TBA, TEOH, BQ, and TEMP were utilized as the trapping for photogenerated holes (h^+), hydroxyl radical (OH), superoxide radical (O_2^-), and singlet oxygen (1O_2) in the photocatalytic reaction, respectively. Before the photocatalytic experiment, 10 mg of LMO/CN-10 catalyst was added into 25 mL quartz test tubes; 1 mmol TEOH, 1 mmol TBA, 1 mmol BQ and 1 mmol TEMP were added into the test tubes, respectively. The degradation of TC was compared by taking samples at an interval of 20 min.

3. Results and Discussion

3.1. Characterization of Photocatalysts

As illustrated in Figure 2a, the surface of the original CN presents an irregular lamellar structure with many folds. Figure 2b exhibits the graininess of pure LMO irregular and agglomerated nanoparticles. After LMO and CN were combined, CN was randomly attached to the surface of LMO. The SEM image is presented in Figure 2c. The tight binding of LMO and CN facilitates the formation of heterojunctions that contribute to interfacial charge transfer and separation and thus superior photocatalytic activity. Additionally, EDS image further indicated that LMO/CN was composed of elements La, Mn, O, C, and N (Figure 2g). All these phenomena suggest that a uniform and tight coupling between LMO nanoparticles and CN nanoparticles is successfully constructed. In other words, a binary heterojunction hybrid is constructed. Such heterojunction makes the contact area between LMO and CN nanosheets large, effectively promoting the transfer of interfacial charge during the photocatalytic reaction. Figure 2d–f imply that LMO/CN-10 maintains a porous structure, and CN nanosheets are attached to LMO particles. Figure 2f demonstrates that the synthesized catalyst maintains clear lattice fringes, consistent with SEM results.

XRD can be used to analyze the crystal structure and image composition of the catalyst prepared. The XRD of CN, LMO, and LMO/CN- x ($x = 5, 10, 15, 20$) is illustrated in Figure 2h. Figure 2h reflects that a significant diffraction peak can be observed at $2\theta = 27.51^\circ$ in the prepared pure CN, which corresponds to that of CN (JCPDS#87-1526) [33]. The original perovskite LMO exhibited seven distinct characteristic peaks at $2\theta = 23.5^\circ, 32.4^\circ, 42.1^\circ, 47.8^\circ, 58.9^\circ, 68.7^\circ$, and 78.1° , corresponding to (012), (110), (202), (024), (214), (208), and (128) crystal planes of rhomboidal perovskite structure LMO (JCPDS#89-8775) [33], respectively. This unveils that the prepared perovskite catalyst is the crystalline form of cubic LMO with good junction crystallinity, and the compound CN does not change the structure of the original LMO.

As observed in Figure S1a, the N_2 absorption and desorption curve of catalyst LCM/CN-10 conforms to type IV isotherm of the H3 hysteresis loop. In other words, the perovskite catalyst has two pore sizes: mesoporous and microporous [34]. This conclusion can also be drawn from the aperture distribution in Figure S1b. Besides, the specific surface area, pore size, and pore volume of the catalyst can be calculated, as listed in Table 1. The pore size of LMO/CN-10 is 23.1663 nm, suggesting the presence of mesoporous pores. LMO/CN-10 presented a lower specific surface area compared to pure LMO. This can be explained as follows. The active sites of the catalyst were lessened since CN was loaded on the surface of the LMO and blocked part of the pores possibly. However, LMO/CN-10 has a larger pore volume, which is conducive to oxidation. Thus, the degradation of pollutants by the catalyst is not solely dependent on the size of the catalyst surface area, but the internal structure. The low specific surface area implies that the reaction of the catalyst is independent of the mass transfer rate.

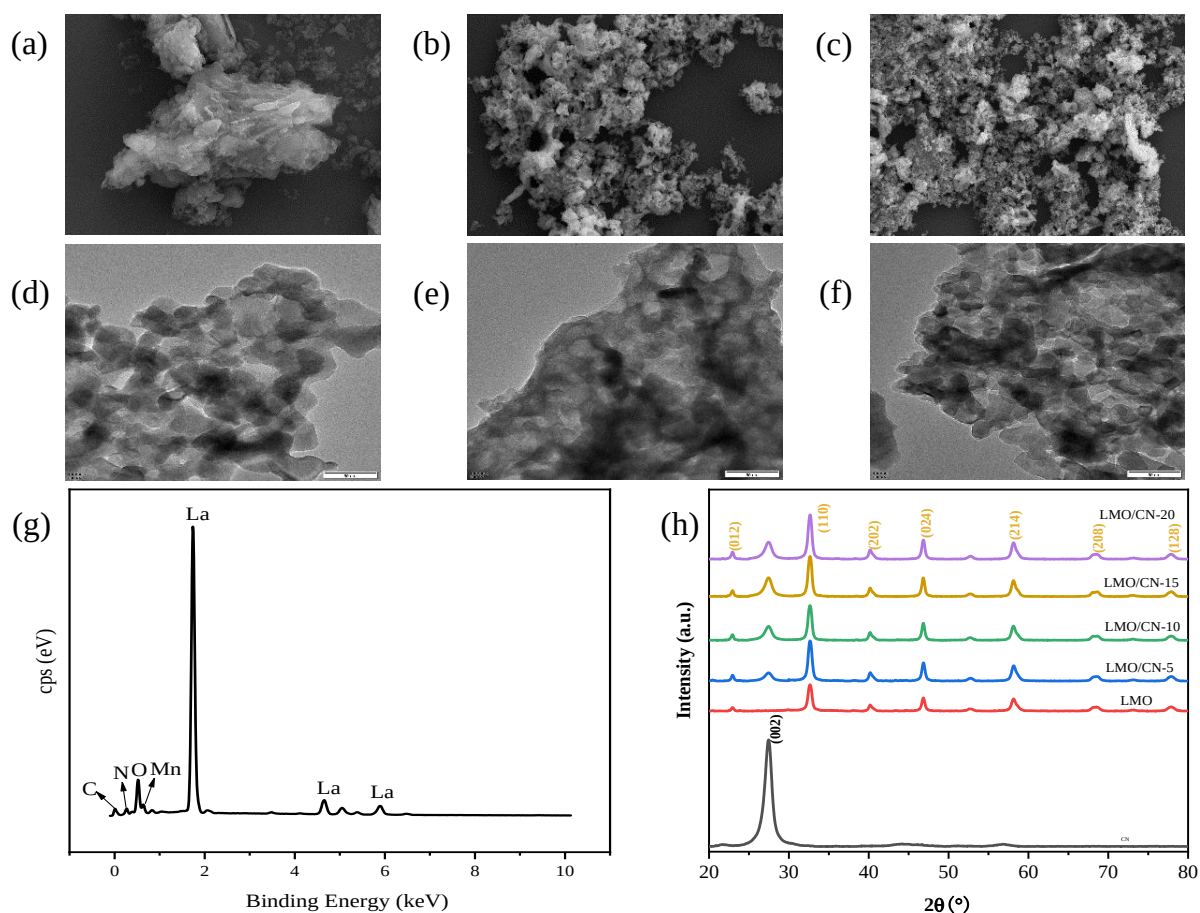


Figure 2. SEM images (Mag = 5.0 k $\times$) of CN (a), LMO (b), LMO/CN-10 (c), TEM images (Mag = 100,000 $\times$) of CN (d), LMO (e), LMO/CN-10 (f), EDS image of LMO/CN-10 (g) and XRD pattern of all samples (h).

Table 1. Specific surface area, pore sizes, and pore volumes of CN, LMO, and LMO/CN-10.

Catalyst	S _{BET} (m ² /g)	Pore Diameter (nm)	Pore Volume (cm ³ /g)
CN	22.4137	22.2745	0.1248
LMO	24.1944	20.8686	0.1262
LMO/CN-10	20.882	23.1663	0.1862

The photocatalytic materials prepared were characterized by XPS to illustrate the interface interaction between LMO and CN and clarify the valence state and chemical composition of the elements of LMO and CN. The characterization results are illuminated in Figure 3. Figure 3a uncovers that elements La, Mn, O, and C exist in LMO, and elements La, Mn, O, C, and N exist in LMO/CN-20. This reflects that CN has been present on the LMO. According to the La 3d XPS spectrum of LMO (Figure 3b), La 3d can fit the four peaks of 834.0 eV, 837.7 eV, 850.7 eV, and 854.5 eV, which belong to the characteristic peaks of 3d_{5/2} and 3d_{3/2} of La, respectively. Hence, the chemical state of La is +3 [35–37]. As observed in the Mn 2p XPS spectra of LMO (Figure 3e), significant characteristic peaks appear at 642.1 eV and 653.6 eV and are attributed to Mn 2p_{3/2} and Mn 2p_{1/2}, respectively, consistent with the previously reported literature [38,39]. In the XPS spectrum of O1s in Figure 3d, three characteristic peaks of 529.3 eV, 530.9 eV, and 532.5 eV are observed, of which, 529.3 eV comes from lattice oxygen (Mn–O) and the other two are mainly from hydroxyl. Furthermore, the characteristic peaks moved toward the direction of lower bond energy from the La 3d, Mn 2p, and O1s spectra of LMO and LMO/CN-20. This would be

the increased electron concentration and enhanced electron shielding effect induced by the heterogeneous structure formed by LMO and CN, which was consistent with the previous reports [40,41].

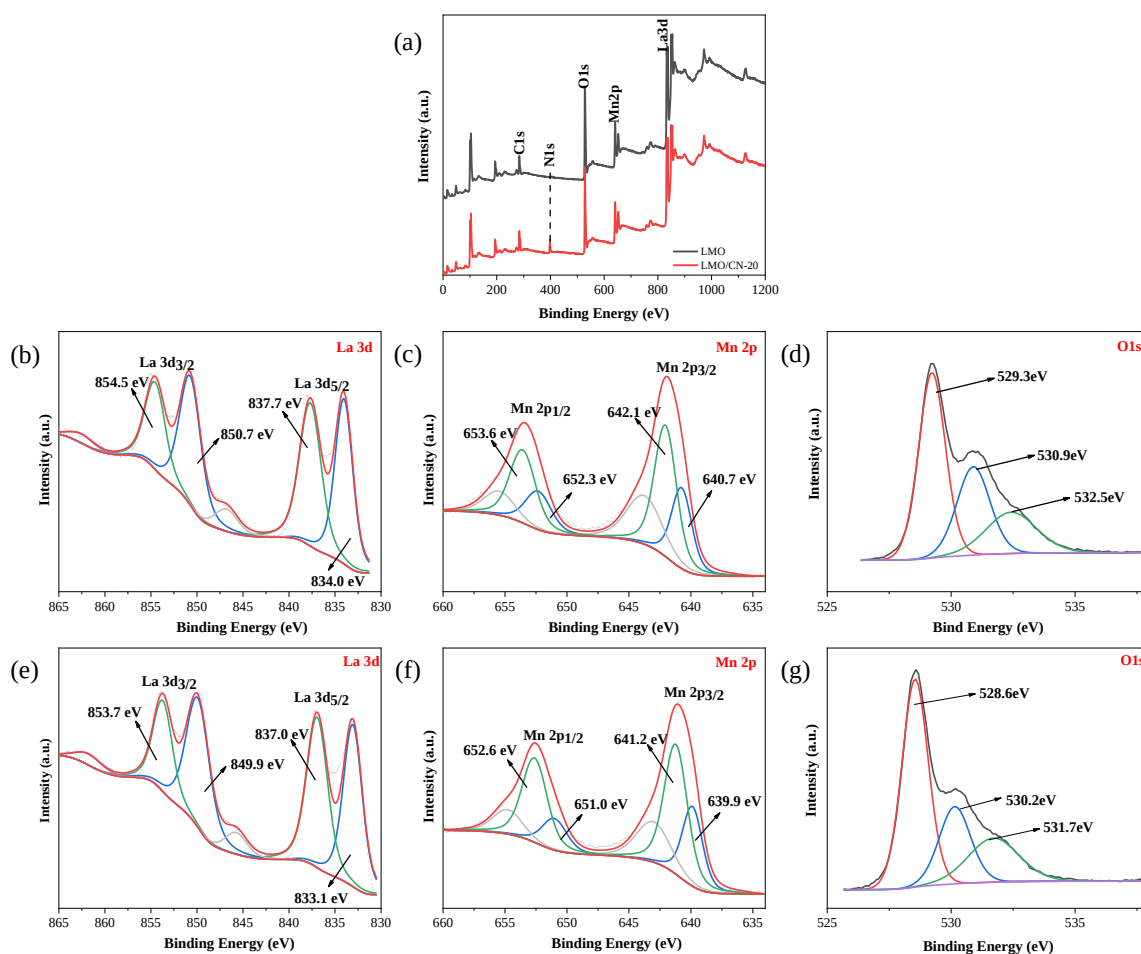


Figure 3. XPS spectra of LMO and LMO/CN-20 (a), LMO La 3d (b), Mn 2p (c), O1s (d); La 3d (e), Mn 2p (f), O1s (g) of LMO/CN-20.

FT-IR is an effective method for the qualitative identification of substances. In this experiment, the prepared composite materials were characterized by FT-IR. The characterization results are provided in Figure 4a. The infrared spectrum of pure CN reveals noticeable absorption peaks at 1248 cm^{-1} , 1335 cm^{-1} , 1414 cm^{-1} , and 1635 cm^{-1} , which may be caused by the stretching of aromatic type C=N and heterocyclic C-N, which is consistent with the literature reports [42–44]. Moreover, the characteristic peak at 811 cm^{-1} is provoked by the tri-s-triazine characteristic respiratory pattern. Concerning pure LMO, there is a strong absorption peak at 618 cm^{-1} , which could be related to the stretching vibration of the Mn-O bond. The infrared spectrum of the LMO/CN composite catalyst demonstrates the corresponding bands in LMO and CN, implying that the composite catalyst of LMO and CN is successfully synthesized, consistent with the results of previous analyses.

The UV–vis DRS was characterized to further understand the effect of the photore-sponse domain of the composite catalyst on the degradation reaction. The characterization results are illustrated in Figure 4b. It can be observed that the absorption edge of pure LMO is about 460 nm, corresponding to the bandgap excitation of LMO [45,46]. The catalysts had strong UV absorption, and a red shift occurred in the composite catalysts. Besides, the photocatalytic performance of all the composites is enhanced compared with pure LMO, which may be the composite effect of LMO and CN. This action would lead to the separation of

the photogenerated carrier and hence improve its photocatalytic performance. With the increasing CN, the absorption intensity of LMO/CN gradually increases, indicating that a load of CN significantly reinforces the visible light absorption capacity of LMO, contributing to more photogenerated electron holes and finally improved photocatalytic activity.

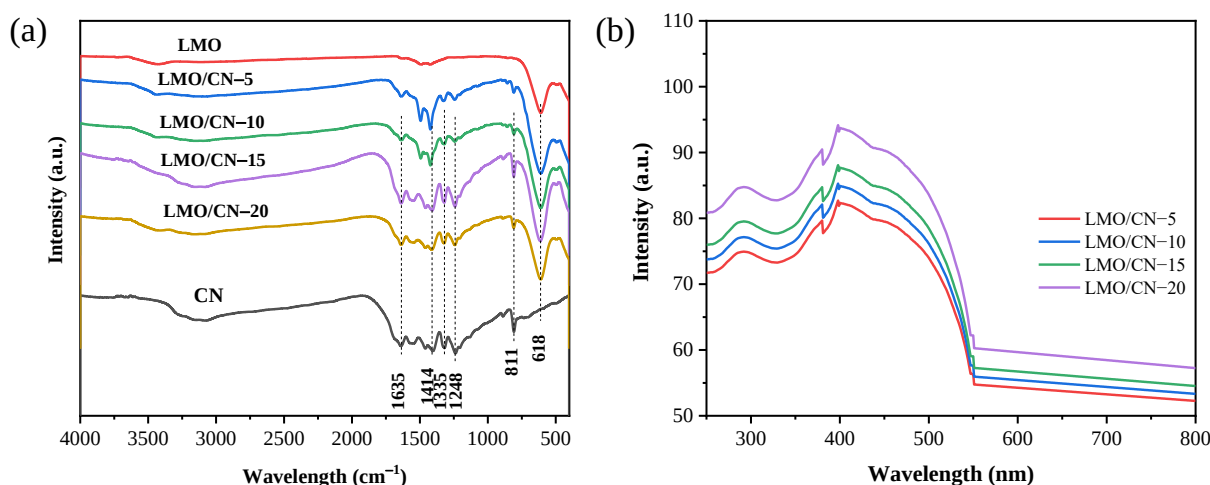


Figure 4. FT-IR spectra of CN, LMO, LMO/CN- x ($x = 5, 10, 15, 20$) (a) and UV-vis DRS spectra of LMO, LMO/CN- x ($x = 5, 10, 15, 20$) (b).

Generally, the activity of photocatalysts is closely associated with the separation and transport capacity of photoexcited carriers [47]. Therefore, the LMO/CN composites were characterized by PL and EIS to further understand the separation and recombination of photoluminescence electron holes on LMO/CN composites. The characterization results are presented in Figure 5. Figure 5a shows the PL spectra of pure LMO and LMO/CN composites. Theoretically, the higher the intensity of PL, the faster the photogenerated carrier recombination rate, and the worse its photocatalytic efficiency [42]. As revealed in Figure 6a, pure LMO has the highest PL strength, and the PL strength of composite catalyst decreases with the load of CN. This verifies that the introduction of CN can significantly reduce the recombination of photogenic hole pairs. Additionally, LMO/CN-10 has the lowest PL intensity, unveiling that the heterogeneous structure of the catalyst effectively promotes charge separation and inhibits the recombination of electron-hole pairs. Thus, it has excellent photocatalytic activity. However, more CN load is not always better considering that the PL strength of LMO/CN-20 composites is immediately higher than that of other composites when the CN load reaches 20%. This suggests that excess CN loading may also contribute to the recombination of photogenic electron holes.

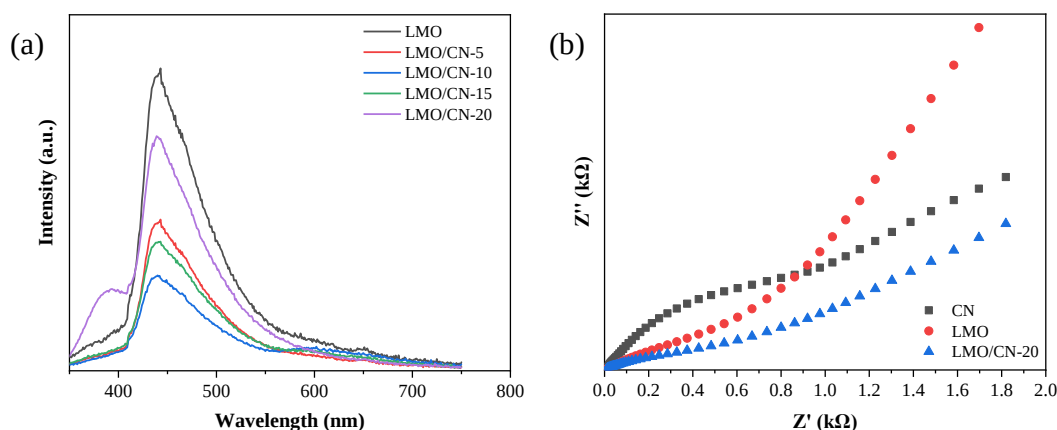


Figure 5. PL of LMO, LMO/CN- x ($x = 5, 10, 15, 20$) (a) and EIS of CN, LMO, LMO/CN-10 (b).

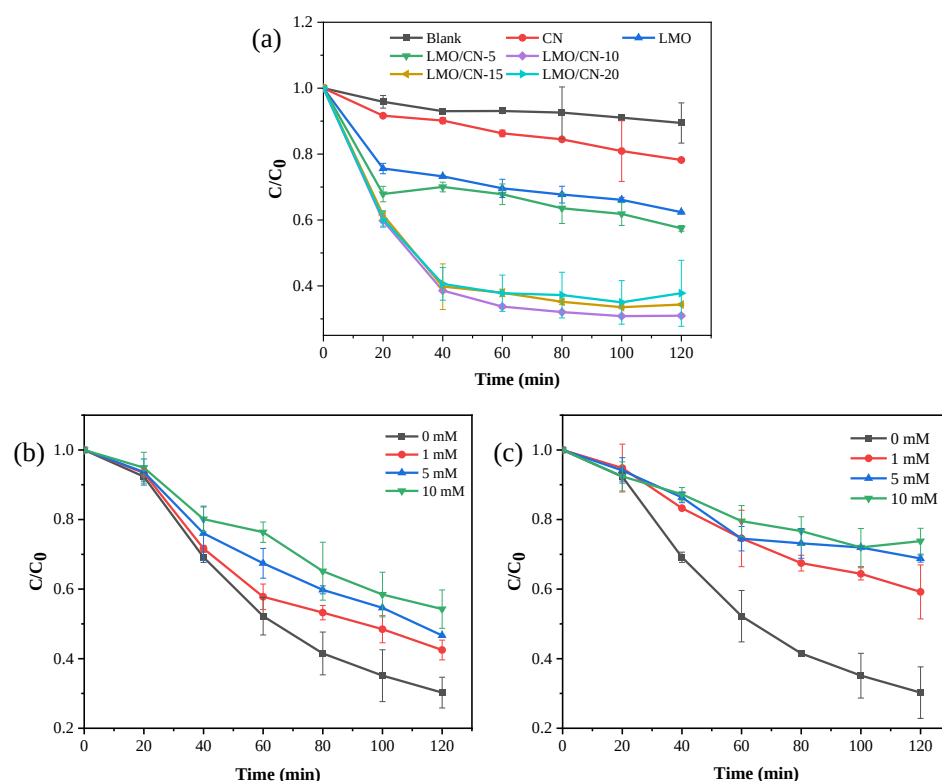


Figure 6. The TC degradation efficiency of CN, LMO, LMO/CN-X ($x = 5, 10, 15, 20$) (a), the effect of Cl^- on TC degradation efficiency (b), and CO_3^{2-} on TC degradation efficiency (c).

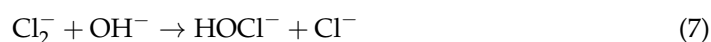
Figure 5b provides the EIS of CN, LMO, and LMO/CN-10. The resistance value of charge transfer is estimated according to the fitting of the Nyquist diagram and equivalent circuit diagram. In this way, the electrode condition of resistance can be directly reflected by the radius of the Nyquist semicircle [48]. The smaller the Nyquist semicircle radius, the smaller the resistance value of the catalyst, and the higher the separation efficiency of the photogenerated electron–hole pairs. As observed in Figure 5b, LMO has the largest resistance value, followed by CN, and LMO/CN-10 has the smallest ring radius, which is considerably lower than that of CN and LMO. These results reveal that LMO/CN-10 has good electrical conductivity and fast electron transfer performance, which can improve the photocatalytic performance of LMO/CN-10. Yuan reported that the combination of CN and ZnO effectively improved the electron transfer performance of the reaction system owing to the change in surface properties and pore structure of the catalyst after the combination [49]. This result is also consistent with PL analysis.

3.2. Photocatalytic Performance for TC Degradation

With TC as the target pollutant in this experiment, the degradation efficiency of different composites on TC was compared under visible light $\lambda > 420$ nm to investigate the photocatalytic performance of LMO/CN composites. The photocatalytic degradation efficiency of TC without catalyst, pure CN, pure LMO, and LMO/CN was managed under the same experimental conditions. After the adsorption equilibrium was achieved in the dark condition, the illumination experiment was performed, as illustrated in Figure 6a. The degradation rate of TC hardly changed when no catalyst was added. In other words, the photodegradation of TC itself can be ignored, TC's molecular structure was relatively stable under visible light irradiation, and the decrease of TC concentration was induced by photocatalysis. With the addition of catalyst, the degradation rates of CN, LMO, LMO/CN-5, LMO/CN-10, LMO/CN-15, and LMO/CN-20 on TC were 20%, 30%, 37%, 70%, 65%, and 60%, respectively. The photocatalytic activity of the catalyst combined with CN and LMO was higher than that of a single catalyst due to the synergistic action of CN and LMO

to form heterojunctions between the interfaces of different components. This effectively improved the formation of photogenerated holes and promoted the separation efficiency of photogenerated carriers and holes. Among them, the photodegradation efficiency of LMO/CN-10 was 2.3 and 3.5 times that of LMO and CN, indicating that the combination of LMO and CN effectively improved the photocatalytic performance. However, the more CN load was not the better. The photocatalytic performance of the LMO/CN-20 catalyst was lower than that of LMO/CN-10 and LMO/CN-15 when the CN load reached 20. This implied that proper CN loading was conducive to the formation of more efficient heterostructures and the transfer and separation of charge carriers at the heterojunction. Additionally, excessive CN may lessen the energy of the effective heterointerface in the LMO/CN composite catalyst and act as the recombination center of photogenerated electrons and holes, which was not favorable for charge transfer and separation and resulted in poor photocatalytic performance, in line with previous literature [50,51]. In conclusion, the construction of Z-scheme LMO/CN heterojunction significantly strengthened the photocatalytic activity of LMO, while a load of CN was the key to obtaining the optimal photocatalytic efficiency of the composites.

Cl^- is one of the most common anions in actual water bodies. Generally, hydroxyl radicals can oxidize halogen ions (such as Cl^-) into less reactive chlorine groups or hypochlorite potential and can react with organic materials to form insoluble chlorides [26]. CO_3^{2-} can be used not only as a pH buffer to adjust solution pH but also as a scavenger to clear $\cdot\text{OH}$ in water. Therefore, it has a vital influence on TC degradation in photocatalytic systems. Since the presence of anions in aquaculture water is inevitable, the effects of two anions, Cl^- , and CO_3^{2-} on TC degradation efficiency were explored in our study. The experimental results are presented in Figure 6b,c. Figure 6b demonstrates that the TC removal rate decreases with the increase in chloride ion concentration. The TC removal rate decreases from 71% to 48% as the chloride ion concentration increases from 0 mM to 10 mM. This is because chloride ions react with hydroxyl radicals in solution to generate reaction products with lower catalytic activity, leading to overall catalytic activity reduction and TC removal rate decrease. The reaction equation is [52]:



Since TC mainly exists as neutral molecule, chloride ions will generate HOCl in water after the addition of chloride ions according to the above equations and the TC solution will be acidic, which may lead to decrease in the concentration of OH^- in water. The concentration of $\cdot\text{OH}$ will also decrease, and this can finally lead to decrease of the TC removal rate.

As suggested in Figure 6c, the removal rate of TC decreases significantly with the increase in concentration of carbonate ions. The removal rate of TC decreases from 75% to 28% as the concentration of carbonate ions increases from 0 mM to 10 mM, owing to the

reaction of carbonate with $\cdot\text{OH}$ to form $\text{CO}_3^{\cdot-}$ in the photocatalytic system. The carbonate ions are hydrolyzed to form OH^- after carbonate ions are added to the solution, which can result in the increase of pH in water. With the increase of the dosage concentration, pH of the solution gradually will be increased and the absorption of LMO/CN-10 is inhibited. The photogenerated holes and OH^- are more likely to form $\cdot\text{OH}$, which leads to the decrease of the content of photogenerated holes in this system. Hydroxy radicals become the dominant factor. Considering that the redox potential of $\text{CO}_3^{\cdot-}$ ($E^0 = 1.78 \text{ V}$) is significantly lower than that of $\cdot\text{OH}$ ($E^0 = 2.5 \text{ V}$), the catalytic activity is weakened [51].

In addition to its photocatalytic performance, stability is also a key factor to be considered. Therefore, the experiment was repeated four times using LMO/CN-10 under the same conditions. The photocatalyst was centrifugally collected from the reaction mixture and then rinsed three times with deionized water and ethanol to remove excess TC solution after each experiment. After washing, it was dried in the oven at 105°C for 12 h, and then a new round of TC solution was added to start the next cycle experiment. The experimental results are rendered in Figure 7a. After four cycles, the photocatalytic degradation efficiency of LMO/CN-10 remained at about 71%. The degradation efficiency may be lowered because of the inevitable weight loss in the process of catalyst recovery. Figure 7b depicts the XRD patterns of LMO/CN-10 before and after the cyclic experiment. Furthermore, the XPS of LMO/CN-10 after four cycles (Figure 8) showed that the characteristic peaks of La 3d, Mn 2p, and O1s were a little weaker than those before cycle, and the characteristic peaks moved toward the direction of higher bond energy. The results showed that there was no significant change in the chemical properties of the samples after circulation. The results demonstrate no significant difference between the structure of LMO/CN-10 after cycling and the original composite material. The cyclic experiment results suggest that the LMO/CN-10 composite has good stability.

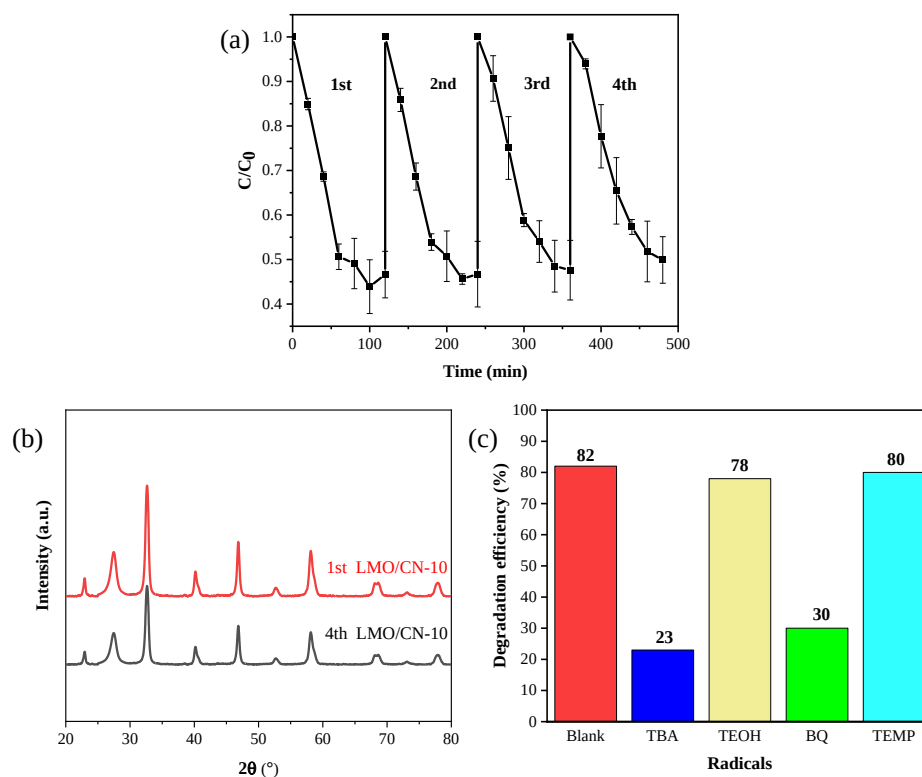


Figure 7. Photocatalytic degradation experiment of TC by LMO/CN-10 (a), XRD pattern of LMO/CN-10 before and after four cycles of reaction (b), and effects of adding different scavengers on TC degradation by LMO/CN-10 (c).

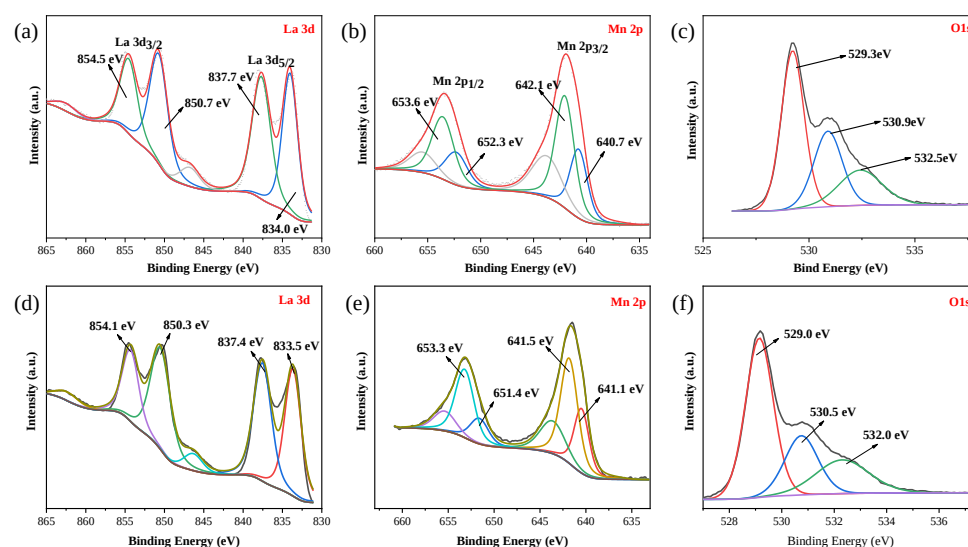


Figure 8. XPS of LMO/CN-10 before (a–c) and after (d–f) four cycles of TC degradation.

3.3. Possible Photocatalytic Mechanism

With the purpose of understanding the mechanism of photocatalysis, LMO/CN-10 composites were subjected to free radical trapping experiments to identify the active oxidation species produced by photocatalysis. In this experiment, TEOH (1 mM), BQ (1 mM), TBA (1 mM) and TEMP (1 mM) were used as scavengers for h^+ , O_2^- , $\cdot OH$ and 1O_2 , respectively [53]. The results of the capture experiment are exhibited in Figure 7c. As observed in the figure, the removal rate of TC decreases from 82% (Blank) to 30% (BQ), 78% (TEOH), 23% (TBA), and 80% (TEMP) after the addition of a trapping agent in the reaction system. Thus, O_2^- and h^+ are the main active species in the catalytic reaction. In addition, the band structure of pure CN and LMO was analyzed in this study to better understand the photocatalytic mechanism of LMO/CN composite catalysts. Generally, the energy band of photocatalysis can be calculated by [54]:

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (9)$$

where A , α , “ ν ”, E_g , and h represent a proportionality constant, absorption coefficient, light frequency, band gap energy, and Planck constant, respectively. The value of n was determined by the type of optical transition of semiconductors ($n = 1$ for direct transition and $n = 4$ for indirect transition). Since both pure CN and LMO are direct transitions, $n = 1$. According to the relationship between $(\alpha h\nu)^2$ and photon energy ($h\nu$), the band gap of pure CN and LMO is 2.68 eV and 1.94 eV according to previous research, respectively [55]. Additionally, the edge potential of the conduction band (CB) and valence band (VB) of the photocatalyst can be calculated by [56,57]:

$$E_{VB} = X - E_e + 0.5E_g \quad (10)$$

$$E_{CB} = E_{VB} - E_g \quad (11)$$

where E_{CB} denotes the CB edge potential; E_{VB} signifies the VB edge potential; X represents the absolute electro-negativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms; E_e stands for the energy of free electrons on the hydrogen scale (about 4.5 eV); E_g is the band gap energy of the semiconductor. X of CN is 4.72 eV [58], the absolute electronegativity of Mn is 3.72 eV, the absolute electronegativity of La is 3.10 eV, and the absolute electronegativity of O is 7.54 eV [59]. Thus, the calculated X of LMO is 5.48 eV. According to the above formula, the E_{CB} and E_{VB} values of CN are -1.12 eV and 1.56 eV, and the E_{CB} and E_{VB} values of LMO are 0.01 eV and 1.95 eV,

respectively. Therefore, CN and LMO have suitable CB and VB, which can form Z-scheme heterojunctions and lessen the recombination of optical carriers.

A direct Z-scheme mechanism was deduced based on the above experimental results to enhance the photocatalytic activity of LMO/CN, as rendered in Figure 9. Under the irradiation of visible light, electrons are excited to transition from VB to CB because of the narrow band gap between LMO and CN, and photoinduced holes are formed on VB.

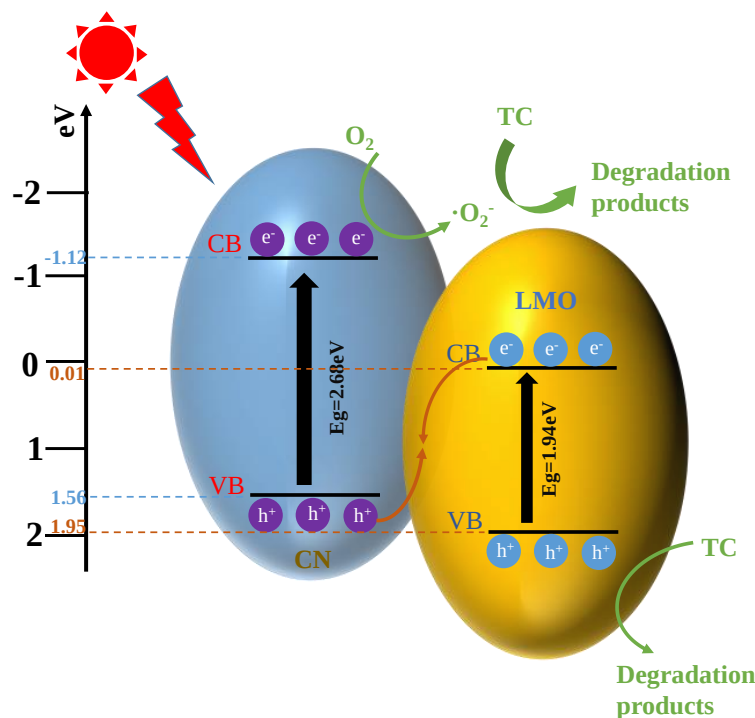


Figure 9. Schematic illustration of the charge separation and transfer process of the $\text{LaMnO}_3/\text{g-C}_3\text{N}_4$.

Excited electrons on LMO combine with electron holes formed on CN, resulting in electron accumulation on CN and hole persistence on LMO. Consequently, the strong reducibility of electrons in CB on CN and the strong oxidation of holes in VB on LMO are maintained. The accumulated electron energy on CB of CN is captured by the dissolved oxygen in the solution to produce $\cdot\text{O}_2^-$. Considering that the CB potential on CN is lower than that of $\text{O}_2/\cdot\text{O}_2^-$, TC can be oxidized and degraded. Concurrently, photogenic holes on LMO can directly oxidize and degrade TC. Therefore, the photocatalytic process is the oxidation reaction between photoholes and superoxide radicals, and the photogenerated carrier is separated in space.

4. Conclusions

In conclusion, Z-scheme heterojunction composites with different contents of $\text{LaMnO}_3/\text{g-C}_3\text{N}_4$ were successfully prepared by the sol-gel method. As revealed in experiments, the degradation rate of TC by LMO/CN-10 under visible light irradiation reached 80%, which was 2.3 and 3.5 times that of a single LMO and CN. This was induced by the formation of a Z-scheme heterostructure that combined the LMO with the CN, which contributed to the accumulation of electrons on the CN and the persistence of holes on the LMO. As a result, the strong reducing property of the electrons in CB on the CN was preserved, as well as the strong oxidation property of the holes in VB on the LMO. Additionally, the TC removal rate decreased with the increase in chloride ion concentration. The TC removal rate decreased from 71% to 48% as the chloride ion concentration increased from 0 mM to 10 mM. The removal rate of TC decreased from 75% to 28% as the carbonate concentration increased from 0 mM to 10 mM. Furthermore, it was verified that super-oxide radicals and holes played key roles in the photocatalytic system by free radical trapping

experiments. Moreover, the newly prepared photocatalytic material demonstrated good stability and recyclability. It is expected to be an effective photocatalyst for environmental water treatment.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w15081627/s1>, Figure S1: Nitrogen adsorption-desorption curve (a) and pore size distribution diagram (b) of LMO/CN-10.

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