Ultrasound-Assisted Hydrothermal Fabrication of AgI/MFeO3/g-C3N4 (M = Y, Gd, La) Nano Sheet–Sphere–Sheet Photocatalysts with Enhanced Photodegradation Activities for Norfloxacin

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Abstract: AgI/MFeO3/g-C3N4 (M = Y, Gd, La) nano sheet–sphere–sheet photocatalysts were synthesized by a simple ultrasound-assisted hydrothermal approach. We characterized the microstructure, surface morphology, and optical absorption capacity of the obtained samples. According to the characterization results, AgI/MFeO3/g-C3N4 (M = Y, Gd, La) nano sheet–sphere–sheet photocatalysts were successfully obtained. MFeO3 nanospheres and AgI nanosheets were dispersed evenly on the surface of g-C3N4 nanosheets. AgI/MFeO3/g-C3N4 showed remarkable photocatalytic. Especially, 95% of NOF was photodegraded over AgI/LaFeO3/g-C3N4 within 3 h and the higher photocatalytic performance still remained after six cycles. Additionally, the N2 adsorption–desorption isotherms of AgI/MFeO3/g-C3N4 showed that AgI/LaFeO3/g-C3N4 possessed the highest specific surface area (79.32 m2/g). The result of scavenging experiment revealed that ·O2−, h+, and ·OH were the main roles in the photodegradation process. Benefitting from the nice energy band matching, MFeO3 acted as the center of photogenerated electrons migration and separation provided more direct electron channels. This work proposes an effective approach for the design and configuration of dual Z-scheme photocatalysts to accomplish the removal of organic contaminants based on g-C3N4.

Keywords: nanocomposite; dual z-scheme photocatalyst; norfloxacin; nanospheres; g-C3N4 nanosheets

1. Introduction

The second-generation synthetic fluoroquinolones antibiotic, norfloxacin (NOF), has been used extensively in medicine, agriculture, and pharmaceutical industries [1]. Since it is extremely difficult to biodegrade NOF by microorganisms in the water, NOF left untreated in lakes, rivers, oceans, wetlands, and groundwater, accumulates and harms the natural environment continually. Traditional wastewater treatment technologies—such as biodegradation, physical adsorption, and chemical precipitation—continue to have low effectiveness and low efficiency in removing NOF. Therefore, it is important to take measures to eliminate NOF with an updated water treatment technology that is effective and efficient.

To solve the growing problems around the world caused by fossil energy shortages and environmental crises, semiconductor photocatalytic materials have been recognized as one of the most serviceable approaches [2]. However, it still deserved to research modified photocatalytic composites for better photoresponse, more efficient reuse retrievability, and higher photocatalytic degradation rate. Based on the previous report, establishing the dual Z-scheme system photocatalyst had been verified as an admirable way to intensify the transfer of photoexcited electrons and separation between electrons.

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and holes [3]. In the process of dual Z-scheme photocatalytic chemistry reaction, the photoexcited charge pairs were separated because of the nice matching of the energy bands belonging to each material within the heterojunction. The oxidation and reduction centers have formed to participate in the photodegradation reaction [4].

Recently, a non-metallic material named g-C$_3$N$_4$ has been recognized as a promising semiconductor photocatalysis for its simple synthesis, environmental innocuity, and reusability [5–8]. However, g-C$_3$N$_4$, before coming into use, requires crucial improvements including photogenerated electrons, holes separation, and charge transfer acceleration [9–12]. Several methods from previous reports were used to enhance the photocatalytic performance of g-C$_3$N$_4$, including metal and non-metal element doping, morphological control, and construction of compound heterojunction. Especially, AgI/g-C$_3$N$_4$ exhibits remarkable photocatalytic performance. However, both AgI and g-C$_3$N$_4$ have similar particle structures, which consist of aggregated sheets attenuating the separation of photoexcited electrons, and the near band gaps also bring the negative generations of charge pairs. Besides, perovskite-type compound modified g-C$_3$N$_4$ was widely used in semiconductor application fields. Especially, MFeO$_3$- and MFeO$_3$-based photocatalysts show excellent photocatalytic degradation of organic contamination [13,14]. They possess higher degradation rate to organic dyes and antibiotics under visible light irradiation than common photocatalysts such as ZnO, CuO, and TiO$_2$. Nevertheless, MFeO$_3$ was confined from application due to rapid recombination of charge pairs, which call on further improvement to reduce the recombination rate.

Herein, we designed dual Z-scheme composite photocatalysts in which MFeO$_3$ nanospheres and AgI nanosheets were assembled on the g-C$_3$N$_4$ nanosheets. The photocatalyst was composed of a nano sheet–sphere–sheet type structure. The intentionally designed heterojunction enables photogenerated charge pairs to be rapidly produced and structurally prevents the recombination of electrons and holes. With the conduction bands (CB) of Z-scheme composites in which benefits from the nice match of energy bands and control of morphological structure, electrons in abundance were excited rapidly, separated efficiently, and accumulated on the conduction of photocatalysts. We researched the photodegradation of NOF over various AgI/MFeO$_3$/g-C$_3$N$_4$, to our knowledge, such comparation has not been reported. With the synergistic effect of MFeO$_3$ (M = Y, Gd, La), AgI, and g-C$_3$N$_4$, the obvious photocatalytic performances can be achieved. This work provides a comprehensive and efficient strategy and design of perovskite-type compound modified g-C$_3$N$_4$ based composites photocatalyst, which can be employed in organic pollution removal.

2. Results and Discussion

2.1. Composition and Structure of Materials

The crystal plane information and crystal structure of as-obtained MFeO$_3$ (M = Y, Gd, La) and AgI/MFeO$_3$/g-C$_3$N$_4$ (M = Y, Gd, La) was investigated by XRD. As shown in Figure 1a, according to (JCPDS No.48-0529) [15], the diffraction peaks valued at 29.44°, 30.54°, 32.22°, 33.3°, 43.02°, 48.92°, 52.28°, 55.40°, 61.86°, and 63.20° were identified as the planes (002), (110), (101), (102), (112), (105), (110), (106), (114), and (202) of YFeO$_3$ respectively. The characteristic peaks located at 23.20°, 23.24°, 25.92°, 32.00°, 33.04°, 33.70°, 34.2°, 39.42°, 40.00°, 41.20°, 42.52°, 47.02°, 47.52°, 48.34°, 48.64°, 53.50°, 57.62°, 58.38°, 59.58°, 64.24°, and 68.94° were well matched to the crystal planes (110), (002), (111), (112), (111), (120), (210), (112), (202), (021), (211), (022), (023), (113), (220), (004), (221), (131), (132), (024), (312), (133), and (224) of GdFeO$_3$ (JCPDS no. 47-0067) [13]. The peaks at 22.7°, 32.26°, 39.72°, 46.18°, 57.54°, 67.4°, and 76.76°, according to the standard XRD patterns LaFeO$_3$ (JCPDS no. 37-1493) [16], corresponded to the planes of (101), (121), (220), (202), (240), and (204). It can be indicated that MFeO$_3$ was successfully synthesized according to the XRD results above.

AgI and g-C$_3$N$_4$ were also examined by XRD and the patterns were revealed in Figure 1b. The two observed characterized peaks at 13.42° and 27.43° of bare g-C$_3$N$_4$ can be indexed to the (100) and (002) planes of standard XRD patterns g-C$_3$N$_4$ (JCPDS no. 87-1526) [17]. Pure AgI showed the diffraction
peaks at 22.12°, 23.22°, 32.30°, 42.28°, and 46.03° were well matched with the (100), (002), (101), (110), (200), and (112) planes of β-AgI (JCPDS no. 09-0374). AgI/MFeO3/g-C3N4 XRD patterns depicted in Figure 1b exhibiting the diffraction peaks of AgI, g-C3N4, and MFeO3 confirmed the successful synthesis of AgI/MFeO3/g-C3N4.

The functional group of AgI/MFeO3/g-C3N4 and g-C3N4 was investigated by FT-IR spectroscopy. The spectra illustrated by the FT-IR analysis were shown in Figure 2. The absorption can be observed centred at 422 cm\(^{-1}\) reflects the vibrations of Ag-I [18]. The absorption peaks at 545 cm\(^{-1}\) denote the stretching vibrational mode of Fe-O bonds [19] in merely AgI/MFeO3/g-C3N4. The sharp characteristic valued 804 cm\(^{-1}\) was symbolizing the triazine rings structure [20] in g-C3N4. The several absorption peaks during the wavenumber of 1197 to 1637 cm\(^{-1}\) were ascribed to typical aromatic C–N stretching vibration mode and surface O–H absorbed on surface [21]. In conclusion, the FT-IR results proved the formation of AgI/MFeO3/g-C3N4 heterojunction—compared with bare g-C3N4 and Fe–O bond (545 cm\(^{-1}\))—and were only ascertained in AgI/MFeO3/g-C3N4, indicating the chemical bond interaction within AgI, MFeO3, and g-C3N4.

![Figure 1](image1.png)

**Figure 1.** (a) The XRD patterns of AgI, g-C3N4, and AgI/MFeO3/g-C3N4 (M = Y, Gd, La) samples and (b) MFeO3 (M = Y, Gd, La).

![Figure 2](image2.png)

**Figure 2.** FT-IR absorbance spectra of obtained samples.
The constituent elements and chemical status of AgI/MFeO$_3$/g-C$_3$N$_4$ (M = Y, Gd, La) photocatalysts were investigated by X-ray photoelectron spectroscopy (XPS). Full integrate spectra of AgI/MFeO$_3$/g-C$_3$N$_4$ composites was illustrated in Figure 3a. The La 3d shown in Figure 3b can be divided into two peaks of 852.1 eV and 835.3 eV which were identified by La 3d$_{3/2}$ and La 3d$_{5/2}$ respectively [23]. As depicted in Figure 3c, the shoulder characteristic peaks located at 1125.5 eV and 1185.0 eV were symbolizing Gd 3d$_{3/2}$ and Gd 3d$_{5/2}$ attributed to Gd$^{3+}$ [24]. In Figure 3d, the binding energy observed at Y 3d$_{3/2}$ and Y 3d$_{5/2}$ were 158.0 eV and 156.5 eV, which was because of Y$^{3+}$ [25]. As demonstrated in Figure 3e, two peaks fitted at 709.1 eV and 721.7 eV of Fe 2p$_x$ and Fe 2p$_y$ were ascribed to Fe$^{3+}$ [23]. Figure 3f reveals that Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$ were symbolized by the peaks at 366.3 eV and 372.4 eV, which were representing Ag$^+$ [26]. C 1s spectrum was displayed in Figure 3g, whose peak fitted at 284.8 eV was ascribed to sp$^3$ C–C bond of carbon from the environment employed for XPS spectra calibration and the peak at 288.4 eV was related to the sp$^2$-bonded carbon (N–C=N). As Figure 3h revealed, there were two peaks located at 614.7 eV and 628.9 eV which were representing I 3d$_{3/2}$ and I 3d$_{5/2}$ belonging to I$^-$, respectively [27]. As investigated by the high-resolution XPS spectrum of La 3d, Gd 3d, and Y 3d, the characteristic peaks were corresponding to La$^{3+}$, Gd$^{3+}$, and Y$^{3+}$ and verifying the presence of LaFeO$_3$, GdFeO$_3$, and YFeO$_3$. The XPS results above ascertain component elements, corresponding chemical status and the present that the MFeO$_3$ couple the AgI/g-C$_3$N$_4$ hybrids demonstratively. The formation of AgI/MFeO$_3$/g-C$_3$N$_4$ heterojunction was further confirmed by XPS characterization.

The morphologies of the product as-obtained were investigated by FESEM and revealed in Figure 4. In Figure 4a, g-C$_3$N$_4$ consists of a typical nanosheet structure with a comparatively transparent and glossy surface. In Figure 4b, AgI was built up by relatively flat and smooth nanosheets which were folded over each other. g-C$_3$N$_4$ and AgI supply more activated areas on their layered structure for the photocatalytic reaction. Figure 4c–e shows MFeO$_3$ with three-dimensional spherical particulates, the diameter of the nanospheres was around 30–70 nm and the particular spherical structure of MFeO$_3$ provides more direct electron channels for photocatalytic activities. After ultrasonic-assisted hydrothermal treatment synthesizing, AgI/MFeO$_3$/g-C$_3$N$_4$, AgI, and MFeO$_3$ nanosheets were assembled on g-C$_3$N$_4$ nanosheet as shown in Figure 4f,g. The FE-SEM results proved the XPS, XRD, and FT-IR analysis.

DRS was employed to investigate the light absorption on samples, which reported the light utilization capability of samples as-prepared. As shown in Figure 5a, the optical absorption edges of pristine g-C$_3$N$_4$ and AgI were examined at 463 nm and 482 nm, respectively. After MFeO$_3$ doped on AgI/g-C$_3$N$_4$ hybrid, compared to bare g-C$_3$N$_4$, all the AgI/MFeO$_3$/g-C$_3$N$_4$ showed redshifts and improved visible light absorption abilities. The absorption edges were shifted to 604 nm (AgI/LaFeO$_3$/g-C$_3$N$_4$), 534 nm (AgI/GdFeO$_3$/g-C$_3$N$_4$), and 484 nm (AgI/YFeO$_3$/g-C$_3$N$_4$). The significant improvement of the visible light absorption was attributed by MFeO$_3$, which experts in supplying more direct electron transfer channels for the composites resulting in a more constructive light-harvesting property of AgI/MFeO$_3$/g-C$_3$N$_4$. The bandgap energy (E$_g$) values of as-obtained composites were calculated by the Tauc formula in Figure 5b [28]. The optical Eg of bare g-C$_3$N$_4$, bare AgI, AgI/YFeO$_3$/g-C$_3$N$_4$, AgI/GdFeO$_3$/g-C$_3$N$_4$, and AgI/LaFeO$_3$/g-C$_3$N$_4$ were calculated to be 2.68, 2.57, 2.56, 2.32, and 2.05 eV respectively. The bandgap was narrowed by AgI and MFeO$_3$ indicating the beneficial bandgap matching and appropriate structure arrangement of AgI/MFeO$_3$/g-C$_3$N$_4$. The bandgap matching and structure arrange will benefit the photogenerated electron migrations and separations from an efficient dual Z-scheme system during the photochemical course.
Figure 3. (a) X-ray photoelectron spectra of full spectra, (b) La 3d, (c) Gd 3d, (d) Y 3d, (e) Fe 2p, (f) Ag 3d, (g) C 1s, and (h) I 3d.
nanosheets which were folded over each other. g-C3N4 and AgI supply more activated areas on their layered structure for the photocatalytic reaction. Figure 4c–e shows MFeO\(_3\) with three-dimensional spherical particulates, the diameter of the nano spheres was around 30–70 nm and the particular spherical structure of MFeO\(_3\) provides more direct electron channels for photocatalytic activities. After ultrasonic-assisted hydrothermal treatment synthesizing, AgI/MFeO\(_3\)/g-C3N4, AgI, and MFeO\(_3\) nanospheres were assembled on g-C3N4 nanosheet as shown in Figure 4f–g. The FE-SEM results proved the XPS, XRD, and FT-IR analysis.

Figure 4. The FESEM microstructure of (a) g-C\(_3\)N\(_4\) nanosheets, (b) AgI, (c) LaFeO\(_3\), (d) GdFeO\(_3\) and (e) YFeO\(_3\) nanospheres, (f) AgI/LaFeO\(_3\)/g-C\(_3\)N\(_4\), (g) AgI/GdFeO\(_3\)/g-C\(_3\)N\(_4\), and (h) AgI/YFeO\(_3\)/g-C\(_3\)N\(_4\).
were demonstrated in Figure 6a. AgI/(PL). Generally, an intense peak means faster recombinations of charge pairs and a weak peak means better separations of electrons and holes. The PL spectra of samples as-prepared suggest that AgI/LaFeO3/g-C3N4, the formation of ternary heterojunction enhances the separations and transmissions of electrons aroused by visible light remarkably. Indicating that it could possess an excellent photocatalytic performance for NOF degradation.

The separation efficiency of photoexcited electron–hole pairs can be reflected by photoluminescence (PL). Generally, an intense peak means faster recombinations of charge pairs and a weak peak means better separations of electrons and holes. The PL spectra of samples as-prepared at room temperature were demonstrated in Figure 6a. AgI/MFeO3/g-C3N4 reveals lower PL emission intensities than original g-C3N4 by comparing the peaks from 450 nm to 470 nm. Especially, AgI/LaFeO3/g-C3N4 shows the lowest emission peaks suggesting that AgI/LaFeO3/g-C3N4, the formation of ternary heterojunction enhances the separations and transmissions of electrons aroused by visible light remarkably. Indicating that it could possess an excellent photocatalytic performance under xenon lamp, sample AgI/LaFeO3/g-C3N4—based on the results of DRS and PI, improvements of visible light absorption abilities and charge pairs separations have been revealed.

The N2 adsorption–desorption isotherms of AgI/MFeO3/g-C3N4 are illustrated in Figure 6b, the hysteresis loops of AgI/MFeO3/g-C3N4 all belong to IV-type isotherms. The BET specific surface area of AgI/LaFeO3/g-C3N4, AgI/GdFeO3/g-C3N4, and AgI/YFeO3/g-C3N4 are 79.32, 57.93, and 45.06 m²/g, respectively. It can be seen that AgI/LaFeO3/g-C3N4 possesses the highest surface area within AgI/MFeO3/g-C3N4 samples suggesting that the photocatalytic performance of AgI/LaFeO3/g-C3N4 is better than that of AgI/GdFeO3/g-C3N4 and AgI/YFeO3/g-C3N4 since the higher surface help to reduce the recombination of charge pairs.

**Figure 5.** (a) DRS of AgI, g-C3N4 and AgI/MFeO3/g-C3N4 (M = Y, Gd, La) and (b) bandgap calculation of obtained samples.

**Figure 6.** (a) The photoluminescence of AgI, g-C3N4 and AgI/MFeO3/g-C3N4 (M = Y, Gd, La) and (b) N2 adsorption–desorption isotherms of AgI/MFeO3/g-C3N4.
2.2. Photocatalytic Performance and Photodegradation Mechanism

The photocatalytic activities of all the samples as-obtained were evaluated through the photodegradation experiments executed under a xenon lamp in quartz beakers with uninterrupted magnetic stirring to maintain uniform distributions of photocatalysts. Before turning on the xenon lamp, the suspension was stirred away from light for 0.5 h to gain the adsorption–desorption equilibrium between solution and photocatalyst. The photocatalytic performance of NOF over g-C$_3$N$_4$, AgI, and AgI/MFeO$_3$/g-C$_3$N$_4$ and the blank experiment (without photocatalysts) were illustrated in Figure 7a,b. For AgI and g-C$_3$N$_4$, the photodegradation rates of NOF were just 35% and 41% for 3 h, respectively. NOF was almost not photodegraded without catalyst irradiated by a xenon lamp. While the photocatalytic efficiencies of NOF were obviously enhanced, reaching 68% over AgI/YFeO$_3$/g-C$_3$N$_4$, 72% over AgI/GdFeO$_3$/g-C$_3$N$_4$, even 95% over AgI/LaFeO$_3$/g-C$_3$N$_4$. It can be concluded that the photocatalytic performance of AgI/LaFeO$_3$/g-C$_3$N$_4$ was the best within the samples obtained.

Benefitting from the construction of ternary heterojunctions, AgI/MFeO$_3$/g-C$_3$N$_4$ samples were able to harvest more visible light than AgI and g-C$_3$N$_4$ because of the red shift of absorption edge, and to reduce the recombination of electrons and holes. AgI/LaFeO$_3$/g-C$_3$N$_4$ possesses enhancements on visible light absorption and larger specific surface area leads improvements on the migrations of charge pairs.

The Langmuir–Hinshelwood model was employed to accurately investigate the reaction kinetics of NOF degradation during the photocatalytic experiment. The model can be interpreted as follows [29],

$$
kt = -\ln(c_0/c_t)
$$

where $c_0$ and $c_t$ were representing the initial concentration and residual concentration at the examined time, and $k$ was pseudo-first-order rate constant. As shown in Figure 8a, the pseudo-first-order rate constants of AgI/YFeO$_3$/g-C$_3$N$_4$, AgI/GdFeO$_3$/g-C$_3$N$_4$, and AgI/LaFeO$_3$/g-C$_3$N$_4$ were calculated to be 0.00481, 0.00640, and 0.0188 min$^{-1}$, respectively. The highest rate constant of AgI/LaFeO$_3$/g-C$_3$N$_4$ was 7.61 times than pristine AgI (0.00247 min$^{-1}$) and 7.01 times than bare g-C$_3$N$_4$ (0.00268 min$^{-1}$), which was beneficial from LaFeO$_3$ nanospheres enhancing the migrations and separations of photogenerated charge pairs within the ternary composites.
The photocatalytic activities were suppressed a little when AgNO₃ was added. While BQ, IPA, and EDTA-2Na were added into the photodegradation process, the photodegradation efficiency reduced extremely. Based on the result of the radicals quenching experiments, -OH, -O₂⁻, and h⁺ were the main roles in the photodegradation process.

The radicals quenching experiments were carried out to further investigate the roles of the reactive species in the AgI/LaFeO₃/g-C₃N₄ photodegradation reaction. P-benzo-quinone (BQ), AgNO₃, ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), and isopropyl alcohol (IPA) were chosen as the scavengers for -O₂⁻, e⁻, h⁺, and -OH. The result was illustrated in Figure 8b, the highest photodegradation rate could be gain when no scavengers participated in the experiment. The photocatalytic activities were suppressed a little when AgNO₃ was added. While BQ, IPA, and EDTA-2Na were added into the photodegradation process, the photodegradation efficiency reduced extremely. Based on the result of the radicals quenching experiments, -OH, -O₂⁻, and h⁺ were the main roles in the photodegradation process.

Figure 8. (a) Reaction kinetics of photocatalytic degradation of AgI/MFeO₃/g-C₃N₄ (M = Y, Gd, La) and (b) radicals quenching experiments.

The stability of AgI/LaFeO₃/g-C₃N₄ photocatalyst was examined by the repeating photocatalytic degradation experiment in 18 h. As displayed in Figure 9a, after six continuous cycles have been completed, the photodegradation rate of AgI/LaFeO₃/g-C₃N₄ remains >92%, indicating the remarkable photostability. As displayed in Figure 9b, the XRD patterns of original and regenerated AgI/LaFeO₃/g-C₃N₄ revealed that the crystalline structure of AgI/LaFeO₃/g-C₃N₄ does not possess a significant change until sequential cycles accomplishing. The entire results above indicated that AgI/LaFeO₃/g-C₃N₄ demonstrate outstanding stability and photocatalytic ability towards NOF in practical applications.

Figure 9. (a) The sixth repetition photocatalytic activities experiment of AgI/MFeO₃/g-C₃N₄ and (b) XRD patterns of fresh and used AgI/LaFeO₃/g-C₃N₄.
To better analyze the photocatalytic oxidation process, it was essential to distinguish the possible band position of each component of the composite photocatalyst. The band position determines the migration and recombination of photo-generated electrons and holes in the interaction with individual components of the composite photocatalyst. The valance band (VB) and conduction band (CB) of AgI/LaFeO$_3$/g-C$_3$N$_4$ can be appraised by the empirical Equations (2) and (3) as shown below [29]

$$E_{VB} = X - E_e + 0.5E_g$$  \hspace{1cm} (2)

$$E_{CB} = E_{VB} - E_g$$ \hspace{1cm} (3)

where $E_{VB}$ and $E_{CB}$ were the VB and CB edge potential respectively, $X$ was the semiconductor absolute electronegativity, represented as the absolute electronegativity of the constituent atoms, and $E_e$ was the energy of free electrons on hydrogen atoms valuing 4.5 eV, approximately. $E_g$ was symbolizing as the bandgap belonging to the semiconductor material. The structure of NOF, possible degradation pathways and the theoretical values of the CB and VB calculated for AgI, LaFeO$_3$, and g-C$_3$N$_4$ and the electron migration within ternary under xenon lamp was illustrated in Figure 10. The $E_{CB}$ and $E_{VB}$ of LaFeO$_3$ were calculated to be 0.37 eV and 2.61 eV, AgI were $-0.90$ eV and 1.66 eV, and g-C$_3$N$_4$ were $-1.13$ eV and 1.45 eV. Depending on the characterization and experiment results above, a possible mechanism in the dual Z-scheme system of AgI/LaFeO$_3$/g-C$_3$N$_4$ was schematically proposed in Figure 10. In the photocatalytic process, enhancing the electrons and holes separation and expediting the electrons migration was a conventional and proven method to ameliorate the photocatalytic behavior for photocatalyst. Just as shown in Figure 10, LaFeO$_3$ acts as the electron transmission intermediary in the dual Z-scheme photocatalytic system in ternary photocatalyst AgI/LaFeO$_3$/g-C$_3$N$_4$. Because of the relative positions, LaFeO$_3$ possesses higher CB than AgI and g-C$_3$N$_4$. During the photocatalytic experiments, the electrons generated in the CB can be transferred to recombine with the holes on the VB of AgI and g-C$_3$N$_4$. Benefitting from interfacial electron transmissions, the electron–hole pairs were separated further. The electrons on the CB of AgI and g-C$_3$N$_4$ will react with O$_2$ dissolved in water forming $\cdot$O$_2^-$ due to their lower potentials than O$_2$/O$_2^-$ ($-0.33$ eV vs. NHE) [30]. Meanwhile, the h$^+$ accumulated on the VB of LaFeO$_3$ could oxidize OH$^-$ or H$_2$O to $\cdot$OH because the VB potential of LaFeO$_3$ was higher than the $\cdot$OH/OH$^-$ potential (+1.99 eV vs. NHE) and H$_2$O/OH$^-$ (+2.27 eV vs. NHE) [31]. With the construction of the dual Z-scheme system, the photogenerated electrons were produced rapidly and the separation of photogenerated charge carriers was effectively enhanced, and the strong redox capability in photocatalytic activities was maintained in AgI/LaFeO$_3$/g-C$_3$N$_4$. The possible reaction process can be expressed by the following equations.

$$\text{AgI/LaFeO}_3/\text{g-C}_3\text{N}_4 + hv \rightarrow \text{AgI/LaFeO}_3/\text{g-C}_3\text{N}_4 + h^+ + e^-$$  \hspace{1cm} (4)

$$\text{H}_2\text{O} \rightleftharpoons H^+ + \text{OH}^-$$ \hspace{1cm} (5)

$$\text{OH}^- + h^+ \rightarrow \text{OH}$$ \hspace{1cm} (6)

$$\text{H}_2\text{O} + h^+ \rightarrow \text{OH} + \text{H}^+$$ \hspace{1cm} (7)

$$\text{O}_2 + e^- \rightarrow \cdot\text{O}_2^-$$ \hspace{1cm} (8)

$$\text{NOF} + \text{O}_2^-/\text{h}^+/\text{OH} \rightarrow \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}$$ \hspace{1cm} (9)
strong redox capability in photocatalytic activities was maintained in AgI/LaFeO$_3$/g-C$_3$N$_4$. The possible reaction process can be expressed by the following equations.

\begin{align*}
\text{AgI/LaFeO}_3/g\text{-C}_3\text{N}_4 \xrightarrow{hv} \text{AgI/LaFeO}_3/g\text{-C}_3\text{N}_4 + h^+ + e^- \quad (4) \\
\text{H}_2\text{O} \xleftrightarrow{} \text{H}^+ + \text{OH}^- \quad (5) \\
\text{OH}^- + h^+ \xrightarrow{} \text{OH} \quad (6) \\
\text{H}_2\text{O} + h^+ \xrightarrow{} \cdot\text{OH} + \text{H}^+ \quad (7) \\
\text{O}_2 + e^- \xrightarrow{} \cdot\text{O}_2^- \quad (8) \\
\text{NOF} + \text{O}_2^- / h^+/\cdot\text{OH} \xrightarrow{} \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad (9)
\end{align*}

Figure 10. The structure of NOF, possible degradation pathways and possible mechanism of AgI/LaFeO$_3$/g-C$_3$N$_4$ composite photocatalyst.

3. Materials and Methods

We used ultrasound-assisted method to prepare the AgI/MFeO$_3$/g-C$_3$N$_4$ and XRD, FESEM, XPS, and BET to characterize the structure of the samples, we also employed DRS and PL to examine the absorption capacity of samples. The photocatalytic ability of the samples obtained was investigated by the photodegradation experiment of NOF under a xenon lamp.

3.1. Materials

Melamine, Y(NO$_3$)$_3$·6H$_2$O, Gd(NO$_3$)$_3$·6H$_2$O, La(NO$_3$)$_3$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, citric acids, KI, and AgNO$_3$ were all analytical purity, provided by MACLIN Chemical Regent Co. Ltd. (Shanghai, China). Norfloxacin (NOF, analytical purity) was provided by ALADDIN Chemical Regent Co. Ltd. (Shanghai, China).

3.2. Preparations of g-C$_3$N$_4$ Nanosheets

g-C$_3$N$_4$ nanosheets were obtained according to the previous report [3]. A moderate amount of melamine was placed in a covered crucible, heated at a temperature of 2 °C to 520 °C, and kept for 2 h. After cooling to room temperature, the crucibles were taken down covers and heated to 520 °C at a temperature of 2 °C and maintained for another 2 h.

3.3. Preparations of MFeO$_3$ Nanospheres

To gain pure MFeO$_3$ nanospheres, typically, 1 mmol Y(NO$_3$)$_3$·6H$_2$O, 1 mmol Gd(NO$_3$)$_3$·6H$_2$O, 1 mmol La(NO$_3$)$_3$·6H$_2$O, 1 mmol Fe(NO$_3$)$_3$·9H$_2$O, and 5 mmol citric acids with 20 mL ethylene glycol were dissolved in deionized water respectively in three different beakers. After being magnetically stirred for 1 h, the mixture solution was sealed into a Teflon-lined reaction autoclave and the temperature was maintained at 180 °C for 12 h. After washed by absolute ethyl alcohol and DI water, the precipitate obtained was dried at 160 °C for 6 h and calcined at 800 °C for 2 h to gain pure MFeO$_3$ (M = Y, Gd, La) nanospheres.
3.4. Preparations of AgI Nanosheets

To obtain AgI nanosheets, 1 mmol KI and 1 mmol AgNO3 were dissolved in DI water away from light and magnetically stirred for 30 min. The water contained in the product was evaporated at 90 °C for 12 h in dark to achieve AgI.

3.5. Preparations of AgI/MFeO$_3$/g-C$_3$N$_4$ Composites

To synthesize AgI/MFeO$_3$/g-C$_3$N$_4$, we selected a facile ultrasound-assisted method. AgI, MFeO$_3$ (M = Y, Gd, La) and g-C$_3$N$_4$ were dispersed in DI water after ultrasonic vibration for 30 min, dried at 80 °C for 5 h and calcined at 320 °C for 2 h to achieve MFeO$_3$/AgI/g-C$_3$N$_4$ (M = Y, Gd, La). The mass ratio of MFeO$_3$ (M = Y, Gd, La), AgI and g-C$_3$N$_4$ was 30:1:100.

3.6. Characterization

The morphologies and microstructure of the photocatalyst prepared were characterized by X-ray diffraction (XRD, Shimadzu LabX-6000 Cu K-alpha radiation $\lambda = 0.15418$ nm) over the 2$\theta$ of 10–80°, Fourier transform infrared spectrum (FT-IR, Bruker Vertex70, Karlsruhe, Germany) in the absorbance range of 4000–450 cm$^{-1}$ with a spectral resolution of 4 cm$^{-1}$, the surface microstructure images were gained on a Hitachi S-4800 field emission scanning electron microscope (FESEM, Tokyo, Japan) at 10 kV, X-ray photoelectron spectroscopy (XPS) measurements were carried out using a VG-Multilab 2000 X-ray Photoelectron Spectrometer Microprobe (Madison, USA) with achromatic Al Kx (1486.6 eV). The optical properties were indicated by photoluminescence (PL) at room temperature and a JASCO UV-2000 UV–vis diffuse reflectance spectroscopy (DRS) spectrophotometer with a wavelength of 200–800 nm (Tokyo, Japan).

3.7. Photodegradation Measurements

To examine the photocatalytic performance of the samples obtained, the photodegradation of NOF experiment was operated under a Xenon lamp (XQ-500W 40 mW/cm$^2$). 100 ml of NOF (20 mg/L) and 0.2 g of photocatalysts, as-prepared, were infused in a beaker and magnetically stirred at the same time. Preliminarily, the turbid liquid obtained was maintained without light for 0.5 h to gain adsorption–desorption equilibrium between NOF and samples in dark. Then the suspension was exposed to a xenon lamp. During the experiment, 5 mL of the mixture was taken out and centrifuged at 8000 rpm for 5 min to get photocatalyst separated each time. The supernatants gained were examined the absorbance at NOF absorption band maximum (280 nm) by an UV–vis spectrum (MAPADA, UV-1800PC, Shanghai, China).

4. Conclusions

To sum up, AgI/MFeO$_3$/g-C$_3$N$_4$ (M = Y, Gd, La) composites were prepared by an ultrasound-assisted hydrothermal method. The photocatalytic activities over these ternary photocatalysts towards NOF were proved to be a remarkable improvement. Compared to AgI/GdFeO$_3$/g-C$_3$N$_4$ and AgI/YFeO$_3$/g-C$_3$N$_4$, AgI/LaFeO$_3$/g-C$_3$N$_4$ possesses higher visible light absorption ability and larger specific surface area. In 180 min, 95% of the NOF was degraded over AgI/LaFeO$_3$/g-C$_3$N$_4$ under a xenon lamp irradiation. A possible enhanced mechanism of dual Z-scheme system was proposed. In the dual Z-scheme system, LaFeO$_3$ nanospheres acting as the electron transmission media after assembled with AgI and g-C$_3$N$_4$ nanosheets, promote the separations and migrations and weaken recombinations of photogenerated electron–hole pairs. This work may provide more informative evidence for the structure designs of lanthanide series perovskite-compound-doped g-C$_3$N$_4$-based dual Z-scheme system ternary photocatalysts for practical applications in water treatment.

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