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Preparation of 2D/2D CoAl-LDH/BiO(OH)_xI_{1-x} Heterojunction Catalyst with Enhanced Visible-Light Photocatalytic Activity for Organic Pollutants Degradation in Water

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Abstract: Hydrotalcite/bismuth solid solution (2D/2D CoAl-LDH/BiO(OH)_xI_{1-x}) heterojunction photocatalysts were fabricated through a hydrothermal route. Because of their identical layered structure and interlayer hydroxides, CoAl-LDH(2D) and BiO(OH)_xI_{1-x}(2D) form a tightly bonded heterojunction, resulting in efficient light absorption, excitation, and carrier migration conversion. At the same time, the large specific surface area and abundant hydroxyl groups of the layered structure make the heterojunction catalyst exhibit excellent performance in the photocatalytic degradation of organic pollutants. Under visible light irradiation and in the presence of 1 g/L of the catalyst, 10 mg/L of methyl orange (MO) in water could be completely degraded within 20 min, and the degradation rate of tetracycline (TC) reached 99.23% within 5 min. CoAl-LDH/BiO(OH)_xI_{1-x} still maintained good photocatalytic degradation activity of tetracycline after five cycles, and the structure of the catalyst did not change. The reaction mechanism related to the degradation of TC by photocatalytic reactions was explored in detail, and the photoexcitation of the semiconductor heterojunction, as well as the subsequent free radical reaction process and the degradation pathway of TC were clarified. This work provides a promising strategy for the preparation of efficient photocatalytic materials and the development of water purification technology.



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Keywords: antibiotics; photocatalysis; heterojunction; organic degradation; high stability; LDH; bismuth oxyhalide

1. Introduction

Tetracycline antibiotics are widely used in clinical applications, animal husbandry, etc. [1]. It has excellent inhibitory effects mainly on a variety of bacteria, viruses, spirochetes, and even protozoa [2]. However, 90% of antibiotics ingested by animals are excreted and released into environmental water bodies through groundwater, surface runoff, and other ways, leading to the development of drug resistance in native bacteria [3], posing a serious threat to environmental water bodies and human health. Therefore, the excessive use of tetracycline has caused great ecological damage [4]. In this context, choosing the right method to remove tetracycline from water has become imperative [5–7]. Among many water purification technologies, photocatalysis is a reliable, feasible, and cost-effective method. In recent years, photocatalysis has become one of the most important means for solving global environmental pollution [8,9]. The synthesis of efficient photocatalysts with broad spectral absorption [10], high charge separation efficiency [11], and high stability [12] is an urgent task. Two-dimensional (2D) nanomaterials have become a subject of interest in the field of photocatalysis because of their unique physicochemical properties (high specific surface area, strong quantum effect, surface exposure of abundant active sites, etc.) [13].

Layered double hydroxide (LDH) is a clay mineral composed of metal cations (including NH₄⁺) and hydroxide ions, which has attracted much attention because of its unique

chemical and physical properties [14,15]. LDH has the advantages of low cost, simple preparation, narrow band gap, large specific surface area, and abundant hydroxyl groups [16–18]. The unique layered structure of LDH promotes photogenerated carrier transport while avoiding nanoparticle agglomeration [15,19]. Among various LDHs, CoAl-LDH exhibits excellent photocatalytic performance because of its visible light trapping ability and suitable redox potential [20], which has attracted widespread attention and has been widely used. Bismuth-based catalysts are visible light catalysts with much better photocatalytic performance than ordinary nanocatalysts [21]. Bismuth oxyhalides (BiOX) consist of alternating layers of $[\text{Bi}_2\text{O}_2]^{2+}$ and inorganic groups [22]. It has a layered structure and can effectively separate photogenerated electron-hole pairs through an internal electrostatic field [23–25]. It is chemically stable, nontoxic, and has a suitable forbidden band gap [26,27]. The solid solution has a layered structure, hydroxides, and more abundant active sites, such as surface hydroxyl groups and oxygen vacancies [28]. Two-dimensional/two-dimensional (2D/2D) heterojunction interfaces effectively broaden the contact area between semiconductors and form a large number of charge transfer channels, which are more favorable for the transfer of photogenerated carriers [18,29]. Inspired by these advantages, this study attempts to synthesize 2D/2D CoAl-LDH/BiO(OH) $_x\text{I}_{1-x}$ heterojunction photocatalysts to improve the photodegradation efficiency of the catalysts effectively.

In this paper, CoAl-LDH/BiO(OH) $_x\text{I}_{1-x}$ was fabricated by a hydrothermal route. The physicochemical properties of CoAl-LDH/BiO(OH) $_x\text{I}_{1-x}$ were characterized and analyzed (morphology, crystal structure, structural composition, and specific surface area). In addition, tetracycline degradation tests were performed in this study to evaluate the degradation efficiency of the photocatalysts under visible light irradiation. Finally, the degradation mechanism of photocatalyst was elucidated by the photoexcitation of the semiconductor, free radical reaction process, and the degradation pathway of TC. The objectives of this study were to effectively retard the electron-hole pair complexation and maintain the maximum redox capacity of the photocatalyst, to effectively remove tetracycline and methyl orange from water under visible light, and to elucidate the photocatalytic capacity, mechanism, and potential applications of CoAl-LDH/BiO(OH) $_x\text{I}_{1-x}$.

2. Materials and Methods

2.1. Materials

The main reagents including bismuth nitrate pentahydrate, urea, sulfa dimethyl pyrimidine, doxycycline, and potassium iodide were supplied by Aladdin Reagent Co., Ltd. (Shanghai, China). Cobalt nitrate hexahydrate was purchased from Zesheng Technology Co., Ltd. (Shanghai, China). Aluminum nitrate enneahydrate, 2-chlorophenol, and tetracycline were supplied by Macklin Chemical Reagent Co., Ltd. (Shanghai, China). All the above materials were analytically pure and were not further purified at the time of use.

2.2. Characterization

X-ray diffraction (XRD) data were obtained by a Shimadzu XRD-6100 diffractometer (Shimadzu, Tokyo, Japan) using Cu K α radiation ($\lambda = 0.154178 \text{ \AA}$) to study the catalyst components with a scanning range of 5° to 90° and a scanning speed of $5^\circ/\text{min}$. Scanning electron microscopy (SEM) was performed on a scanning electron microscope (Thermo Fisher Quattro S, Thermo, Waltham, MA, USA) to observe the microstructure of the catalysts. Transmission electronic microscopy (TEM) images were recorded using a FEI Talos F200x transmission electron microscope (FEI, Hillsboro, OR, USA). X-ray photoelectron spectrometry (XPS) was determined by a Thermo Fisher Scientific K-Alpha spectrometer, and all binding energies were calibrated by the C1s peak at 284.80 eV. UV-Vis diffuse reflectance spectra (UV-Vis DRS) were carried out on a Shimadzu 3600-plus instrument. N_2 adsorption-desorption tests were carried out using a Quantachrome Autosorb-iQ analyzer (Anton Paar QuantaTec Inc., Boynton Beach, FL, USA) to study the surface area and pore structure parameters. The electron spin resonance (ESR) was obtained using a Bruker EMXnano Paramagnetic Resonance Spectrometer (Bruker, Karlsruhe, Germany).

2.3. Catalyst Preparation

First, 1.2 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was completely dissolved in 20 mL of acetic acid solution (6 mL of acetic acid mixed with 14 mL of H_2O) as solution A. Then, 0.42 g of KI was dissolved in 200 mL of ammonia solution (4 mL of ammonia mixed with 196 mL of H_2O) as solution B. Solution A was added dropwise to solution B, and the precipitates were collected after 12 h of magnetic stirring. The precipitates were washed with water to pH neutral and dried at 70 °C.

Next, 0.5 g dried solid powder was weighed and ultrasonically dispersed in 20 mL aqueous solution containing 0.032 g urea as solution C. An appropriate amount of cobalt nitrate and aluminum nitrate was dissolved in 60 mL ultrapure water as solution D. The C solution was mixed with the D solution and stirred for 30 min, transferred to a 100 mL reactor, and hydrothermally heated at 150 °C for 24 h. The solid generated was collected, washed clean, and dried to obtain the CoAl-LDH/ $\text{BiO}(\text{OH})_x\text{I}_{1-x}$ composite, referred to as CoAl-LDH/BiSS.

By adjusting the amount of cobalt nitrate and aluminum nitrate, CoAl-LDH/ $\text{BiO}(\text{OH})_x\text{I}_{1-x}$ composites with CoAl-LDH contents of 5%, 8%, 10%, 15%, and 20% were obtained, respectively. $\text{BiO}(\text{OH})_x\text{I}_{1-x}$ solid solution material, referred to as BiSS, was obtained without adding nitrate, with all other steps being consistent.

Finally, 2.91 g of cobalt nitrate and 1.88 g of aluminum nitrate were dissolved in 80 mL of ultrapure water, followed by the addition of 0.72 g of urea and stirring for 30 min. Subsequently, the mixed solution was transferred to a 100 mL reactor and reacted at a constant temperature of 150 °C for 12 h. After natural cooling, the resulting solid was collected, washed clean, and dried to obtain CoAl-LDH samples.

2.4. Photocatalytic Degradation Experiment

The photocatalytic degradation experiment was carried out in 50 mL 10 mg/L tetracycline solution and a 50 mL 10 mg/L methyl orange solution with 50 mg catalyst. The beaker was wrapped tightly with tin foil paper and placed on a magnetic stirrer, and the adsorption–desorption equilibrium was reached after 30 min of stirring protected from light. A xenon lamp was used as the light source (Beijing China Au-light Technology Co., Ltd., Beijing, China, $\lambda > 400$ nm), and 2 mL of the liquid was taken at regular intervals. The transparent liquid was filtered through a 0.22 μm filter, and then the change in tetracycline concentration in the solution was analyzed by high-performance liquid chromatography (Agilent 1260, Agilent, Santa Clara, CA, USA). For free radical trapping experiments, tert-butanol (t-BuOH), p-benzoquinone (BQ), disodium ethylenediaminetetraacetic acid (EDTA-2Na), and $\text{K}_2\text{S}_2\text{O}_8$ were added as active species scavengers to the reaction solution. In the stabilization experiments, the photocatalysts were recovered and added to the new cycle.

2.5. Optical Performance Testing

In this three-electrode system, ITO conductive glass was used as the working electrode, platinum wire as the counter electrode, saturated calomel electrode as the reference electrode, and 0.1 M Na_2SO_4 solution as the electrolyte. The excitation light source was a xenon lamp, which was carried out on a CHI660E workstation (Shanghai Chenhua Apparatus Co., Ltd., Shanghai, China). The transient photocurrent (I–t) curve, electrochemical impedance spectroscopy (EIS) curve, and Mott–Schottky equation of the prepared materials were tested.

3. Results and Discussion

3.1. Structure, Morphology, and Surface Properties

The XRD patterns of BiSS, CoAl-LDH, and the 5~15% composites are depicted in Figure 1. In the BiSS spectrum, it can be seen that the characteristic peak of the layered material appears at the 2θ 12° position. CoAl-LDH has four characteristic peaks located at 11.5°, 23.2°, 34.6°, and 38.8°, corresponding to the (003), (006), (012), and (015) crystal

planes, which conforms to the standard card [19] (JCPDS PDF#51–0045). This demonstrated the successful synthesis of CoAl-LDH. The diffraction peak of CoAl-LDH in the composite at the 2θ value of 38.8° is covered by the diffraction peak of BiSS. The composites with different proportions have similar peak shapes and consistent peak positions but different peak intensities. The results show that 10% CoAl-LDH/BiSS has the highest peak intensity and the best crystallinity. All the diffraction peaks of the composites corresponded to the characteristic peaks of BiSS and CoAl-LDH, which proves that the composites were successfully synthesized.

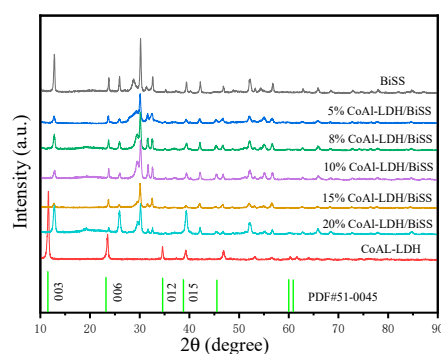


Figure 1. XRD patterns of the synthesized catalysts.

Figure 2 shows SEM images of the BiSS, CoAl-LDH, 10% CoAl-LDH/BiSS, and 15% CoAl-LDH/BiSS composites. BiSS has a rectangular layered structure and a large amount of stacking (Figure 2a). A large accumulation of nanosheets with a hexagonal structure can be seen in Figure 2b, which is a typical feature of CoAl-LDH. Figure 2c shows the morphology of the composite containing 10% CoAl-LDH. It can be observed that obvious LDH nanosheets are attached to the surface of BiSS and dispersed inside it, and LDH and BiSS are tightly bonded. When the content of hydrotalcite increases, independent hydrotalcite nanosheets appear in the composite (Figure 2d).

To further investigate the microscopic and structural morphology of the 10% CoAl-LDH/BiSS sample, TEM analysis was performed. The results are shown in Figure 3. The photocatalyst is composed of CoAl-LDH nanosheets and BiSS nanosheets and forms a heterogeneous structure. As shown in Figure 3a,b, the rectangular block is considered to be BiSS nanosheets, and the fine irregular nanosheets are considered to be CoAl-LDH nanosheets. The CoAl-LDH nanosheets and BiSS are tightly bound together, and the two sheet structures are stacked layer by layer. According to the electron-selected area diffraction results, it is found that the crystalline spots present a diffraction ring pattern, indicating that the fabricated catalyst has a polycrystalline structure [30] (Figure 3c). Two kinds of uniformly distributed lattice stripes can be clearly found in the TEM images. The lattice fringes of the samples are shown in Figure 3d–f. The results show that the lattices of CoAl-LDH and BiSS can be observed on 10% CoAl-LDH/BiSS, where 0.2766 nm corresponds to the (012) crystalline plane, which also corresponds to the results of the XRD diffraction peaks. The results of the TEM tests indicate that CoAl-LDH and BiSS were successfully synthesized and well-composited together with good contact.

As depicted in Figure 4, BiSS, CoAl-LDH, and 10% CoAl-LDH/BiSS display obvious IV isotherms with H₃-type hysteresis loops, indicating that both materials have mesoporous features. The S_{BET} of 10% CoAl-LDH/BiSS ($27.903 \text{ m}^2/\text{g}$) is larger than that of BiSS ($25.384 \text{ m}^2/\text{g}$). The increase in specific surface area of 10% CoAl-LDH/BiSS could be attributed to the unique architecture of CoAl-LDH. The pore sizes of BiSS, CoAl-LDH, and 10% CoAl-LDH/BiSS are 3.056 nm, 3.830 nm, and 3.820 nm, whereas the corresponding pore volumes are 0.122, 0.123, and $0.379 \text{ cm}^3/\text{g}$, respectively. The larger specific surface area and pore volume facilitated the adsorption of pollutants and provided more active sites, thereby obtaining better photocatalytic performance.

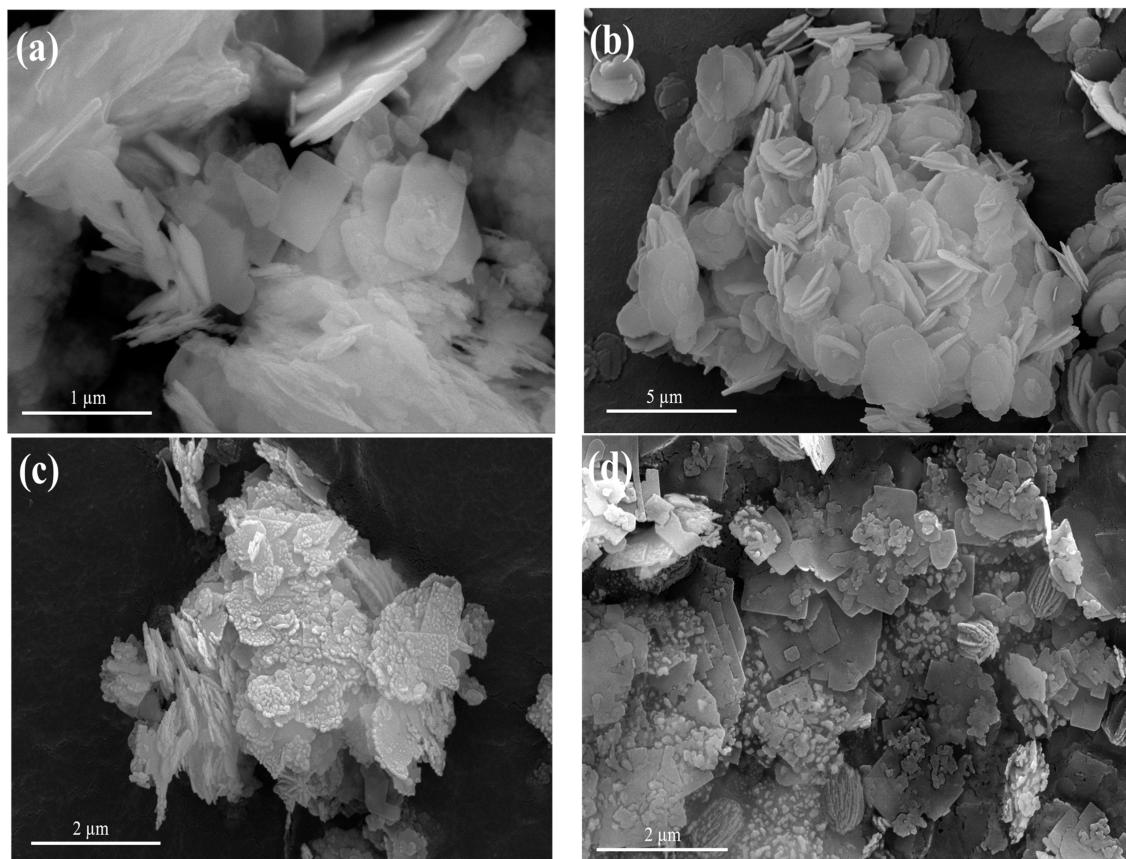


Figure 2. SEM images of (a) BiSS, (b) CoAl-LDH, (c) 10% CoAl-LDH/BiSS, and (d) 15% CoAl-LDH/BiSS.

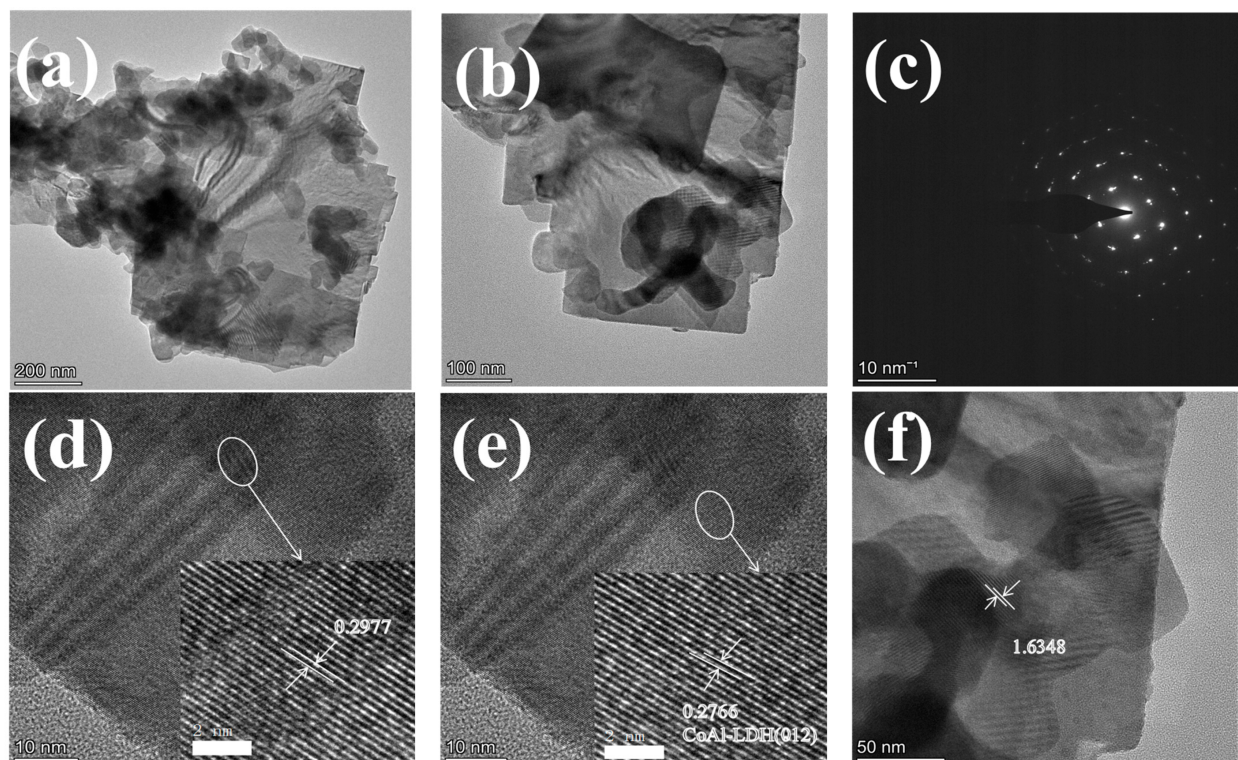


Figure 3. TEM (a,b,f), SAED (c) and HRTEM (d,e) images of 10% CoAl-LDH/BiSS.

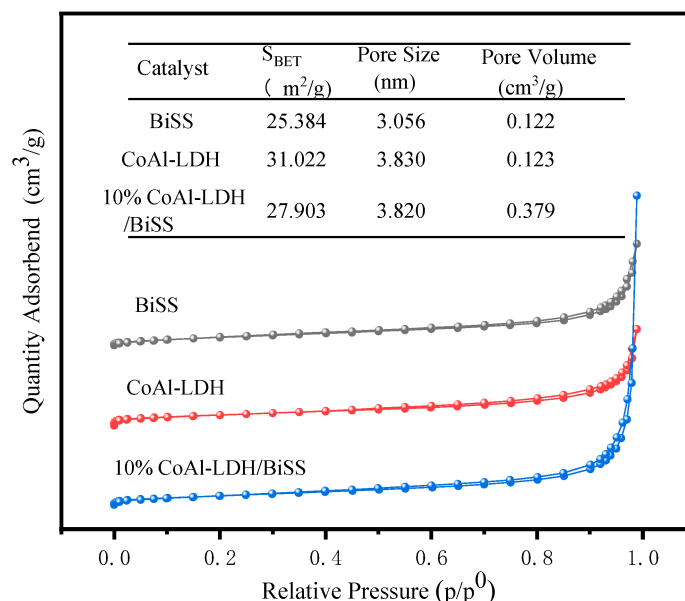


Figure 4. N_2 adsorption–desorption isotherm and the corresponding S_{BET} , pore size, and pore volume of the BiSS, CoAl-LDH, and 10% CoAl-LDH/BiSS samples.

The chemical compositions and states of the photocatalysts and the interactions between BiSS and CoAl-LDH were investigated by XPS. The characteristic peaks of elements Co, Al, O, Bi, and I were detected in the composites (Figure 5a). High-resolution spectra of O 1s in BiSS, CoAl-LDH, and 10% CoAl-LDH/BiSS are shown in Figure 5b. The O 1s orbitals are classified as 530.96, 531.62, and 531.48 eV. The O 1s of BiSS are attributed to low-oxygen coordination defects [31,32], and the O 1s of both LDH and composites are attributed to hydroxyl bonds [32,33]. This result is due to the fact that most of the oxygen present in CoAl-LDH is present in the form of interlayer hydroxides and affects the composite. From the high-resolution spectrum of Bi 4f (Figure 5c), it can be seen that the characteristic peaks located at 163.77 eV, 164.50 eV and 158.53 eV, 159.24 eV correspond to Bi 4f_{7/2} and Bi 4f_{5/2}, respectively, indicating the presence of Bi³⁺ [10,34]. The four characteristic peaks at 630.64 eV, 630.72 eV and 619.16 eV, 619.15 eV are attributed to I 3d_{3/2} and I 3d_{5/2}, respectively (Figure 5d), which belong to the I element [35]. The high-resolution spectra of Al in CoAl-LDH are demonstrated in Figure 5e. The characteristic peak at 73.82 eV of CoAl-LDH belongs to Al 2p, indicating that Al exists in the form of Al³⁺ [36]. In the composite, the Al 2p peak (74.27 eV) shows a significant positive shift [15] (Figure 5f). The characteristic peaks of CoAl-LDH at 781.81 eV and 797.53 eV correspond to Co 2p_{3/2} and Co 2p_{1/2}, and two satellite peaks appear at 787.11 eV and 802.85 eV, respectively (Figure 5g), which correspond to the high-spin Co²⁺ species in CoAl-LDH [36,37]. The Co peak is not easily captured because of the low content of hydrotalcite in the composite material. The change in binding energy indicates that there is a strong interfacial chemical interaction between CoAl-LDH and BiSS, which may be due to electron transfer. Compared with CoAl-LDH, the binding energy of O 1s in CoAl-LDH/BiSS is transferred to a lower energy level, and the binding energy of Al 2p is transferred to a higher energy level. Compared with the BiSS, the binding energy of I 3d in the composite catalyst CoAl-LDH/BiSS is transferred to a lower energy level, and the binding energy of O 1s and Bi 4f is transferred to a higher energy level. These results indicate that the migration of photogenerated electrons in the catalyst through the heterojunction interface conforms to the law of heterojunctions [38]. The formation of the CoAl-LDH/BiSS heterojunction catalyst was proven.

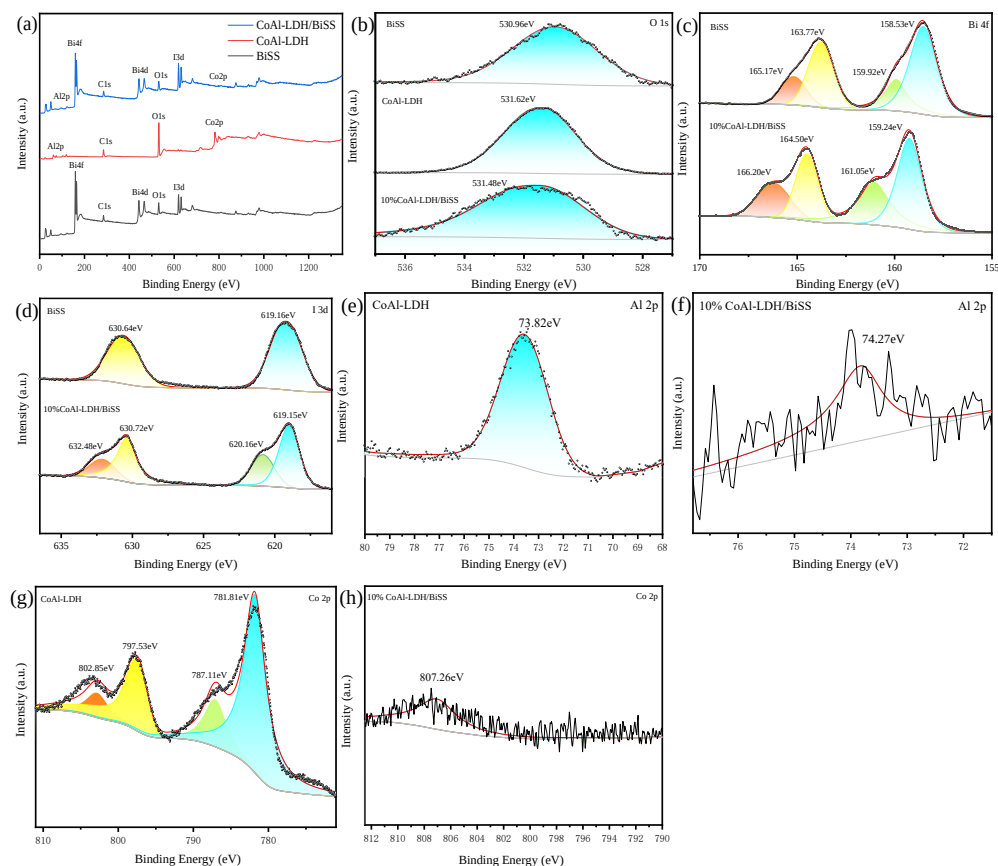


Figure 5. XPS high-resolution spectrogram of CoAl-LDH, BiSS, 10% CoAl-LDH/BiSS ((a) full spectra, (b) O 1s, (c) Bi 4f, (d) I 3d, (e,f) Al 2p, and (g,h) Co 2p).

3.2. Photocatalytic Degradation Activity

Photocatalytic degradation experiments were carried out at room temperature. It was observed that the photocatalytic degradation of the composites improved compared with that of pure BiSS, and the catalytic activity was optimal for 10% CoAl-LDH/BiSS. As shown in Figure 6a, in the methyl orange degradation experiment, 10% CoAl-LDH/BiSS was completely degraded in 20 min, and the degradation rate of pure BiSS was only 76.80%. The degradation of tetracycline by the composite material could reach 98.98% in three minutes, compared with 93.18% for the single BiSS (Figure 6b). The degradation reaction follows pseudo-first-order kinetics (Equation (1)):

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (1)$$

where C is the concentration of pollutants at time t , C_0 is the initial concentration of pollutants, and k is the pseudo-first-order kinetic rate constant (min^{-1}).

Figure 6c,d show the fitting results for photocatalytic degradation. Tables S1 and S2 display the reaction rate constants (k) and correlation coefficients (R^2). The R^2 values were all greater than 0.9, indicating a good fit. From the analysis of the reaction rate constant, it can be seen that the first-order reaction rate constants of the 10% CoAl-LDH/BiSS catalyst for the degradation of methyl orange and tetracycline were the largest at 0.1563 min^{-1} and 1.3381 min^{-1} , respectively. Compared with the BiSS catalyst, they increased by 1.88 times and 1.70 times, respectively. Table S3 presents a comparative table of the results of the degradation of contaminants in water using different catalysts, including removal efficiency and rate constant, to illustrate the advantages of the catalysts developed in this work. Compared with the previous study, our work in the case of photocatalytic activity is satisfactory, and the rate constant is the largest.

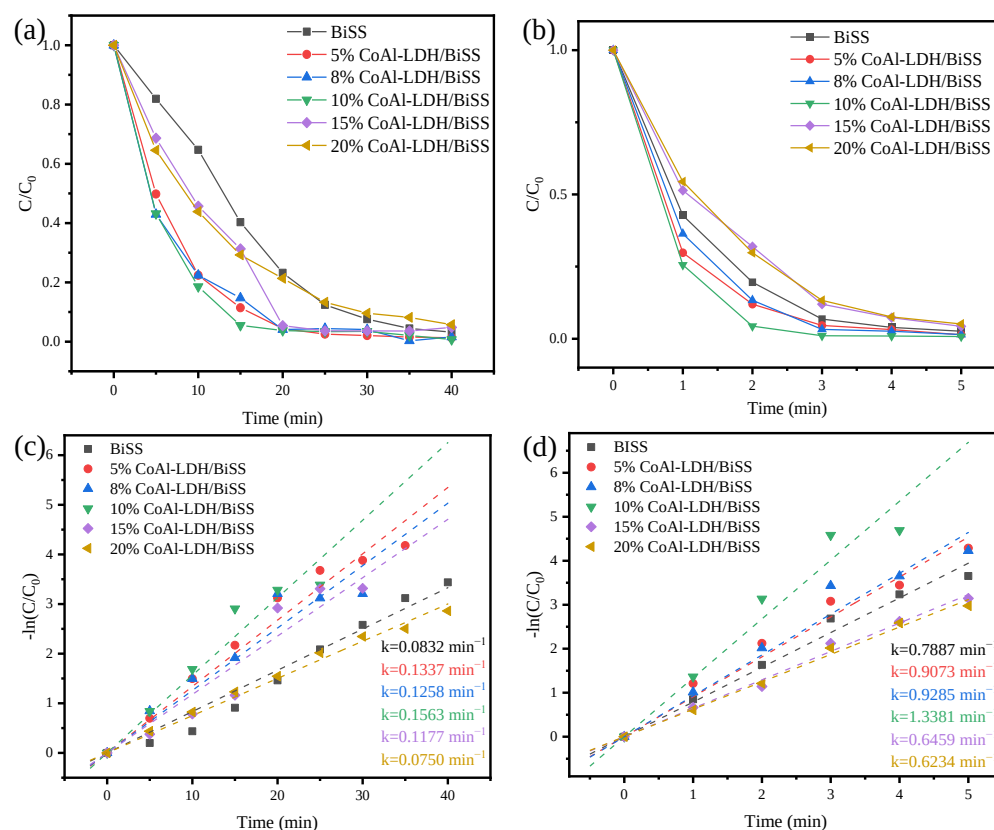


Figure 6. Complex-catalyst degradation: (a) curve of MO (50 mL, 10 mg/L), (b) TC (50 mL, 10 mg/L) degradation curve, (c) reaction rate constants associated with MO degradation, and (d) reaction rate constants associated with TC degradation.

3.3. Effect of Different Reaction Conditions on Photocatalytic Degradation Activity

The effect of different catalyst dosages on the photocatalytic degradation efficiency is shown in Figure 7a. The degradation rates of tetracycline were 77.99%, 86.13%, 90.17%, 99.23%, 84.97%, and 92.21% at catalyst dosages of 10 mg, 20 mg, 40 mg, 50 mg, 60 mg, and 70 mg, respectively. This illustrates that the photocatalytic effect increases with the amount of catalyst, as more catalyst provides more active sites. The best catalytic effect is obtained when the amount of catalyst is 50 mg. However, when the catalyst exceeds 50 mg, the catalytic efficiency decreases instead, which may be due to some catalyst agglomerates in the photocatalytic process, which affects the activity of the catalyst. The effect of the antibiotic concentration on the degradation efficiency is exhibited in Figure 7b. The degradation efficiency decreased from 99.31% to 79.94% with an increase in tetracycline concentration. The active sites on the catalyst surface were occupied by a high concentration of TC molecules, which reduced the generation of active groups and decreased the degradation efficiency. However, the catalytic effect of the catalyst was still considerable, indicating that the catalyst is applicable to high concentrations of tetracycline but more suitable for the degradation of low concentrations of antibiotics.

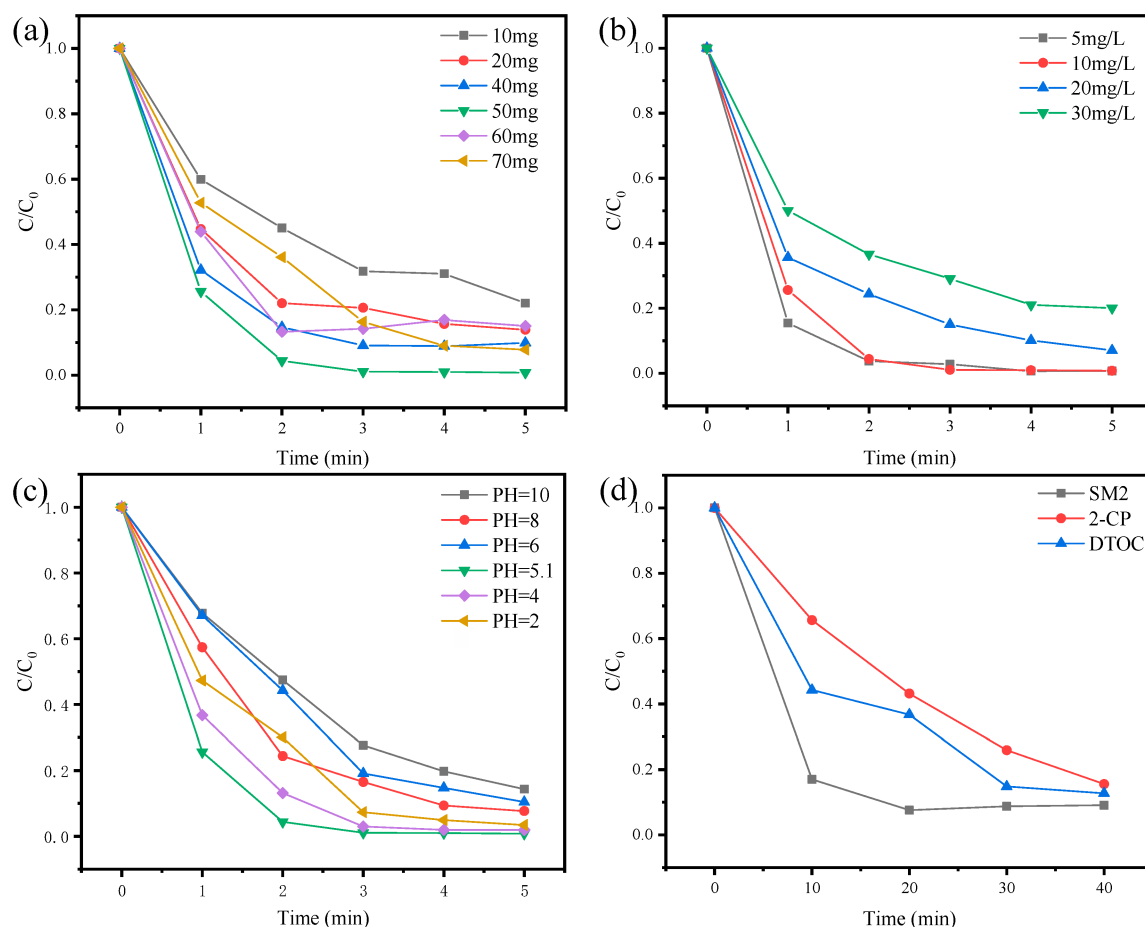


Figure 7. Effect of different reaction conditions on TC (50 mL, 10 mg/L) degradation: (a) dosage of catalyst, (b) initial concentrations of TC, (c) pH, and (d) different kinds of antibiotics (50 mL, 10 mg/L).

In order to evaluate the effect of the initial solution pH on the degradation performance, photocatalytic activity experiments with CoAl-LDH/BiSS were carried out at different initial pH values of the reaction solution. The initial pH of the reaction solution was adjusted to five different values of 2, 4, 6, 8, and 10 by adding appropriate amounts of HCl or NaOH solution. Without the addition of HCl or NaOH solution, the initial pH of tetracycline was 5.1. The catalyst exhibited the highest TC degradation activity (99.23%) at pH 5.1, and the removal efficiency of tetracycline was almost independent of pH. Still, it showed better catalytic activity in a weakly acidic environment (Figure 7c). The degradation rates of sulfa dimethyl pyrimidine (SM2), doxycycline (DTOC), and 2-chlorophenol (2-CP) were 90.95%, 87.29%, and 84.47%, respectively, after 40 min of reaction (Figure 7d), which shows that 10% CoAl-LDH/BiSS has good degradation activity for different types of antibiotics.

3.4. Stability of CoAl-LDH/BiSS

The stability of the catalyst was checked by the cycling test, in which the efficiency of the catalyst decreased from 99.23% to 88.72% after five cycles, which was only 10.51% lower, indicating that the catalyst has excellent stability (Figure 8a). The XRD pattern and SEM image after five cycles of the tetracycline degradation experiment are represented in Figure 8b. After the photodegradation cycling experiments, the XRD pattern and SEM image of 10% CoAl-LDH/BiSS did not change significantly, which also indicated the good stability of this catalyst.

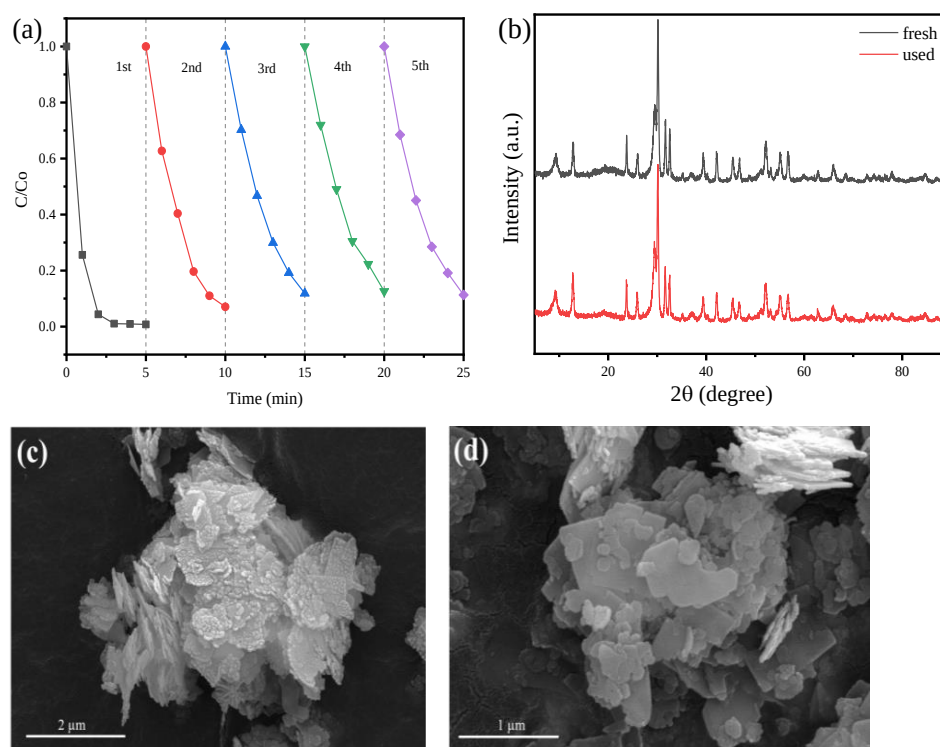


Figure 8. (a) Cyclic experiment of 10% CoAl-LDH/BiSS photocatalytic degradation of TC (50 mL, 10 mg/L), (b) XRD pattern before and after catalysis, and (c,d) SEM images of 10% CoAl-LDH/BiSS before and after catalysis.

3.5. Mechanism of Photocatalytic Degradation

Photocatalytic degradation involves many processes, such as the generation of electrons and holes by semiconductors under light excitation, the transfer of photogenerated carriers, the generation of free radicals, and the degradation of organic matter. Therefore, this work investigates the relevant processes, and the specific results are as follows:

3.5.1. Photoelectric Response and Charge Separation Efficiency

Figure 9a shows the UV–vis DRS spectra of 10% CoAl-LDH/BiSS and the other two materials. It can be seen that all the catalysts exhibit good absorbance in the ultraviolet and visible light range. The absorption edges of BiSS, CoAl-LDH, and 10% CoAl-LDH/BiSS are approximately 538 nm, 594 nm, and 665 nm, respectively, indicating that all the catalysts can be excited by visible light. And 10% CoAl-LDH/BiSS has a larger range of absorption intensities and responses to light. Figure 9b depicts the transient photocurrent test results of 10% CoAl-LDH/BiSS and the other two materials. Compared with BiSS and CoAl-LDH, 10% CoAl-LDH/BiSS has a faster light response. The composite of BiSS and CoAl-LDH shows a substantial increase in the photocurrent intensity of the catalysts, which suggests that the composites have a stronger light excitation capability. As shown in Figure 9c,d, to evaluate the photogenerated charge transfer resistance in the BiSS, CoAl-LDH, and CoAl-LDH/BiSS composites, the EIS semicircle radii of the three samples are arranged as follows: BiSS > CoAl-LDH > 10% CoAl-LDH/BiSS. The smaller the radius corresponding to the circle, the smaller the resistance and the higher the separation efficiency, so the composites have a stronger photogenerated electron transfer capability. The above results show that the composite material has good light absorption ability, light excitation ability, and light-induced charge separation efficiency.

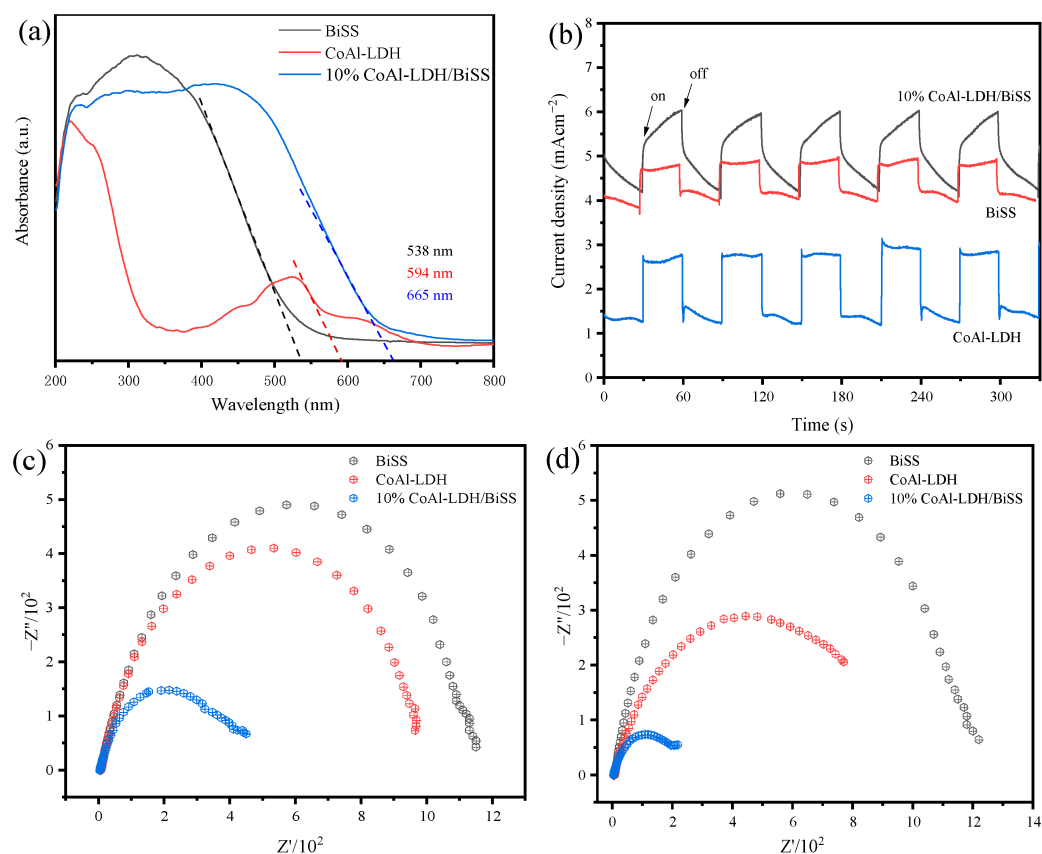


Figure 9. (a) UV-vis DRS spectra of BiSS, CoAl-LDH, and CoAl-LDH/BiSS, (b) transient photocurrents, (c) EIS under dark conditions, and (d) EIS under lighting conditions.

3.5.2. Free Radical Capture Experiment

The free radical capture experiments were carried out on the major radicals involved in the antibiotic degradation experiments. In the experiments, 1 mmol of tert-butanol (t-BuOH), p-benzoquinone (BQ), disodium ethylenediaminetetraacetic acid (EDTA-2Na), and K₂S₂O₈ were added to limit hydroxyl radicals ($\cdot\text{OH}$), superoxide radicals ($\text{O}_2^{\bullet-}$), photogenerated holes (h^+), and electron holes (e^-), respectively. Figure 10a shows that after the addition of EDTA-2Na and BQ, the photodegradation efficiency decreased to 9.66% and 69.51%, respectively. After the addition of tert-butanol (92.556%) and K₂O₂S₈ (94%), the degradation efficiency changed little compared to the system without any inhibitor (Figure 10a). The experimental results show that h^+ and $\text{O}_2^{\bullet-}$ are the main free radicals in the photolysis process. In order to further verify the types of free radicals generated during the photocatalytic process of the composite catalysts, a study was carried out using ESR. The single linear oxygen ($^1\text{O}_2$) signal of the CoAl-LDH/BiSS composite photocatalyst can be clearly detected in the light conditions (Figure 10b), but the signal of the superoxide radical ($\text{O}_2^{\bullet-}$) can only be weakly detected (Figure 10c). The observed intensity ratios of the TEMP- $^1\text{O}_2$ and DMPO- $\text{O}_2^{\bullet-}$ signals are 1:1:1 and 1:2:2:1, respectively. The characteristic peaks of the TEMP- $^1\text{O}_2$ and DMPO- $\text{O}_2^{\bullet-}$ signals were not detected in the dark. These results indicate that under dark conditions, there was no production of $^1\text{O}_2$ or $\text{O}_2^{\bullet-}$, and the photocatalytic degradation of tetracycline solution under visible light produced $^1\text{O}_2$ and $\text{O}_2^{\bullet-}$ reactive substances, similar to the results of the capture experiments described above. BMPO- $\cdot\text{OH}$ signals were not detected for the CoAl-LDH/BiSS composite photocatalysts under either light or dark conditions (Figure 10d). As shown in Figure 10e, TEMPO- h^+ exhibits three signal peaks, but the intensity of the h^+ produced in the system under light conditions is weaker than under dark conditions. This is because the excitation of h^+ by light will produce adducts with weaker signals [39].

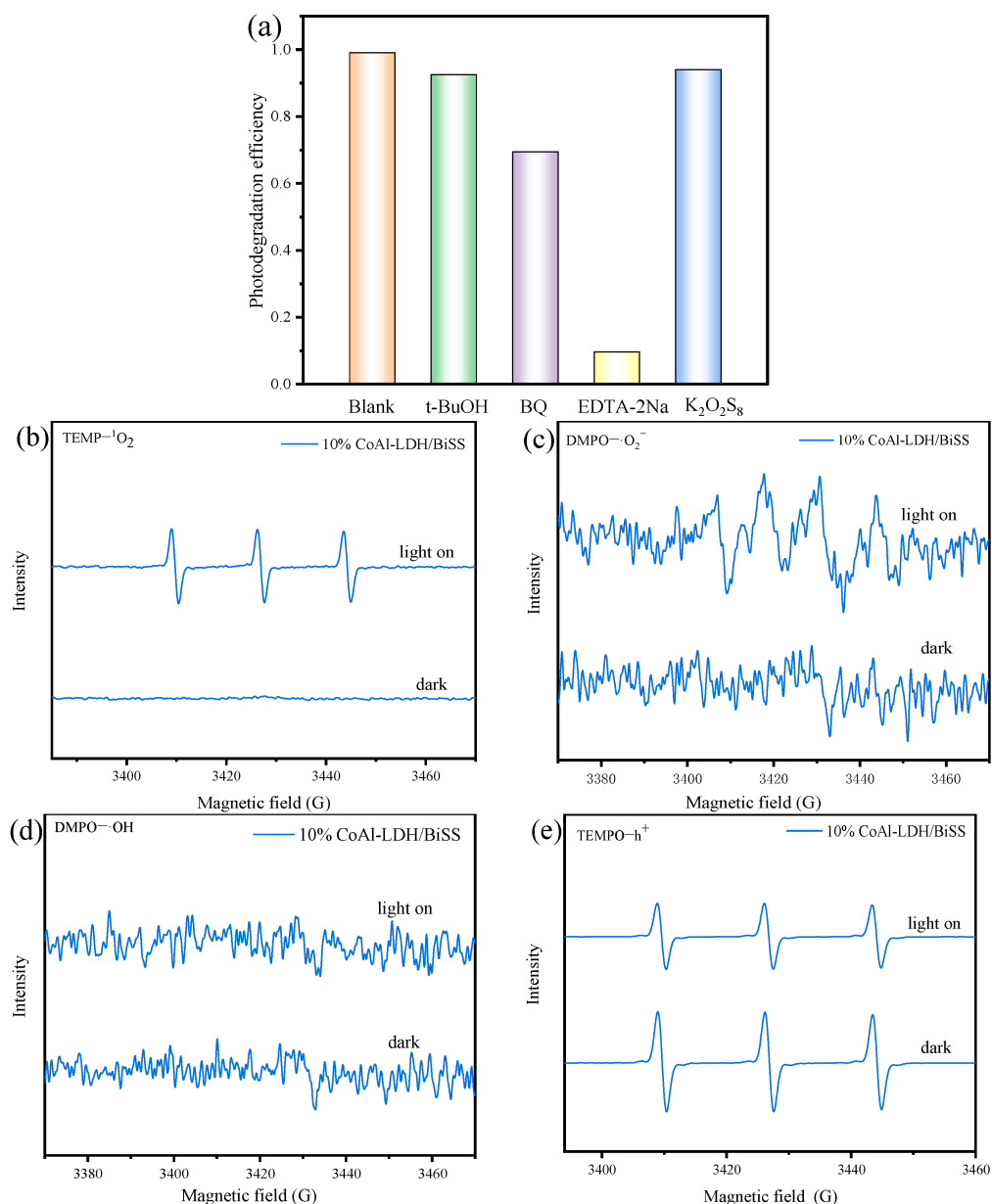


Figure 10. (a) Plot of the photodegradation efficiency versus scavengers and ESR spectra of (b) TEMPO-¹O₂, (c) DMPO-O₂^{•-} adducts, (d) DMPO-OH adducts, and (e) TEMPO-h⁺ for 10% CoAl-LDH/BiSS.

3.5.3. Band Structure Calculation

Tauc plots of BiSS and CoAl-LDH were obtained via the Kubelka–Munk method (Figure 11a), and the optical energy band gaps (E_g) were measured to be 2.0 eV and 2.17 eV for BiSS and CoAl-LDH, respectively. Mott–Schottky curves were measured to obtain the flat-band potentials of the samples, and the energy-band structures were estimated according to the relationship among the conduction band, valence band, and flat-band potential of the samples, as well as from the results of the UV–Vis diffuse reflectance spectra. The flat-band potentials (E_{fb}) of BiSS and CoAl-LDH are −0.56 eV and −0.44 eV, respectively, as shown by the Mott–Schottky curves (Figure 11b). The flat-band potential of the semiconductor is approximately equal to the Fermi energy level (E_f) [40]. The result shown in the XPS valence spectrum is the energy difference between the Fermi energy levels and the valence band positions [41], and the energy differences between the valence band and E_f are close to 0.56 and 0.72 eV for BiSS and CoAl-LDH, respectively (Figure 11c).

The E_{VB} was calculated to be 0.24 eV and 0.52 eV (relative to NHE). According to the formula $E_{CB} = E_{VB} - Eg$, the conduction band (CB) positions of BiSS and CoAl-LDH are -1.76 eV and -1.65 eV, respectively.

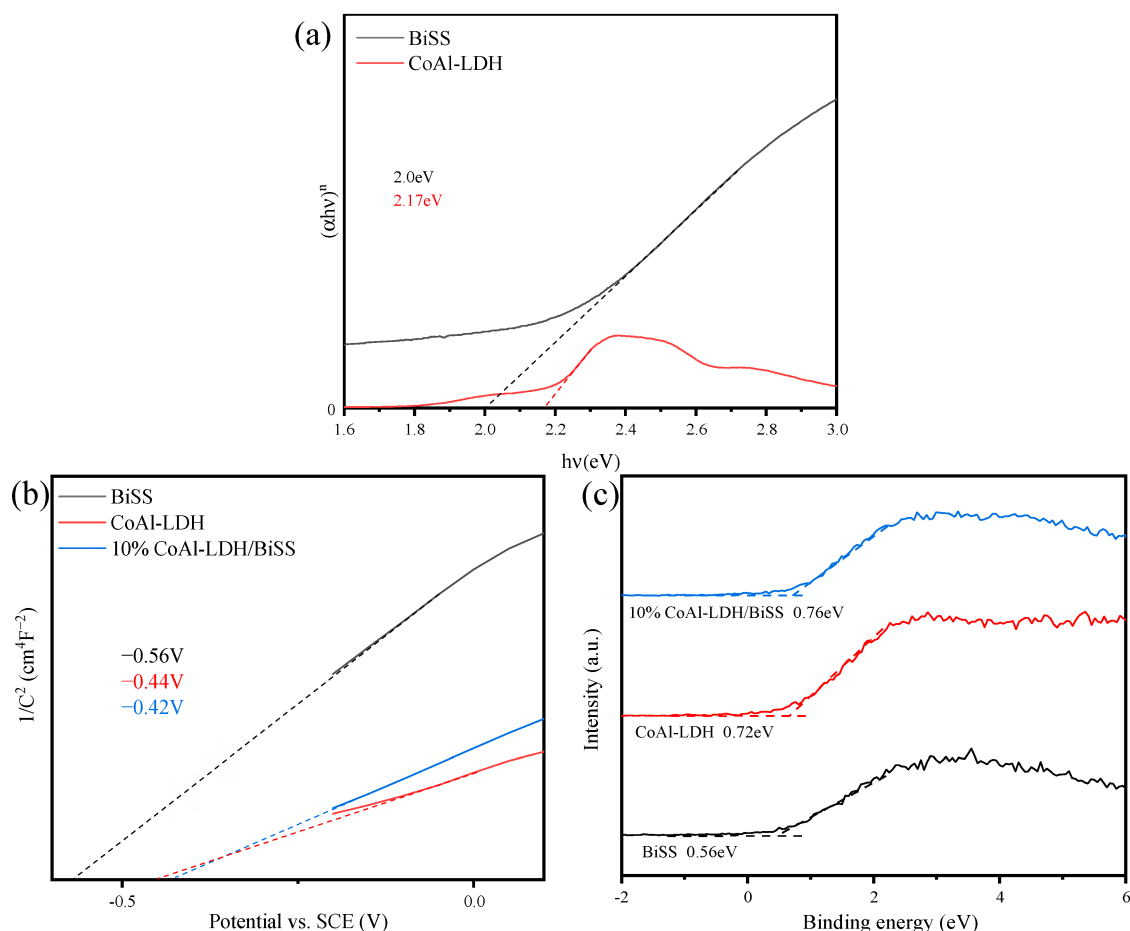


Figure 11. (a) Tauc plot of BiSS and CoAl-LDH, (b) Mott-Schottky plots, and (c) VB-XPS.

The mechanistic diagram of the CoAl-LDH/BiSS composite catalyst under visible light irradiation is shown in Figure 12. BiSS is closely combined with CoAl-LDH nanosheets, and during the photocatalytic reaction, the catalyst is excited by light to produce a large number of electron-hole pairs and undergoes segregation and migration. Under visible light irradiation, the electrons (e^-) in the valence band of BiSS and CoAl-LDH transition from photoexcitation to the conduction band, while equal amounts of h^+ remain in the valence band. The CoAl-LDH CB is higher than the BiSS CB, and electrons in the BiSS conduction band migrate to the CoAl-LDH conduction band. The BiSS VB is lower than the CoAl-LDH VB, and holes in the CoAl-LDH valence band are transferred to the BiSS valence band. The compounding of electrons and holes is effectively prevented, and the photogenerated carrier lifetime is prolonged. The e^- in CB reacts with O_2 to generate superoxide radicals. $O_2^{\bullet-}$ and h^+ are directly involved in the degradation of TC. The composite catalysts were prepared by introducing CoAl-LDH, which not only increased the specific surface area of the catalysts but also effectively promoted the migration of photogenerated carriers, thus improving the photocatalytic degradation ability.

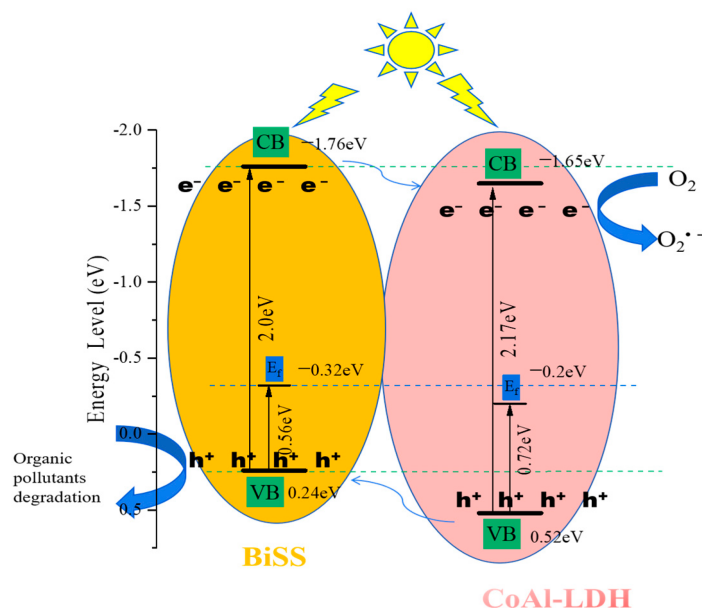


Figure 12. Proposed photocatalytic mechanism for the CoAl-LDH/BiSS photocatalyst under visible light irradiation.

3.5.4. Possible Degradation Pathways of TC

To understand the possible degradation pathways of tetracycline, the intermediates in the photocatalytic degradation process were investigated by the LC–MS technique. The proposed TC photocatalytic degradation pathways are shown in Figure 13. On the one hand, the TC molecule ($m/z = 445$) is demethylated to B ($m/z = 429$) by electrophilic attack [42]. After B is attacked by free radicals, it causes B to lose hydroxyl, amino, and aldehyde groups and to convert to C ($m/z = 339$). Subsequently, C undergoes further oxidation and ring-opening conversion to D ($m/z = 282$), E ($m/z = 169$), and F ($m/z = 129$).

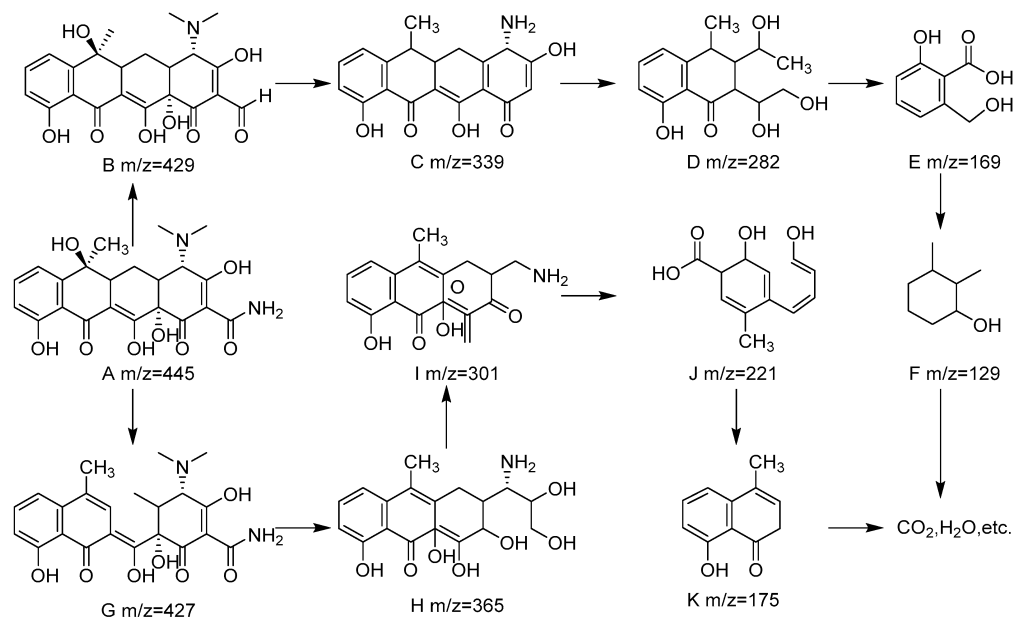


Figure 13. Degradation path of tetracycline.

On the other hand, the TC molecule ($m/z = 445$) is dehydrated and converted to intermediate G ($m/z = 427$) under the action of h^+ or $\cdot OH$ [43]. The intermediate product G is oxidized by h^+ or $\cdot OH$ and undergoes demethylation, hydroxylation, and deamidation to

give the ring-opening product H ($m/z = 365$) [44]. Product H is converted to intermediate I ($m/z = 301$) by oxidation. Subsequently, compound I generates J ($m/z = 221$) and K ($m/z = 175$) by the stepwise reaction of $\cdot\text{OH}$ [45]. As the photocatalytic reaction continues, F and K are eventually oxidized to small molecules of organic matter, CO_2 , and H_2O .

4. Conclusions

CoAl-LDH/BiSS doped with different ratios of CoAl-LDH were successfully synthesized by adopting a hydrothermal method, and the photoactivity of the prepared CoAl-LDH/BiSS heterojunction composites was evaluated by their ability to degrade tetracycline and methyl orange under visible light. The results showed that 10% CoAl-LDH/BiSS exhibited the best photocatalytic degradation performance of pollutants, which could completely degrade MO within 20 min, and the degradation efficiency of tetracycline could reach 99.23% within 5 min. Compared with BiSS, the degradation activity of methyl orange and tetracycline was increased by 1.88 and 1.70 times, respectively. The photocatalytic degradation cycling experiments also proved that the composite exhibited good stability. The effects of catalyst dosage, antibiotic concentration, and pH on the degradation of tetracycline were systematically investigated. Composite materials had good degradation efficiency for various antibiotics. In addition, it was demonstrated that h^+ , $\text{O}_2^{\bullet-}$, and $^1\text{O}_2$ were the main active substances in the photocatalytic reaction. The synthesis of a heterojunction structure between CoAl-LDH and BiSS can effectively prevent the complexation of electrons and holes, improve degradation efficiency, and completely degrade tetracycline into small molecules.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/w16111467/s1>, Table S1: Kinetic data model of the photocatalytic degradation of methyl orange by catalysts with different components; Table S2: Kinetic data model of the photocatalytic degradation of tetracycline by catalysts with different components; Table S3: Comparison of the rate constants of different photocatalysts for photocatalytic degradation. References [19,36,46–51] are cited in the Supplementary Materials.

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