Article

Novel $\text{LaAO}_x/\text{g-C}_3\text{N}_4$ ($\text{A} = \text{V}, \text{Fe}, \text{Co}$) Heterojunctions with Enhanced Photocatalytic Degradation of Norfloxacin under Visible Light

Jiwen Jiang and Yonghua Li *

School of Geography, Liaoning Normal University, Dalian 116029, China; lusedujw@163.com

* Correspondence: dydl@lnnu.edu.cn; Tel.: +86-131-9428-3155

Abstract: In this study, novel photocatalysts $\text{LaAO}_x/\text{g-C}_3\text{N}_4$ ($\text{A} = \text{V}, \text{Fe}, \text{Co}$) were prepared by the hydrothermal method, through which LaAO_x and $\text{g-C}_3\text{N}_4$ were mixed and ultrasonically oscillated to gain heterojunction catalysts. All the samples were characterized by XRD, SEM, FT-IR, XPS, DRS, and PL to ensure the successful integration of LaAO_x with $\text{g-C}_3\text{N}_4$. The obtained results showed that $\text{LaAO}_x/\text{g-C}_3\text{N}_4$ ($\text{A} = \text{V}, \text{Fe}, \text{Co}$) could effectually improve the separation efficiency of photogenerated carriers during the photodegradation process, thus improving the photodegradation efficiency, while among them, $\text{LaFeO}_3/\text{g-C}_3\text{N}_4$ showed the best photocatalytic performance and degradation of norfloxacin under visible light, reaching up to 95% in 180 min, which was 9.32 times higher than pristine $\text{g-C}_3\text{N}_4$. From the discussed results above, the possible mechanism of the photodegradation process was put forward. This study supplies a promising method to gain $\text{g-C}_3\text{N}_4$ -based photocatalysts for antibiotics removal.

Citation: Jiang, J.; Li, Y. Novel $\text{LaAO}_x/\text{g-C}_3\text{N}_4$ ($\text{A} = \text{V}, \text{Fe}, \text{Co}$) Heterojunctions with Enhanced Photocatalytic Degradation of Norfloxacin under Visible Light. *Crystals* **2021**, *11*, 1173. <https://doi.org/10.3390/cryst11101173>

Academic Editor: Marilena Carbone

Received: 28 July 2021

Accepted: 22 September 2021

Published: 27 September 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: heterojunction photocatalyst; nanocomposite; norfloxacin; graphitic carbon nitride

1. Introduction

In recent decades, with the intensive research and production quantity, a significant number of antibiotic drugs have been widely used in agriculture, animal husbandry, aquaculture, clinical therapy, etc. [1]. One serious consequence of this are the increasing numbers of antibiotic residues in the natural environment. Among them, norfloxacin is a representative antibiotic [2–4] which is clinically prescribed in humans and animals for a wide range of diseases. Meanwhile, during the process of its production, massive wastewater is discharged directly into natural waters without treatment, which often contains antibiotics and can also cause serious ecological pollution [5,6]. Therefore, the rapid and effective removal of antibiotic residues from water has become an important research topic [7].

In order to solve the energy crisis and water pollution problems that limit contemporary human development, photocatalysis is a popular and promising research topic today. In 1972, Honda and Fujishima discovered that TiO_2 could decompose water molecules into hydrogen when exposed to ultraviolet light [8], which could be noted as the beginning of heterogeneous photocatalysts. In addition, as research further developed, more photocatalytic materials with a high visible light activity were successfully prepared [9], making it possible to utilize the high-energy visible light as the light source in the photocatalytic system.

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) is an organic semiconductor polymer material with a graphite-like structure, consisting of tri-s-triazine units formed from sp^2 , hybridized by C and N atoms, and interconnected by amino radicals [10]. Layer-to-layer interaction by van der Waals forces have demonstrated the structure by density functional theory (DFT) calculations [11]. $\text{g-C}_3\text{N}_4$ is endowed with excellent thermal, physical, as well as chemical stability. In addition, a bandgap of (~ 2.7 eV) makes $\text{g-C}_3\text{N}_4$ makes it possible to exhibit

catalytic activities easily under visible light [12]. Since Wang [13] reported its application in photocatalytic water splitting in 2009, g-C₃N₄ has been extensively researched in the field of photocatalytic removal of refractory organic contamination. Nevertheless, its development in photocatalysis is still being restricted by such aspects: its difficulty in absorbing visible light specifically refers to wavelengths above 460 nm, the short lifetime of photogenerated carriers, its low electrical conductivity, as well as its small, specific surface area. In response to this situation, different strategies have been devised to improve the photocatalytic efficiency of g-C₃N₄, such as metal doping [14], non-doping [15], the regulation of its nanostructure [16], and construction of heterojunctions [17], among others.

Compared to other semiconductor modification methods, compounding two or more semiconductor materials to form a heterojunction photocatalyst can not only enhance the separation efficiency of photogenerated electrons and holes, but also regulate the redox chemistry and photocatalytic stability, thereby effectively increasing the photocatalytic activity, which is regarded as a simple, stable, and efficient modification method [18]. As we know about a photocatalyst, the photocatalytic activity is mainly limited to the adsorption efficiency, the photoresponse range, and the separation efficiency of the photogenerated electron-hole pairs. Inspired by plant photosynthesis in nature, Z-scheme heterojunction photocatalysts are considered as one of the most efficient photocatalytic systems [19]. In particular, the synthesis of the Z-scheme photocatalyst has been reported as an effective way to enhance the photocatalytic efficiency. Due to the appropriate energy band matching between each component materials, the photogenerated electrons are transferred and separated from holes effectively, which accumulate at the respective valence band (VB) and conduction band (CB) to form the redox centers. In the photocatalytic degradation process, the organic contaminants are decomposed into harmless small inorganic small molecules. Furthermore, the morphology of the photocatalysts also play a crucial role in the photodegradation process. As reported [20], the heterojunction photocatalysts with multilevel structure exhibit better photocatalytic performance than those with a single structure, mainly due to the interconnectedness of the multilevel nanostructures, which provide more multi-dimensional channels for the transport and diffusion of reactants, as well as the fact that they can be reflected or refracted on the surface of the multilevel structured composites, which contributes to the light utilization efficiency. The multilevel structure provides larger surface areas and active sites, improves the adsorption capacity, and helps the morphology to be maintained.

Therefore, the selection of suitable materials for the synthesis of Z-scheme composite photocatalysts for the degradation of norfloxacin is a highly desirable topic. Nowadays, nanometer-sized transition metal oxide particles have achieved a wide range of applications in the fields such as environmental protection [5], energy production and storage [14], and electronic devices [21]. Especially, perovskites presenting the atomic structure of ABO_x are the focus of research. Among such perovskite compounds, LaAO_x (A = V, Fe, Co), is a promising material with excellent catalytic oxidation capability, thermal stability, light absorption, electron migration efficiency, low-cost and no environmental impact. Graphite phase carbon nitride (g-C₃N₄) possesses high photo-sensitive and photosensitivity, is often combined with other semiconductor materials to form heterojunction photocatalysts to enhance the optical absorption and electron migration efficiency of the photodegradation system [22].

In this work, a novel Z scheme photocatalyst was synthesized by a facile ultrasound-assisted hydrothermal method, combining LaAO_x (A = V, Fe, Co) with g-C₃N₄ to form a binary LaCoO₃/g-C₃N₄ hybrid. Further, the crystal structure, surface morphology, optical properties and chemical composition of the samples obtained were investigated by XRD, SEM, FTIR, XPS, DRS and PL. The photocatalytic activities were investigated by the degradation of norfloxacin aqueous solution under visible light. Benefited by the construction of Z-scheme heterojunction, the optical absorption, and photogenerated electron transfer efficiency were enhanced, which increased the photocatalytic degradation activities over the samples obviously. This work provides a feasibility for the application

of solar energy to remove the antibiotic contaminants from water over the g-C₃N₄ based ternary photocatalyst.

2. Experiment

2.1. Materials

Melamine, La(NO₃)₃·6H₂O, NH₄VO₃, Fe(NO₃)₃·9H₂O, Co(NO₃)₃·6H₂O, NaOH, and citric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shenyang, China). Norfloxacin was obtained from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China).

2.2. Synthesis of g-C₃N₄

Typically, 10 g of melamine was placed in a sealed crucible and heated to 550 °C for 4 h, at a rate of 2 °C/min, then cooled down naturally, and then it was heated at 520 °C for 4 h at a rate of 2 °C/min in air to obtain g-C₃N₄ nanosheets [23].

2.3. Synthesis of LaAO_x (A = V, Fe, Co)

In order to obtain pure pin-like LaVO₄, 0.52 g of sodium hydroxide and 1.52 g of NH₄VO₃ were added to 30 mL of deionized water and dissolved by stirring to obtain aqueous solution of sodium metavanadate (A solution for short). Then, for LaVO₄, 5.84 g of lanthanum nitrate hexahydrate was added to a certain amount of water and dissolved by stirring to obtain B solution. The yellow suspension was formed by adding B solution to A solution, slowly. After mixing and stirring for 30 min, we added the yellow suspension to the 200 mL Teflon-lined reaction autoclave and the temperature was kept at 200 °C for 48 h, then cooled naturally to room temperature. The milky white product was centrifuged and washed successively with water and anhydrous ethanol for three times. Finally, the obtained products were dried at 80 °C for 24 h to form pure white LaVO₄ powder.

As for pure LaCoO₃, La(NO₃)₃·6H₂O, Co(NO₃)₃·6H₂O, and citric acid were mixed in 100 mL deionized water at a molar ratio of 1: 1: 5 and stirred magnetically for 30 min with adding 20 mL ethylene glycol. The mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 180 °C for 16 h. The obtained precipitate was washed with deionized water and anhydrous ethanol several times, dried at 80 °C for 6 h, then calcined at 900 °C for 2 h to gain pure LaCoO₃ nanospheres. LaCoO₃ and g-C₃N₄ were mixed at a 30: 100 mass ratio, then poured into deionized water, and ultrasonically shaken for 2 h. The mixture was dried at 80 °C for 2 h and calcined at 500 °C for 2 h to prepare LaCoO₃/g-C₃N₄ hybrid.

For pure LaFeO₃, 1 mmol Fe(NO₃)₃·6H₂O and 5 mmol citric acids with 20 mL ethylene glycol were dissolved in deionized water in a beaker. The mixed solution was stirred for 1 h and transferred onto the Teflon-lined reaction autoclave; the temperature was adjusted to 180 °C and kept for 12 h. The obtained solution was washed by deionized water and alcohol for 3 times, respectively. Then, the precursor was dried at 160 °C for 6 h and calcined at 850 °C for 4 h to obtain the LaFeO₃.

2.4. Synthesis of LaAO_x/g-C₃N₄ (A = V, Fe, Co)

LaAO_x/g-C₃N₄ (A = V, Fe, Co) composites were synthesized by ultrasonic dispersion method. We took a certain amount of g-C₃N₄ pure into 20 mL methanol in three different beakers, and the ultrasonic dispersing lasted for 30 min at room temperature. After 30 min we added a certain amount of LaVO₄, LaFeO₃, and LaCoO₃ powder, respectively, and stirred for 2 h under the fume hood. Then the resulting mixture was dried at 80 °C for 10 h. Finally, we placed the product in the crucible in muffle furnace at 5 °C per minute to 250 °C and kept for 1 h, letting it cool naturally to room temperature. The LaAO_x/g-C₃N₄ (A = V, Fe, Co) composites were obtained.

2.5. Characterization of the Samples

For all the samples obtained, the microstructure and chemical composition were characterized by X-ray Diffraction Analysis (XRD, Rigaku, Dmax-2000, Tokyo, Japan), Fourier transformed infrared (FTIR, Bruker AXS, TENSOR-27, Karlsruhe, Germany), and (XPS, Thermo VG, ESCALAB-250, Waltham, MA, USA). The surface morphology was investigated by scanning electron microscopy (SEM, Hitachi, S-4800, Tokyo, Japan) and transmission electron microscopy (TEM, Hitachi, H-600, Japan). The optical capacity was measured by UV-vis diffuse reflection spectroscopy (DRS, PerkinElmer, Lambda-35, Waltham, MA, USA) and Photoluminescence (PL, Shimadzu, RF-540, Kyoto, Japan) spectra.

2.6. Photocatalytic Activity Examination

The photocatalytic activities of all the samples prepared were measured by the degradation of norfloxacin in aqueous solution under visible light illumination. In order to prove the degradation ability of La under visible light, we added a filter on the xenon lamp. The light source was provided by a xenon lamp with a 420 nm cutoff filter. 20 mg of all the samples obtained was mixed with 100 mL of 20 mg/L norfloxacin solution, magnetically stirred for 1 h to reach the adsorption-desorption equilibrium on the sample surface. Then, the xenon lamp was turned on, 5 mL of the suspension liquid was withdrawn, centrifuged and the absorbance of the supernatant was measured by a UV-Vis spectrophotometer at 275 nm.

3. Result and Discussion

3.1. Characterization Results of Catalysts

The crystal phase structure of the catalyst prepared was analyzed using XRD, and the results are shown in Figure 1. As can be seen, the pure g-C₃N₄ (JCPDS 87-1526) shows two diffraction peaks of (100) and (002) planes at 13.02° and 27.56° [12], the diffraction peaks of LaVO₄ (JCPDS 50-0367) are observed at 18.28°, 20.36°, 24.46°, 26.16°, 27.76°, 29.0°, 30.12°, 32.88°, 35.1°, 39.66°, 40.42°, 41.28°, 45.06°, 46.5°, 47.24°, 49.48°, 50.8°, 51.96°, 53.98°, 55.5°, 57.56°, 67.78°, 70.24° and 73.32°, respectively, which corresponded to (011), (11-1), (020), (200), (120), (210), (012), (20-2), (21-2), (031), (31-1), (211), (212), (13-2), (103), (32-2), (132), (140), (40-2), (41-2), (21-4), (51-1), (41-4), and (33-4) planes [24]. Furthermore, the peaks of LaFeO₃ were observed as 22.7°, 32.24°, 39.83°, 46.19°, 57.53°, 67.41°, and 76.75°, which were matched to the planes (101), (121), (220), (202), (240), (242) and (204) of LaFeO₃ (JCPDS no. 37-1493) [25]. Nevertheless, the LaCoO₃ (JCPDS 48-0123) has strong diffraction peaks at 22.64°, 33.26°, 39.78°, 46.22°, 57.44°, 68.94°, and 69.96° were well matched with (012), (110), (202), (024), (214) and (208) planes [26]. In the XRD patterns of the LaAO_x/g-C₃N₄ composite catalysts, the characteristic diffraction peaks of LaVO₄, LaFeO₃ and LaCoO₃ and g-C₃N₄ can be observed clearly and simultaneously. No impurity diffraction peaks were observed which confirmed the successful synthesis of LaAO_x/g-C₃N₄ (A = V, Fe, Co).

Figure 1. XRD patterns of obtained samples.

The morphologies of obtained samples were tested by scanning electron microscopy (SEM). In Figure 2a, pure LaVO_4 presents a pin-like structure and has a length about 200–300 nm. It can be seen in Figure 2c,e, that pure LaFeO_3 and LaCoO_3 show spherical particulates, and the nanospheres having a diameter about 70–150 nm, which can provide a rich space for electrons transport. As shown in Figure 2g, pure $\text{g-C}_3\text{N}_4$ presents smooth sheet structure, which provides well conditions for loading LaAO_x ($A = \text{V, Fe, Co}$). For $\text{LaVO}_4/\text{g-C}_3\text{N}_4$, we can clearly observe that pin-like LaVO_4 was grown on $\text{g-C}_3\text{N}_4$ nanosheet in Figure 2b. From Figure 2d,f, we can conclude that LaFeO_3 and LaCoO_3 nanosphere was evenly distributed on the $\text{g-C}_3\text{N}_4$ nanosheet. Based on the above analysis, the SEM results proved $\text{LaAO}_x/\text{g-C}_3\text{N}_4$ ($A = \text{V, Fe, Co}$) were successfully prepared.

The functional group of $\text{LaAO}_x/\text{g-C}_3\text{N}_4$ ($A = \text{V, Fe, Co}$) was examined by FT-IR spectroscopy. The spectra illustrated by FT-IR analysis were shown in Figure 3, which shows that there is absorption at whole spectra. For bare $\text{g-C}_3\text{N}_4$, the distribution of main characteristic peaks at 1100 cm^{-1} to 1700 cm^{-1} , which were corresponding to aromatic C-N stretching vibration modes [27]. The peak related to N-H stretching vibration modes was shown at 3000 cm^{-1} to 3700 cm^{-1} , which was consistent with previous reports [28]. For LaVO_4 , the two characteristic peaks at 810 and 440 cm^{-1} could be attributed to vibration of VO_4^{3-} , and La-O [29]. As for LaFeO_3 , the Fe-O bond was observed as 501 cm^{-1} . Apart from above peaks, another sharp peak at 808 cm^{-1} can be attributed to bending vibration modes of the triazine ring units and C = N stretching vibration modes [10]. No other intermediate phases are existed in the FTIR spectra, which corresponds with the XRD results [30].

Figure 2. SEM images of all samples: (a) Pure LaVO_4 , (b) $\text{LaVO}_4/\text{g-C}_3\text{N}_4$, (c) Pure LaFeO_3 , (d) $\text{LaFeO}_3/\text{g-C}_3\text{N}_4$, (e) Pure LaCoO_3 , (f) $\text{LaCoO}_3/\text{g-C}_3\text{N}_4$ and (g) Pure $\text{g-C}_3\text{N}_4$.

Figure 3. FT-IR absorbance spectra of obtained samples.

The surface chemical composition and chemical state of the $\text{LaAO}_x/\text{g-C}_3\text{N}_4$ ($A = \text{V, Fe, Co}$) catalyst were characterized through XPS. Figure 4a shows the X-ray photoelectron spectroscopy of the $\text{LaAO}_x/\text{g-C}_3\text{N}_4$ ($A = \text{V, Fe, Co}$) catalyst. All the signals of La, V, Fe, Co, O, C, and N were observed in the survey spectra of $\text{LaAO}_x/\text{g-C}_3\text{N}_4$ catalyst, which indicates its composite structure and tallies with the results of the XRD. Figure 4b–h show the high resolution X-ray photoelectron spectroscopy of La 3d, V 2p, Fe 2p, Co 2p, O 1s, C 1s and N 1s respectively. In Figure 4b, the binding energy (BE) of La 3d shows two pairs of diffraction peaks at 832.7, 836.8 eV, and 849.4, and 853.6 eV represent La 3d_{5/2} and La 3d_{3/2} [31]. As Figure 4c shows, the BE peaks at 522.5 and 514.7 eV are ascribed to V 2p_{1/2} and V 2p_{3/2}, and the V 2p peak is assigned to V⁵⁺ [32]. In Figure 4d, the BE peaks at 708.9 eV and 722.8 eV of Fe 2p_{3/2} and Fe 2p_{1/2} were assigned to Fe³⁺ [33]. Moreover, the Co 2p XPS spectra shows in Figure 4e which present three primary peaks at 778.3, 787.1 and 795.7 eV, which corresponds with Co 2p_{3/2} and Co 2p_{1/2}, indicating that all Co ions are present as Co³⁺ [27]. As for the element O 1s, shown in Figure 4f, the peak at 527.9 eV was attributed to the lattice oxygen, while the peak at 529.8 eV was assigned to surface adsorbed oxygen. In the high-resolution C 1s XPS spectrum shown in Figure 4g, the peak at 281.8 eV is attributed to the sp²-type C-C bonds from the environment, the peak at 285.2 eV is assigned to the sp²-type C = N bonds [19]. We can observe in Figure 4h that the N 1s peak at 395.7 eV to the C-N bonds and the peak at 398.3 eV to the sp²-type C=N bonds, the peak at 401.5 eV is identified as originating from nitrogen surrounded by three carbons in an amorphous C-N network (N-(C)₃) [34]. In a nutshell, the XPS analysis proves that the $\text{LaAO}_x/\text{g-C}_3\text{N}_4$ ($A = \text{V, Fe, Co}$) composite catalysts were successfully prepared.

Figure 4. (a) XPS spectra of $\text{LaAO}_x/\text{g-C}_3\text{N}_4$ ($A = \text{V, Fe, Co}$) nanocomposites a survey of the samples, (b) La 3d, (c) V 2p, (d) Fe 2p, (e) Co 2p, (f) O 1s, (g) C 1s, and (h) N 1s.

Figure 5 is the UV–vis diffuse reflectance spectra of $\text{g-C}_3\text{N}_4$, LaAO_x , and $\text{LaAO}_x/\text{g-C}_3\text{N}_4$ ($A = \text{V, Fe, Co}$) composite photocatalyst, and it is apparent that in Figure 5a, at the wavelength range from 300 to 800 nm, pristine LaCoO_3 and LaFeO_3 revealed an intense absorption over the total visible light range. It could be seen that the absorption edges

of g-C₃N₄ are at about 490 nm. It could also be seen that the LaAO_x/g-C₃N₄ (A = V, Fe, Co) shows stronger absorption than pristine g-C₃N₄ and LaFeO₃. Among them, it can be clearly observed that the LaFeO₃/g-C₃N₄ composite showed a wide absorption range, approximately at 615 nm.

Figure 5. (a) DRS spectra of g-C₃N₄, LaVO₄, LaFeO₃, LaCoO₃, and LaAO_x/g-C₃N₄ (A = V, Fe, Co) composite photocatalyst and the band gaps of (b) LaVO₄, (c) LaFeO₃, (d) LaCoO₃, (e) g-C₃N₄, (f) LaVO₄/g-C₃N₄, (g) LaFeO₃/g-C₃N₄, and (h) LaCoO₃/g-C₃N₄.

The band gap energies of all samples, as shown in Figure 5b–h, are determined according to the Kubelka-Munk equation; herein, the band gap (E_g) values of bare $g\text{-C}_3\text{N}_4$, LaVO_4 , LaFeO_3 and LaCoO_3 are 2.68, 3.46, 2.02 and 2.72 eV, respectively. Furthermore, the values of E_g for $\text{LaVO}_4/g\text{-C}_3\text{N}_4$, $\text{LaFeO}_3/g\text{-C}_3\text{N}_4$, and $\text{LaCoO}_3/g\text{-C}_3\text{N}_4$ composite were calculated to be 2.98, 3.06 and 2.85 eV, indicating that the co-existence of LaAO_x ($A = \text{V, Fe, Co}$) and $g\text{-C}_3\text{N}_4$ materials.

Photoluminescence (PL) emission spectra of as-prepared samples, shown in Figure 6, study the transfer behavior of the photogenerated electrons and holes and understand the separation and recombination of photogenerated charge carriers [35]. Generally speaking, PL emission is the result of recombination of electrons and holes. In other words, a lower PL intensity is the same as a lower recombination rate and higher photocatalytic activity. Therefore, the PL spectra demonstrate that $\text{LaFeO}_3/g\text{-C}_3\text{N}_4$ has the best photocatalytic performance.

Figure 6. The photoluminescence of $g\text{-C}_3\text{N}_4$ and $\text{LaAO}_x/g\text{-C}_3\text{N}_4$ ($A = \text{V, Fe, Co}$).

3.2. Photocatalytic Performance

After the above analysis, it can be found that the visible-light absorption capacity of $\text{LaAO}_x/g\text{-C}_3\text{N}_4$ ($A = \text{V, Fe, Co}$) composites and the separation efficiency of photogenerated carriers are significantly improved compared with $g\text{-C}_3\text{N}_4$, which may be beneficial to the improvement of photocatalytic performance. In order to verify the photodegradation performance of $\text{LaAO}_x/g\text{-C}_3\text{N}_4$ ($A = \text{V, Fe, Co}$), we studied the photocatalytic performance of NOF as target pollutant. In Figure 7, among them, the C_0 is the initial concentration, and the C_t is the concentration at t min. As can be seen, all the samples can degrade NOF for less than 8% after 30 min, while the pure $g\text{-C}_3\text{N}_4$, LaVO_4 , LaFeO_3 , and LaCoO_3 can

only degrade 25%, 34%, 50%, and 39% NOF after 180 min visible-light illumination. As for $\text{LaAO}_x/\text{g-C}_3\text{N}_4$ ($A = \text{V, Fe, Co}$) composites, under the same conditions, $\text{LaVO}_4/\text{g-C}_3\text{N}_4$, $\text{LaFeO}_3/\text{g-C}_3\text{N}_4$, and $\text{LaCoO}_3/\text{g-C}_3\text{N}_4$ show higher photocatalytic efficiency, reached 80%, 95%, and 57%, respectively. Specifically, $\text{LaFeO}_3/\text{g-C}_3\text{N}_4$ composites show the highest photocatalytic efficiency, which can degrade 95% NOF after 180 min of visible-light illumination.

Figure 7. Photocatalytic performance of all samples.

In addition, we calculated the kinetic curve of photocatalytic degradation of NOF by the equation as follow:

$$-\ln(C_t/C_0) = kt \quad (1)$$

where C_0 is the initial concentration, the C_t is the concentration for t min, k is the rate constant and t is the reaction time. The calculation results are shown in Figure 8 and Table 1. As we can see clearly that the reaction time and concentration of NOF degradation conform to the first order kinetics. Combining Figure 8 and Table 1, it can be concluded that the kinetic constants of NOF photodegradation over $\text{LaFeO}_3/\text{g-C}_3\text{N}_4$ (0.01371 min^{-1}) is 9.32 times that of pristine $\text{g-C}_3\text{N}_4$ (0.00147 min^{-1}), indicating that the coupling $\text{g-C}_3\text{N}_4$ with LaFeO_3 extremely enhances photodegradation efficiency of NOF among these photocatalysts.

Figure 8. Kinetic curves of all samples.

Table 1. Photocatalytic results of all samples.

Samples	Degradation	k	R ²
g-C ₃ N ₄	25%	0.00147	0.98475
LaVO ₄	34%	0.00210	0.97228
LaFeO ₃	50%	0.00322	0.96608
LaCoO ₃	39%	0.00250	0.98143
LaVO ₄ /g-C ₃ N ₄	80%	0.00789	0.94428
LaFeO ₃ /g-C ₃ N ₄	95%	0.01371	0.94997
LaCoO ₃ /g-C ₃ N ₄	57%	0.00417	0.97579

3.3. Photodegradation Possible Mechanism

In order to explore the electron hole transfer path between LaFeO₃ and g-C₃N₄ under visible-light illumination, we proposed a possible photodegradation mechanism, as shown in Figure 9. According to previous reports [10], using the formula $E_{VB} = X - E_e + 0.5E_g$, and $E_{VB} = E_{CB} + E_g$, the conduction band (CB) potential and valence band (VB) potential of g-C₃N₄ were determined to be -1.01 eV and 1.57 eV. LaFeO₃ were calculated to -0.37 eV and 1.65 eV, respectively. Furthermore, the CB of both g-C₃N₄ and LaFeO₃ are more negative than the reduction potential (-0.33 eV vsNHE) of $O_2/\bullet O_2^-$, which could be explained that electrons reacted with O_2 to produced $\bullet O_2^-$ [33], at the same time, $\bullet O_2^-$ participated in the NOF photodegradation process under visible-light illumination.

Figure 9. Photodegradation possible mechanism of LaFeO₃/g-C₃N₄.

In simple terms, under illumination, the electrons on g-C₃N₄ and LaFeO₄ are photoexcited into their respective CB, leaving holes on the VB, thereby generating photogenerated electrons-hole pair. The e[−] on the conduction band of LaFeO₄ rapidly transported to the valence band of LaFeO₄, while the h⁺ on the VB of the g-C₃N₄ reacts with the OH[−] to form the •OH, and the e[−] stayed on the CB of the g-C₃N₄ can react with O₂ generates •O₂[−], and the finally formed •OH, •O₂[−] and h⁺ participate in the photocatalytic degradation reaction of NOF, so that NOF can be transformed into products such as CO₂ and H₂O, and the Z-scheme mechanism formed effectively avoids photo-generated electrons and improves the separation efficiency of electron-hole pairs, thus, the photocatalytic degradation efficiency was improved.

4. Conclusions

In conclusion, a novel LaAO_x/g-C₃N₄ (A = V, Fe, Co) nanocomposite material was prepared by a facile hydrothermal method. This novel photocatalyst has the activity of initiating the decomposition of NOF under visible light illuminate. As shown in the XRD and FT-IR results, there were no impurity diffraction peaks observed, which confirmed the successful synthesis of LaAO_x/g-C₃N₄ (A = V, Fe, Co). We also observed that, in the SEM results, both the pin-like LaVO₄, spherical LaFeO₃ and LaCoO₃ were successful in loading on the sheet g-C₃N₄, respectively. And the results of DRS and PL characterization showed that LaAO_x has more efficient visible light response ability. In addition, it also exhibits excellent photocatalytic performance under visible light illumination. The enhanced photocatalytic performance of LaFeO₃/g-C₃N₄ is not only related to the energy band potential of LaFeO₃ and g-C₃N₄, but also related to the interconnected nanocrystalline heterojunction of g-C₃N₄. This study may provide an important strategy for the designation and preparation of high-performance photocatalysts induced by visible light.

Author Contributions: Methodology, Y.L.; writing—original draft preparation, J.J. Both authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: This study did not report any data.

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

References

- Zhu, W.; Gao, X.; Li, Q.; Li, H.; Chao, Y.; Li, M.; Mahurin, S.M.; Li, H.; Zhu, H.; Dai, S. Controlled Gas Exfoliation of Boron Nitride into Few-Layered Nanosheets. *Angew. Chem.-Int. Ed.* **2016**, *55*, 10766–10770. [CrossRef]
- Lafin, J.T.; Sarsour, E.H.; Kalen, A.L.; Wagner, B.A.; Buettner, G.R.; Goswami, P.C. Methylseleninic acid induces lipid peroxidation and radiation sensitivity in head and neck cancer cells. *Int. J. Mol. Sci.* **2019**, *20*, 225. [CrossRef] [PubMed]
- Lv, X.; Yan, D.Y.S.; Lam, F.L.Y.; Ng, Y.H.; Yin, S.; An, A.K. Solvothermal synthesis of copper-doped BiOBr microflowers with enhanced adsorption and visible-light driven photocatalytic degradation of norfloxacin. *Chem. Eng. J.* **2020**, *401*, 126012. [CrossRef]
- Zhuang, Y.; Luan, J. Improved photocatalytic property of peony-like InOOH for degrading norfloxacin. *Chem. Eng. J.* **2020**, *382*, 122770. [CrossRef]
- Feng, M.; Zhang, P.; Zhou, H.C.; Sharma, V.K. Water-stable metal-organic frameworks for aqueous removal of heavy metals and radionuclides: A review. *Chemosphere* **2018**, *209*, 783–800. [CrossRef]
- Ghasemi, S.; Setayesh, S.R.; Habibi-Yangjeh, A.; Hormozi-Nezhad, M.R.; Gholami, M.R. Assembly of CeO₂-TiO₂ nanoparticles prepared in room temperature ionic liquid on graphene nanosheets for photocatalytic degradation of pollutants. *J. Hazard. Mater.* **2012**, *199–200*, 170–178. [CrossRef]
- Cao, S.; Low, J.; Yu, J.; Jaroniec, M. Polymeric Photocatalysts Based on Graphitic Carbon Nitride. *Adv. Mater.* **2015**, *27*, 2150–2176. [CrossRef]
- Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *240*, 37–38. [CrossRef]
- Wen, J.; Xie, J.; Chen, X.; Li, X. A review on g-C₃N₄-based photocatalysts. *Appl. Surf. Sci.* **2017**, *391*, 72–123. [CrossRef]
- Zhang, J.; Zhu, Z.; Jiang, J.; Li, H. Ultrasound-Assisted Hydrothermal Fabrication of AgI/MFeO₃/g-C₃N₄ (M = Y, Gd, La) Nano Sheet-Sphere-Sheet Photocatalysts with Enhanced Photodegradation Activities for Norfloxacin. *Catalysts* **2020**, *4*, 373. [CrossRef]
- Dzyaloshinskii, I.E.; Lifshitz, E.M.; Pitaevskii, L.P. General theory of van der Waals' forces. *Sov. Phys. Uspekhi* **1961**, *73*, 153–176. [CrossRef]
- Mohini, R.; Lakshminarasimhan, N. Coupled semiconductor nanocomposite g-C₃N₄/TiO₂ with enhanced visible light photocatalytic activity. *Mater. Res. Bull.* **2016**, *76*, 370–375. [CrossRef]
- Wang, X.; Maeda, K.; Chen, X.; Takanabe, K.; Domen, K.; Hou, Y.; Fu, X.; Antonietti, M. Polymer semiconductors for artificial photosynthesis: Hydrogen evolution by mesoporous graphitic carbon nitride with visible light. *J. Am. Chem. Soc.* **2009**, *131*, 1680–1681. [CrossRef] [PubMed]
- Qin, J.; Huo, J.; Zhang, P.; Zeng, J.; Wang, T.; Zeng, H. Improving the photocatalytic hydrogen production of Ag/g-C₃N₄ nanocomposites by dye-sensitization under visible light irradiation. *Nanoscale* **2016**, *8*, 2249–2259. [CrossRef] [PubMed]
- Mamba, G.; Mishra, A.K. Graphitic carbon nitride (g-C₃N₄) nanocomposites: A new and exciting generation of visible light driven photocatalysts for environmental pollution remediation. *Appl. Catal. B Environ.* **2016**, *198*, 347–377. [CrossRef]
- Yan, J.; Wu, H.; Chen, H.; Zhang, Y.; Zhang, F.; Liu, S.F. Fabrication of TiO₂/C₃N₄ heterostructure for enhanced photocatalytic Z-scheme overall water splitting. *Appl. Catal. B Environ.* **2016**, *191*, 130–137. [CrossRef]
- Guo, S.; Deng, Z.; Li, M.; Jiang, B.; Tian, C.; Pan, Q.; Fu, H. Phosphorus-Doped Carbon Nitride Tubes with a Layered Micro-nanostructure for Enhanced Visible-Light Photocatalytic Hydrogen Evolution. *Angew. Chem.-Int. Ed.* **2016**, *55*, 1830–1834. [CrossRef]
- Zhu, W.; Li, X. Graphene quantum dots/LaCoO₃/attapulgite heterojunction photocatalysts with improved photocatalytic activity. *Appl. Phys. A Mater. Sci. Process.* **2017**, *123*, 1–10. [CrossRef]
- Guo, J.; Li, P.; Yang, Z. A novel Z-scheme g-C₃N₄/LaCoO₃ heterojunction with enhanced photocatalytic activity in degradation of tetracycline hydrochloride. *Catal. Commun.* **2019**, *122*, 63–67. [CrossRef]
- Li, Y.; Fang, Y.; Cao, Z.; Li, N.; Chen, D.; Xu, Q.; Lu, J. Construction of g-C₃N₄/PDI@MOF Heterojunctions for the Highly Efficient Visible Light-Driven Degradation of Pharmaceutical and Phenolic Micropollutants; Elsevier B.V.: Amsterdam, The Netherlands, 2019; Volume 250, ISBN 5126588036.
- Masih, D.; Ma, Y.; Rohani, S. Graphitic C₃N₄ based noble-metal-free photocatalyst systems: A review. *Appl. Catal. B Environ.* **2017**, *206*, 556–588. [CrossRef]
- Fu, J.; Yu, J.; Jiang, C.; Cheng, B. g-C₃N₄-Based Heterostructured Photocatalysts. *Adv. Energy Mater.* **2018**, *8*, 1–31. [CrossRef]
- Jiang, L.; Yuan, X.; Zeng, G.; Chen, X.; Wu, Z.; Liang, J.; Zhang, J.; Wang, H.; Wang, H. Phosphorus- and Sulfur-Codoped g-C₃N₄: Facile Preparation, Mechanism Insight, and Application as Efficient Photocatalyst for Tetracycline and Methyl Orange Degradation under Visible Light Irradiation. *ACS Sustain. Chem. Eng.* **2017**, *5*, 5831–5841. [CrossRef]
- Huang, H.; Li, D.; Lin, Q.; Zhang, W.; Shao, Y.; Chen, Y.; Sun, M.; Fu, X. Efficient degradation of benzene over LaVO₄/TiO₂ nanocrystalline heterojunction photocatalyst under visible light irradiation. *Environ. Sci. Technol.* **2009**, *43*, 4164–4168. [CrossRef] [PubMed]
- Wu, Y.; Wang, H.; Tu, W.; Liu, Y.; Tan, Y.Z.; Yuan, X.; Chew, J.W. Quasi-polymeric construction of stable perovskite-type LaFeO₃/g-C₃N₄ heterostructured photocatalyst for improved Z-scheme photocatalytic activity via solid p-n heterojunction interfacial effect. *J. Hazard. Mater.* **2018**, *347*, 412–422. [CrossRef] [PubMed]

26. Fu, X.; Chen, Y.; Yu, G.Q.; Yu, C.; Wang, H.Z.; Zhang, G. De Preparation, characterization and photocatalysis properties of ultrafine perovskite-type LaCoO₃. *Adv. Mater. Res.* **2011**, *197–198*, 935–942. [[CrossRef](#)]
27. Lin, K.Y.A.; Chen, Y.C.; Lin, T.Y.; Yang, H. Lanthanum cobaltite perovskite supported on zirconia as an efficient heterogeneous catalyst for activating Oxone in water. *J. Colloid Interface Sci.* **2017**, *497*, 325–332. [[CrossRef](#)]
28. Che, H.; Ngaw, C.K.; Hu, P.; Wang, J.; Li, Y.; Wang, X.; Teng, W. Fabrication of molybdenum doped carbon nitride nanosheets for efficiently photocatalytic water splitting. *J. Alloys Compd.* **2020**, *849*, 156440. [[CrossRef](#)]
29. Xu, Y.; Liu, J.; Xie, M.; Jing, L.; Xu, H.; She, X.; Li, H.; Xie, J. Construction of novel CNT/LaVO₄ nanostructures for efficient antibiotic photodegradation. *Chem. Eng. J.* **2019**, *357*, 487–497. [[CrossRef](#)]
30. Zhu, Z.; Liu, F.; Zhang, W. Fabricate and characterization of Ag/BaAl₂O₄ and its photocatalytic performance towards oxidation of gaseous toluene studied by FTIR spectroscopy. *Mater. Res. Bull.* **2015**, *64*, 68–75. [[CrossRef](#)]
31. Veldurthi, N.K.; Eswar, N.K.R.; Singh, S.A.; Madras, G. Cocatalyst free Z-schematic enhanced H₂ evolution over LaVO₄/BiVO₄ composite photocatalyst using Ag as an electron mediator. *Appl. Catal. B Environ.* **2018**, *220*, 512–523. [[CrossRef](#)]
32. Thakur, H.; Singh, B.P.; Kumar, R.; Gathania, A.K.; Singh, S.K.; Singh, R.K. Synthesis, structural analysis, upconversion luminescence and magnetic properties of Ho³⁺/Yb³⁺ co-doped GdVO₄ nanophosphor. *Mater. Chem. Phys.* **2020**, *253*, 123333. [[CrossRef](#)]
33. Ye, Y.; Yang, H.; Wang, X.; Feng, W. Photocatalytic, Fenton and photo-Fenton degradation of RhB over Z-scheme g-C₃N₄/LaFeO₃ heterojunction photocatalysts. *Mater. Sci. Semicond. Process.* **2018**, *82*, 14–24. [[CrossRef](#)]
34. Zhang, Z.; Huang, J.; Zhang, M.; Yuan, Q.; Dong, B. Ultrathin hexagonal SnS₂ nanosheets coupled with g-C₃N₄ nanosheets as 2D/2D heterojunction photocatalysts toward high photocatalytic activity. *Appl. Catal. B Environ.* **2015**, *163*, 298–305. [[CrossRef](#)]
35. Dong, F.; Zhao, Z.; Xiong, T.; Ni, Z.; Zhang, W.; Sun, Y.; Ho, W.K. In situ construction of g-C₃N₄/g-C₃N₄ metal-free heterojunction for enhanced visible-light photocatalysis. *ACS Appl. Mater. Interfaces* **2013**, *5*, 11392–11401. [[CrossRef](#)] [[PubMed](#)]