

Article

Synthesis of a Novel Photocatalyst $MVO_4/g-C_3N_4$ ($M = La, Gd$) with Better Photocatalytic Activity for Tetracycline Hydrochloride Degradation under Visible-Light Irradiation

Zhengru Zhu, Songlin Han, Yongqiang Cao * and Junchao Jiang

School of Geography, Liaoning Normal University, Dalian 116029, China; zhengruzhu@lnnu.edu.cn (Z.Z.); mochawei475@163.com (S.H.); jiangjunchao@lnnu.edu.cn (J.J.)

* Correspondence: caoyongqiang@lnnu.edu.cn; Tel.: +86-0411-82159593

Abstract: In this study, novel photocatalysts $MVO_4/g-C_3N_4$ ($M = La, Gd$) were prepared by the hydrothermal method, through which different loading amounts of 10–50% MVO_4 and $g-C_3N_4$ were mixed and ultrasonically oscillated to gain heterojunction catalysts. All the samples were characterized by XRD, SEM, TEM, FT-IR, XPS, Us-vis, and PL to ensure the successful integration of $LaVO_4$ and $GdVO_4$ with $g-C_3N_4$. The obtained results showed that $MVO_4/g-C_3N_4$ could effectually improve the separation efficiency of photogenerated carriers during the photodegradation process, thus improving the photodegradation efficiency, while among them, 40% $GdVO_4/g-C_3N_4$ showed the best photocatalytic performance and degradation of tetracycline hydrochloride, reaching up to 91% for 3 h, which was 3.64 times higher than pristine $g-C_3N_4$. From the discussed results above, the possible mechanism of the photodegradation process was put forward. This study supplies a promising method to gain $g-C_3N_4$ -based photocatalysts for antibiotics removal.

Keywords: heterojunction photocatalyst; vanadate; graphitic carbon nitride; antibiotic degradation



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1. Introduction

In recent years, antibiotic pollutants represented by tetracycline have been frequently detected in water, posing a great threat to the ecological environment and human health [1–4]. It is worth noting that compared with other antibiotics, tetracycline has the following features: biological accumulation and a long cycle [5]; natural attenuation with the passage of time, parts of the residual will not be degraded in environmental mediums but rather enter the body through the food chain [6]; it is a potential threat to the human body, the excessive intake may even affect human body physiology because it has severe carcinogenic, teratogenic and mutagenic consequences [7]. Therefore, finding a way to remove the tetracycline hydrochloride (TC) residues in the water environment is an urgent issue. At present, the methods used to remove tetracycline from wastewater and soil mainly include a physical method, chemical oxidation method [8], biodegradation method, etc. However, some traditional processing methods are limited in practical application due to their disadvantages, such as a complex process, high operating costs, and unstable effects. As of now, the application of advanced oxidation technology, especially semiconductor photocatalysis technology, in tetracycline wastewater treatment has been widely studied, and some research results have been achieved.

For a photocatalytic system with excellent performance, it is necessary to have a wide solar absorption range, high carrier separation and transmission efficiency, and strong redox capacity. Due to its simple synthesis method, unique electron band structure, and excellent photocatalytic cycling stability, $g-C_3N_4$ has become a hot research object of novel photocatalysts [9]. However, in actuality, the photocatalytic activity of $g-C_3N_4$ monomer materials is limited by the low utilization of sunlight and the high recombination rate of photogenerated electron holes [10,11]. Based on the semiconductor composite modification

of energy level matching, the interface heterojunction can be constructed by combining $g\text{-C}_3\text{N}_4$ with another semiconductor to improve the separation and transmission efficiency of photogenerated carriers, thus improving the photocatalytic efficiency [12].

In the present work, we prepared novel $\text{MVO}_4/g\text{-C}_3\text{N}_4$ ($M = \text{La, Gd}$) photocatalysts via the hydrothermal method. All the samples were further characterization by XRD, SEM, TEM, FT-IR, XPS, DRS, and PL. Moreover, TC was selected as a target pollutant and photodegradation experiments were performed under visible light irradiation. This study concentrated on the design of the novel heterojunction and its speculative mechanism of TC photodegradation under visible light.

2. Materials and Methods

2.1. Materials

Lanthanum nitrate hexahydrate, gadolinium nitrate hexahydrate, ammonium vanadate, melamine, ammonium hydroxide, sodium hydroxide, and tetracycline hydrochloride were purchased from China National Pharmaceutical Group Chemical Reagent Co. Ltd. (Shanghai, China). All the chemicals were analytic reagents.

2.2. Preparation of $\text{MVO}_4/g\text{-C}_3\text{N}_4$ ($M = \text{La, Gd}$) Nanocomposite

First, 15.0 g of melamine was placed into a covered crucible and heated to 550 °C, kept for 2 h, then cooled to room temperature. The obtained yellow powder was ground thoroughly for 10 min to get $g\text{-C}_3\text{N}_4$ nanosheets [13].

LaVO_4 and GdVO_4 were prepared via the hydrothermal method [14]. First, 0.52 g of sodium hydroxide and 1.52 g of NH_4VO_3 were added to 30 mL of deionized water and dissolved by stirring to obtain an aqueous solution of sodium metavanadate (A solution for short). Then, for LaVO_4 , 5.84 g of lanthanum nitrate hexahydrate was added to a certain amount of water and dissolved by stirring to obtain B_1 solution. For GdVO_4 , 5.62 g gadolinium nitrate hexahydrate was added into deionized water and stirred to obtain B_2 solution. The yellow suspension was formed by adding B_1 and B_2 solution to A solution slowly and respectively. After mixing and stirring for 30 min, the yellow suspension was added 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 100 °C to form pure white LaVO_4 and GdVO_4 powder.

$\text{MVO}_4/g\text{-C}_3\text{N}_4$ composites were synthesized by ultrasonic dispersion method. A certain amount of pure $g\text{-C}_3\text{N}_4$ was added into 20 mL methanol, and the ultrasonic dispersion lasted for 30 min at room temperature. After 30 min, a certain amount of LaVO_4 and GdVO_4 powder were added, stirring the mixture 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 a muffle furnace, heating from 5 °C per minute to 250 °C and kept for 1 h, then naturally cooling to room temperature. The $\text{MVO}_4/g\text{-C}_3\text{N}_4$ composites were obtained. Lastly, 10%, 20%, 30%, 40%, and 50% $\text{MVO}_4/g\text{-C}_3\text{N}_4$ composite catalysts were prepared by adjusting the mass ratios of $g\text{-C}_3\text{N}_4$ and MVO_4 [15].

2.3. Characterization of Samples

For all the samples obtained, the X-ray powder diffraction patterns of the samples were measured on a Shimadzu LabX-6000 X-ray diffractometer equipped with Cu K α radiation ($\lambda = 0.15418$ nm). A scanning electron microscope (SEM, Hitachi, S-4800, Tokyo, Japan) and transmission electron microscope (TEM, Hitachi, H-600, Japan) were utilized to characterize morphologies and nanostructures of the prepared samples. The functional groups and networks could be identified by the Fourier transform infrared (FT-IR, Bruker AXS, TENSOR-27, Karlsruhe, Germany) spectra, X-ray photoelectron spectroscopy (XPS, Thermo VG, ESCALAB-250, Waltham, MA, USA) measurements. 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. The total organic carbon (TOC) was measured on a TOC analyzer (Analytik Jena AG, MultiN/C2100TOC/TN, Jena, Germany).

2.4. Photodegradation Measurements

The photocatalytic activities of all the samples prepared were measured by the degradation of tetracycline in aqueous solution under visible light illumination. The light source was provided by a xenon lamp (CEAULIGHT, CEL-S500, Beijing, China) with a 420 nm cutoff filter. Then 20 mg of all the samples obtained was mixed with 100 mL of 20 mg/L tetracycline solution and 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 and centrifuged and the absorbance the supernatant was measured by a UV–Vis spectrophotometer (MAPADA, UV-1800PC, Shanghai, China) at 356 nm.

3. Results and Discussion

3.1. Characterization Studies

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 $g\text{-C}_3\text{N}_4$ (JCPDS 87-1526) [16] showed two diffraction peaks of (100) and (002) planes at 13.06° and 27.56° . The diffraction peaks of GdVO_4 were loaded at 18.67° , 24.66° , 33.28° , 35.2° , 37.7° , 40.08° , 44.64° , 47.74° , 49.16° , 50.5° , 57.1° , 61.9° , 64.1° , 69.78° , and 73.18° , which were matched to crystal plane (101), (200), (112), (220), (202), (301), (103), (321), (312), (400), (420), (332), (204), (224), and (512) of GdVO_4 (JCPDF No. 17-0260) [17]. LaVO_4 (JCPDS 50-0367) [18] was 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. Nevertheless, the intensity of peaks at 20.26° , 27.76° , 30.12° , 35.1° , 45.06° , and 67.78° increased clearly with the amount of the LaVO_4 loading, indicating that more LaVO_4 particles were deposited on the surface of $g\text{-C}_3\text{N}_4$. In the XRD patterns of the $\text{MVO}_4/g\text{-C}_3\text{N}_4$ ($M = \text{La}, \text{Gd}$) composite catalysts, no impurity diffraction peaks were observed, which confirmed the successful synthesis of $\text{MVO}_4/g\text{-C}_3\text{N}_4$.

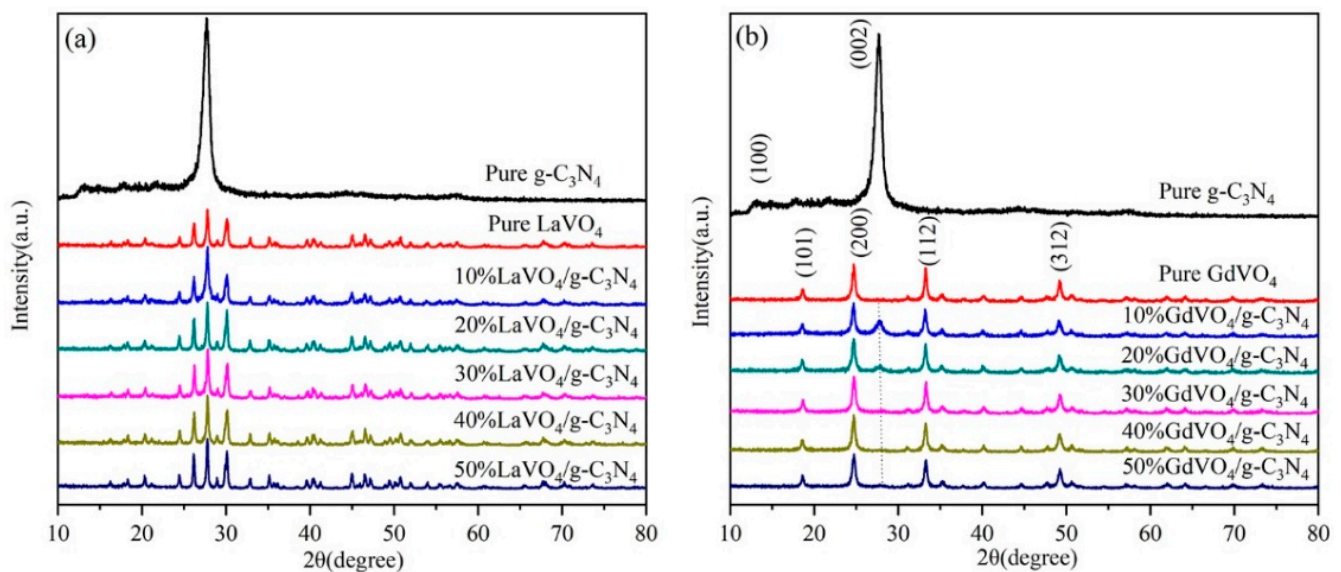


Figure 1. XRD patterns of (a) $g\text{-C}_3\text{N}_4$, LaVO_4 , and 10–50% $\text{LaVO}_4/g\text{-C}_3\text{N}_4$, (b) $g\text{-C}_3\text{N}_4$, GdVO_4 , and 10–50% $\text{GdVO}_4/g\text{-C}_3\text{N}_4$

To investigate the morphology and microstructure of the composite and its component parts. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images are shown in Figure 2. As shown in Figure 2a, $g\text{-C}_3\text{N}_4$ exhibits nanosheet structure with a smooth surface. As seen in Figure 2b, pure GdVO_4 powders display a coral-like structure. It can be concluded from the TEM graph of $\text{GdVO}_4/g\text{-C}_3\text{N}_4$ (Figure 2c) that the composite catalyst has two parts, one with a black color and coral-like structure, belonging to the GdVO_4 , and others with a French grey color and sheet-like structure of the $g\text{-C}_3\text{N}_4$. The morphology of pure LaVO_4 has a pin-like nanostructure, as shown in Figure 2d. In Figure 2e and the TEM graph of $\text{LaVO}_4/g\text{-C}_3\text{N}_4$ (Figure 2f), both LaVO_4 and $g\text{-C}_3\text{N}_4$ can be easily observed and LaVO_4 particles are well adhered to the surface of $g\text{-C}_3\text{N}_4$. Therefore, the constitution of $\text{MVO}_4/g\text{-C}_3\text{N}_4$ ($M = \text{La}, \text{Gd}$) composite is obviously recognizable, which is beneficial to the efficient transport of charge carriers in comparison to pure MVO_4 ($M = \text{La}, \text{Gd}$).

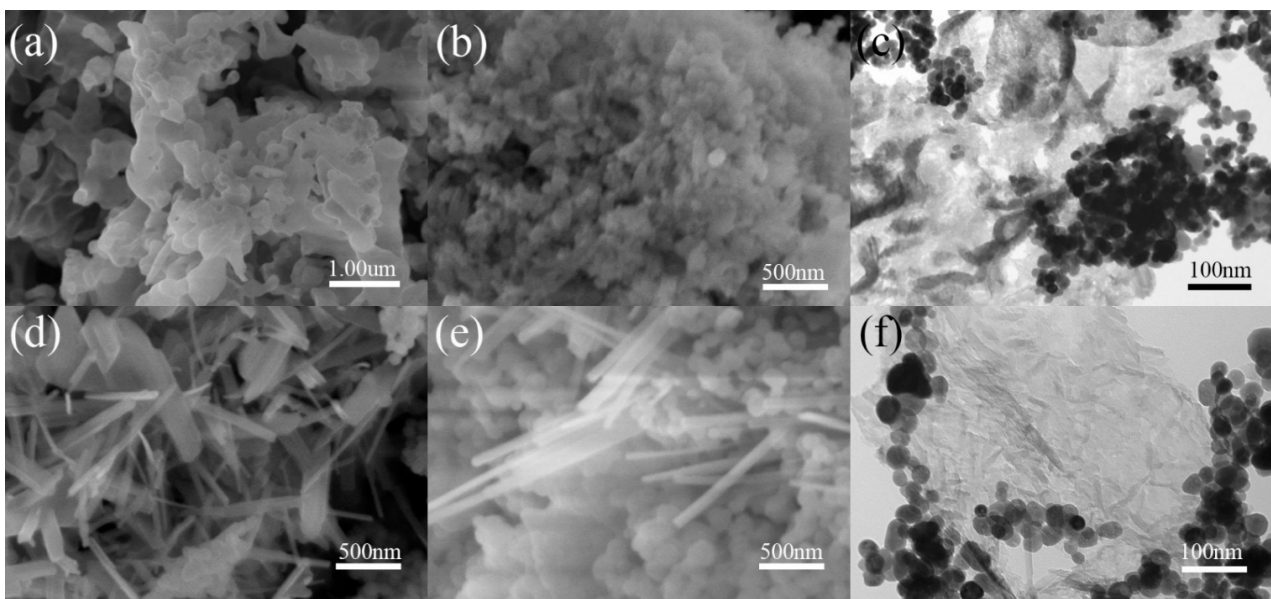


Figure 2. The SEM images of (a) $g\text{-C}_3\text{N}_4$, (b) GdVO_4 , (d) LaVO_4 , and (e) $\text{LaVO}_4/g\text{-C}_3\text{N}_4$ and the TEM images of (c) $\text{GdVO}_4/g\text{-C}_3\text{N}_4$ and (f) $\text{LaVO}_4/g\text{-C}_3\text{N}_4$.

FT-IR spectra of these synthesized samples are shown in Figure 3. In the case of MVO_4 ($M = \text{La}, \text{Gd}$), the two characteristic peaks at 810 and 440 cm^{-1} could be attributed to vibration of VO_4^{3-} [19], La-O [20] and Gd-O [21]. For pristine $g\text{-C}_3\text{N}_4$, the sharp peak at 1245 , 1233 , 1547 , and 1633 cm^{-1} was vested in characteristic peak bands of C-N heterocyclic compounds. Apart from above peaks, the peak at 808 cm^{-1} is the characteristic absorption peak of the triazine ring. In addition, the multiple peaks at $3000\text{--}3700\text{ cm}^{-1}$ and $1100\text{--}1700\text{ cm}^{-1}$ are assigned to N-H stretching vibration and the C=N and C-N heterocyclic rings, respectively. Obviously, according to the results above, it was concluded that heterojunctions consist of MVO_4 ($M = \text{La}, \text{Gd}$) and $g\text{-C}_3\text{N}_4$.

In order to study surface chemical composition and oxidation state of all the obtained samples, XPS measurement was performed on $\text{MVO}_4/g\text{-C}_3\text{N}_4$ ($M = \text{La}, \text{Gd}$). As can be seen in Figure 4a, in which the XPS spectra of $\text{MVO}_4/g\text{-C}_3\text{N}_4$ ($M = \text{La}, \text{Gd}$) samples are displayed, these characteristic peaks of Gd, La, V, O, C, and N were observed expressly. In Figure 4b, the binding energy peaks at 168.3 eV , 144.9 , and 139.3 eV are due to $\text{Gd}4d_{5/2}$ and $\text{Gd}4d_{3/2}$ [22]. In Figure 4c, the characteristic peaks at 853.6 and 849.4 eV are attributable to $\text{La } 3d_{3/2}$, and the binding energy of 836.8 and 832.7 eV corresponds to $\text{La } 3d_{5/2}$. As shown in the V 2p spectrum in Figure 4d, the binding energy peaks at 522.5 and 514.7 eV are ascribed to $\text{V } 2p_{1/2}$ and $\text{V } 2p_{3/2}$, and the V 2p peak is assigned to V^{5+} [23]. Moreover, the O 1s peaks at 529.8 eV and 527.9 eV in Figure 4e are in line with the O^{2-} and hydroxylated

oxygen atom adsorbed on the surface of MVO_4 ($M = La, Gd$), respectively. Then, the C 1s spectrum, as can be seen in Figure 4f, is fitted to two peaks at 285.2 eV and 281.8 eV, respectively, belonging to C-C coordination and sp^2 hybridized adventitious carbon atom in $g-C_3N_4$ or incompletely polymerized precursors [24]. For N 1s, Figure 4g shows three characteristic peaks of 401.5, 398.3, and 395.7 eV, which indicate that the nitrogen atom bonded to the surface hydrogen atom (N-H) and the tertiary nitrogen atom (N-(C)₃), and the nitrogen atom bonded to two carbon atom (C-N-C), respectively. Combining the XPS results above, we can conclude that $MVO_4/g-C_3N_4$ ($M = La, Gd$) composite were successfully synthesized.

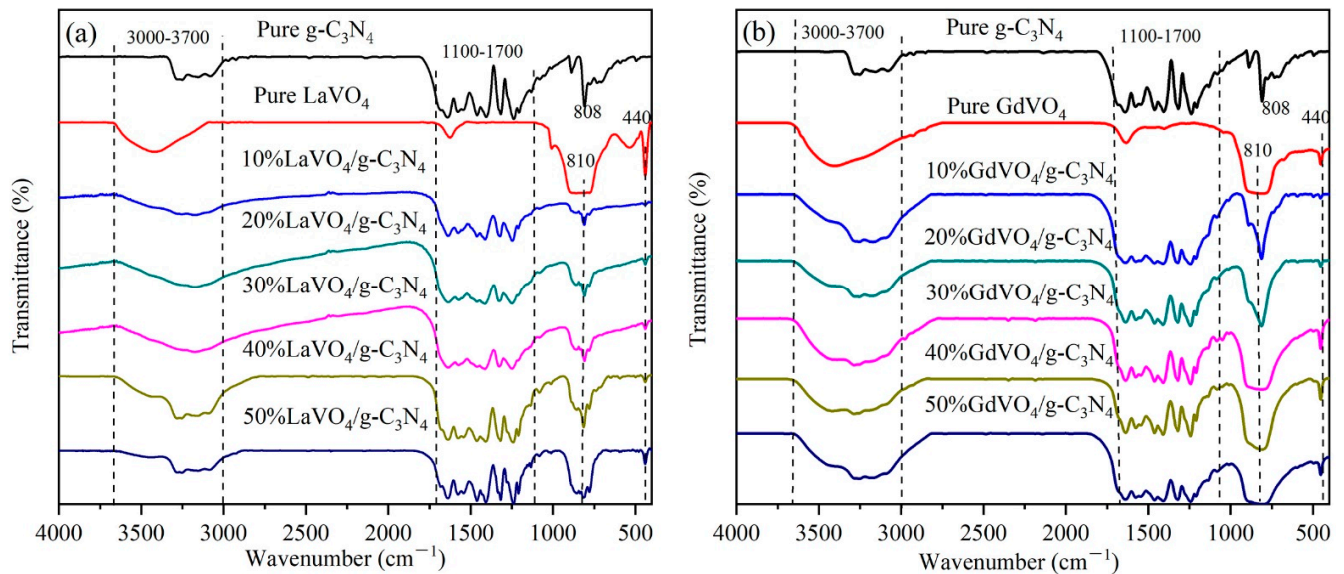


Figure 3. FT-IR absorbance spectra of (a) $g-C_3N_4$, $LaVO_4$, and 10–50% $LaVO_4/g-C_3N_4$, (b) $g-C_3N_4$, $GdVO_4$, and 10–50% $GdVO_4/g-C_3N_4$.

A comparison of UV-vis diffuse reflection spectra (DRS) of $g-C_3N_4$, $LaVO_4$, $GdVO_4$, and $MVO_4/g-C_3N_4$ ($M = La, Gd$) composite is shown in Figure 5a,b, and it is apparent that pure $g-C_3N_4$ displays efficient absorption at 460 nm. Compared with $g-C_3N_4$, MVO_4 ($M = La, Gd$) exhibits a wider band gap. As for $MVO_4/g-C_3N_4$ ($M = La, Gd$), it reveals stronger visible light absorption ability than pure $g-C_3N_4$. Overtly, with the amount of MVO_4 ($M = La, Gd$) increasing, absorption edges show a redshift, which contribute to formation of the heterojunction between MVO_4 ($M = La, Gd$) and $g-C_3N_4$, sequentially under the visible light range, and the absorption effective is significantly improved. In addition, the band gap value of all samples was estimated by Tauc formula.

As shown in Figure 5c–e, the bandgap energies of pure $g-C_3N_4$, pure $LaVO_4$, and pure $GdVO_4$ are 2.86, 3.47, and 3.54 eV, respectively, which are in keeping with the previous reports [25,26]. Moreover, the bandgap value of 20% $LaVO_4/g-C_3N_4$ was calculated to be 2.94 eV, severally. The bandgap value for 40% $GdVO_4/g-C_3N_4$ was 3.50 eV. Previous reports have suggested that lower band gap can promote the excitation and transition of electrons [27,28], thus improving the photocatalytic performance of the obtained materials.

Photoluminescence (PL) is another indicator of recombination of photogenerated electrons and holes [29], where low PL intensity suggests high separation of electron–hole pairs. The PL spectra of pristine $g-C_3N_4$, $LaVO_4$, $GdVO_4$, and different loadings of $MVO_4/g-C_3N_4$ ($M = La, Gd$) composite are displayed in Figure 6. Pure $g-C_3N_4$ has the highest PL spectral intensity, indicating that it is not an excellent photocatalyst because the carrier has the highest recombination intensity. The lowest PL intensity was observed for 40% $GdVO_4/g-C_3N_4$, which proves that this is probably the best photocatalyst studied in this study. Therefore, the observed quenching of luminescence intensity leads us to predict that $MVO_4/g-C_3N_4$ ($M = La, Gd$) has

higher photocatalytic activity. Therefore, so far, the above analyses confirm that both MVO_4 ($M = La, Gd$) and $g-C_3N_4$ coexist in the composite photocatalysts.

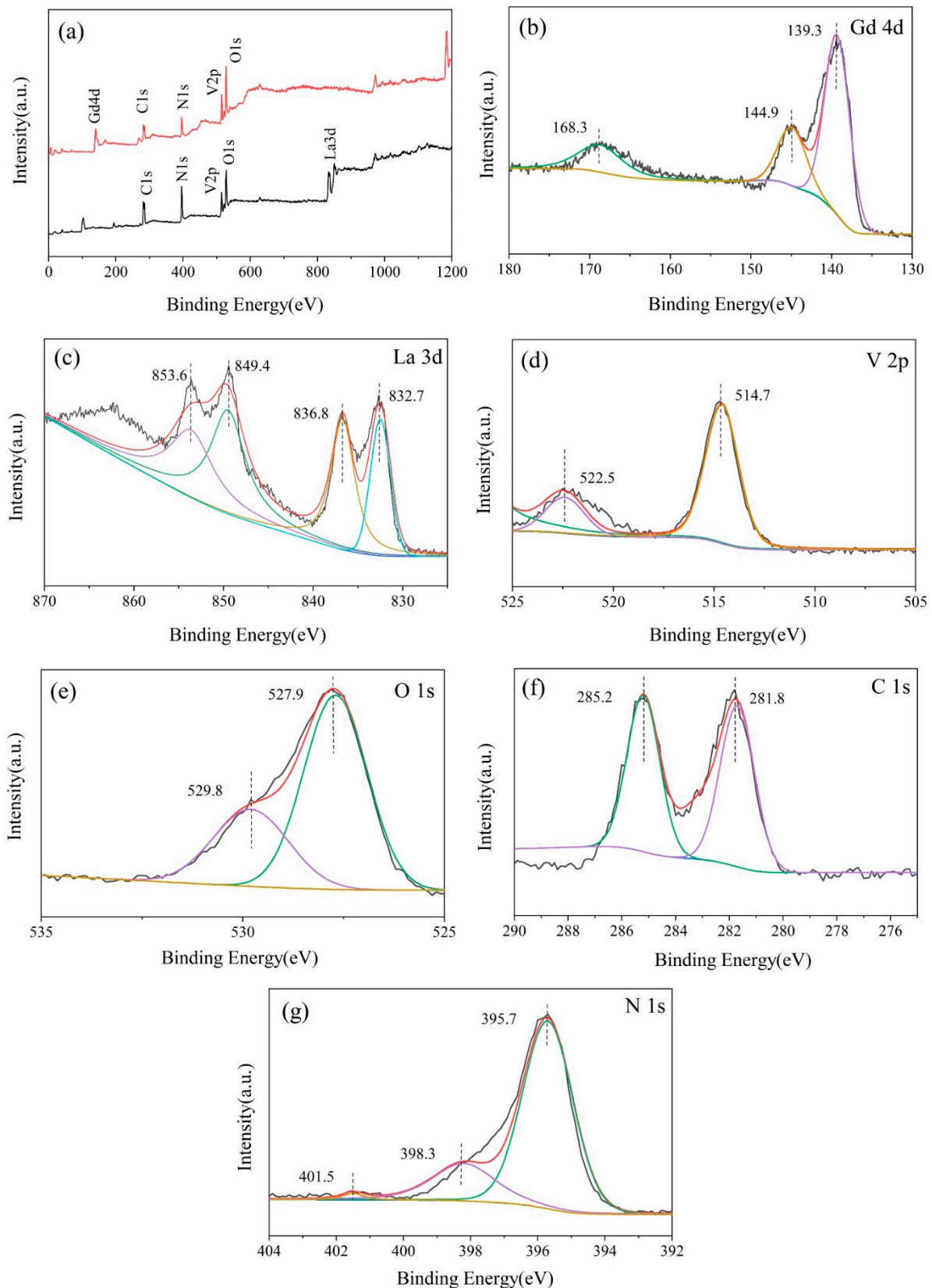


Figure 4. (a) XPS spectra of $MVO_4/g-C_3N_4$ ($M = La, Gd$) nanocomposites in a survey of the samples, (b) Gd 4d, (c) La 3d, (d) V 2p, (e) O 1s, (f) C 1s, and (g) N 1s.

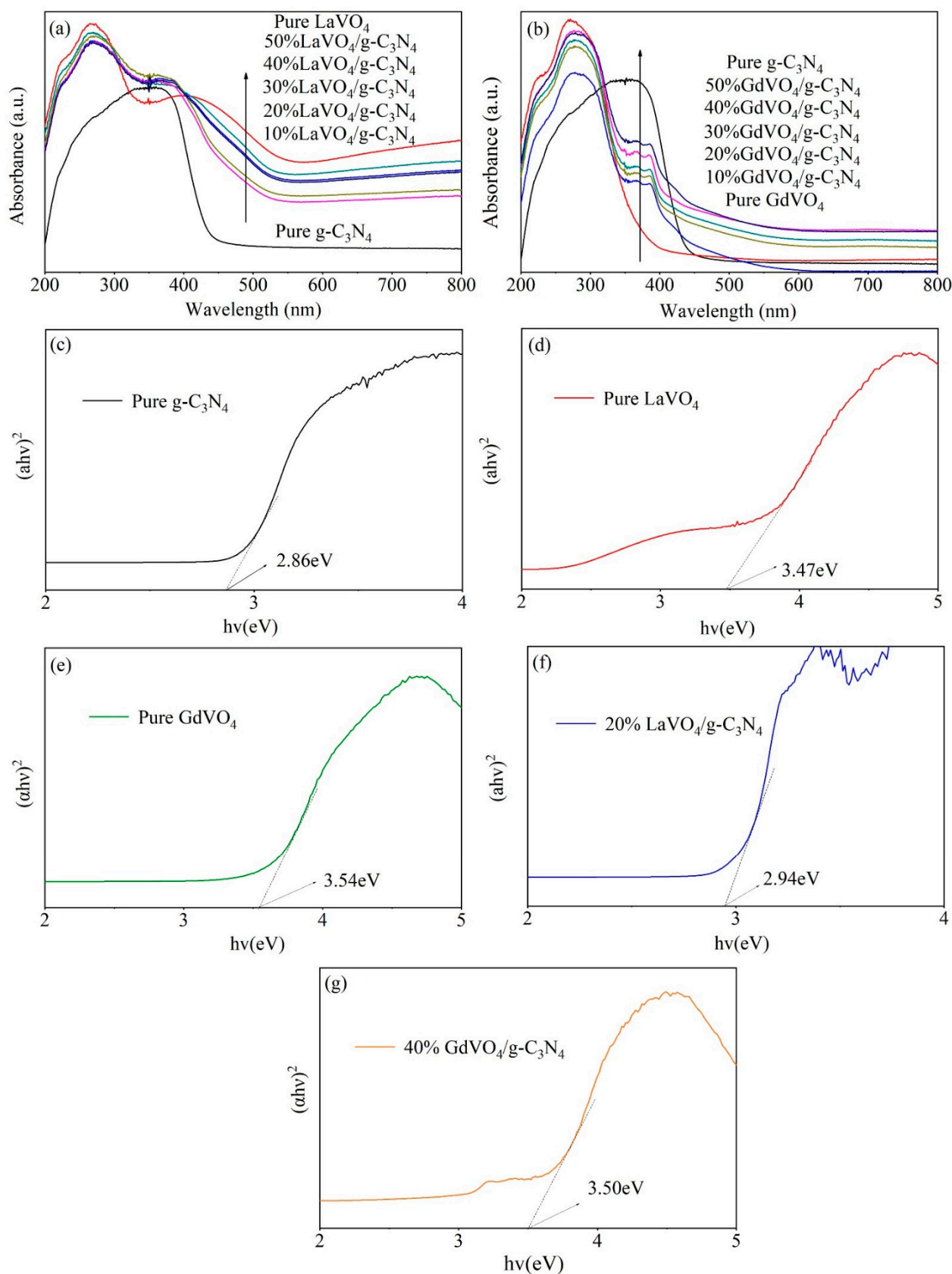


Figure 5. DRS spectra of (a) 10–50% LaVO₄/g-C₃N₄, (b) 10–50% GdVO₄/g-C₃N₄, and the band gaps of (c) g-C₃N₄, (d) LaVO₄, (e) GdVO₄, (f) 20% LaVO₄/g-C₃N₄, and (g) 40% GdVO₄/g-C₃N₄.

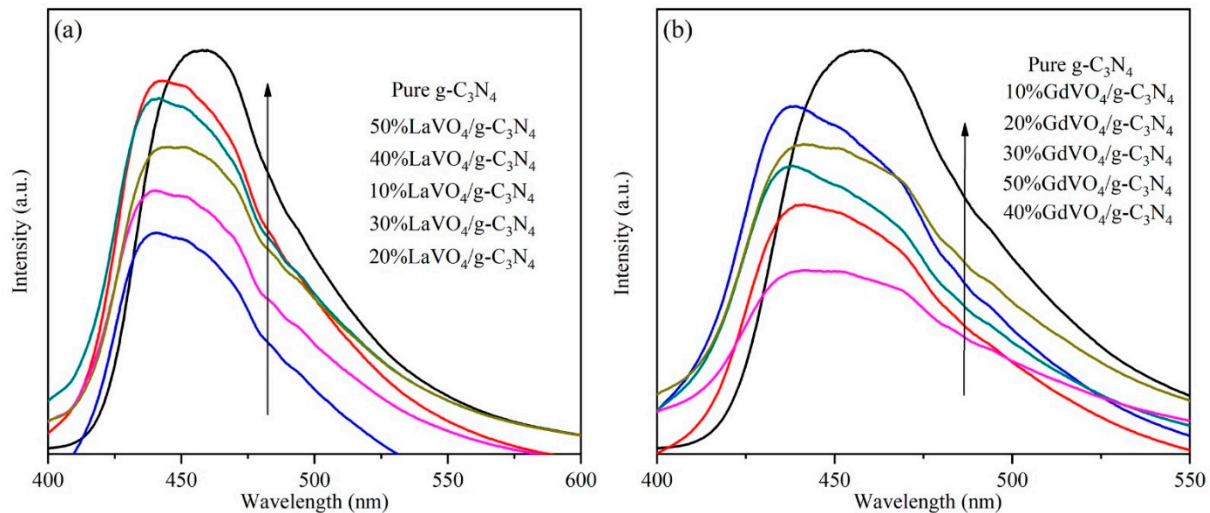


Figure 6. The photoluminescence of (a) $g\text{-C}_3\text{N}_4$ and 10–50% $\text{LaVO}_4/g\text{-C}_3\text{N}_4$, (b) $g\text{-C}_3\text{N}_4$ and 10–50% $\text{GdVO}_4/g\text{-C}_3\text{N}_4$.

3.2. Photocatalytic Performance

The photocatalytic performance of the obtained samples was evaluated by photooxidation degradation of TC under visible light. As displayed in Figure 7a, for the $g\text{-C}_3\text{N}_4$, LaVO_4 , and GdVO_4 , the photocatalytic degradation efficiencies of TC are just 25.3%, 32.8%, and 51.0% under visible light for 3 h, respectively. Based on the loading amount of LaVO_4 , from 10% to 50%, the degradation efficiencies of TC, improved, reaching to 63.2%, 79.1%, 69.8%, 53.6%, and 52.4%. As for a 10–50% loading amount of GdVO_4 the degradation efficiencies of TC reached to 68.0%, 73.4%, 82.4%, 91%, and 84.9% respectively. It can be easily observed that 40% $\text{GdVO}_4/g\text{-C}_3\text{N}_4$ has the best photodegradation efficiency among these obtained samples. The reasons why the $\text{GdVO}_4/g\text{-C}_3\text{N}_4$ composite can enhance photocatalytic activities are assigned to the following: (1) with the increase of GdVO_4 , the $\text{GdVO}_4/g\text{-C}_3\text{N}_4$ heterojunctions could obtain more visible light, which leads to red shift of absorption edges; (2) the $\text{GdVO}_4/g\text{-C}_3\text{N}_4$ heterojunctions would efficiently restrain recombination of photogenerated charge pairs. In addition, the Langmuir–Hinshelwood model formula is as follows, which was used to fit reaction kinetics:

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

where C_0 , C_t , and t represent the original concentration, final concentration, and reaction time, respectively, and k is the kinetic constant. Combining Figure 7b and Table 1, it can be concluded that the kinetic constants of TC photodegradation over 40% $\text{LaVO}_4/g\text{-C}_3\text{N}_4$ (0.01302 min^{-1}) is 7.44 times that of pristine $g\text{-C}_3\text{N}_4$ (0.00175 min^{-1}), indicating that the coupling $g\text{-C}_3\text{N}_4$ with GdVO_4 extremely enhances photodegradation efficiency of TC among these photocatalysts.

Moreover, the changes in the TOC reflected the degree of mineralization of an organic molecule during testing period. To further prove the photocatalytic degradation effect, we measured the degree of mineralization before and after the degradation of the target pollutants. The results showed that if there was no impurity in the TC solution, the TOC concentration was 21.09 mg/L, and after degradation with 40% $\text{GdVO}_4/g\text{-C}_3\text{N}_4$ as photocatalysts, the residual TOC was about 4.37 mg/L. Apparently, the TOC results indicated that the 40% $\text{GdVO}_4/g\text{-C}_3\text{N}_4$ could not only degrade TC but also mineralize it under visible light irradiation, working as an efficient photocatalyst to degrade TC in wastewater.

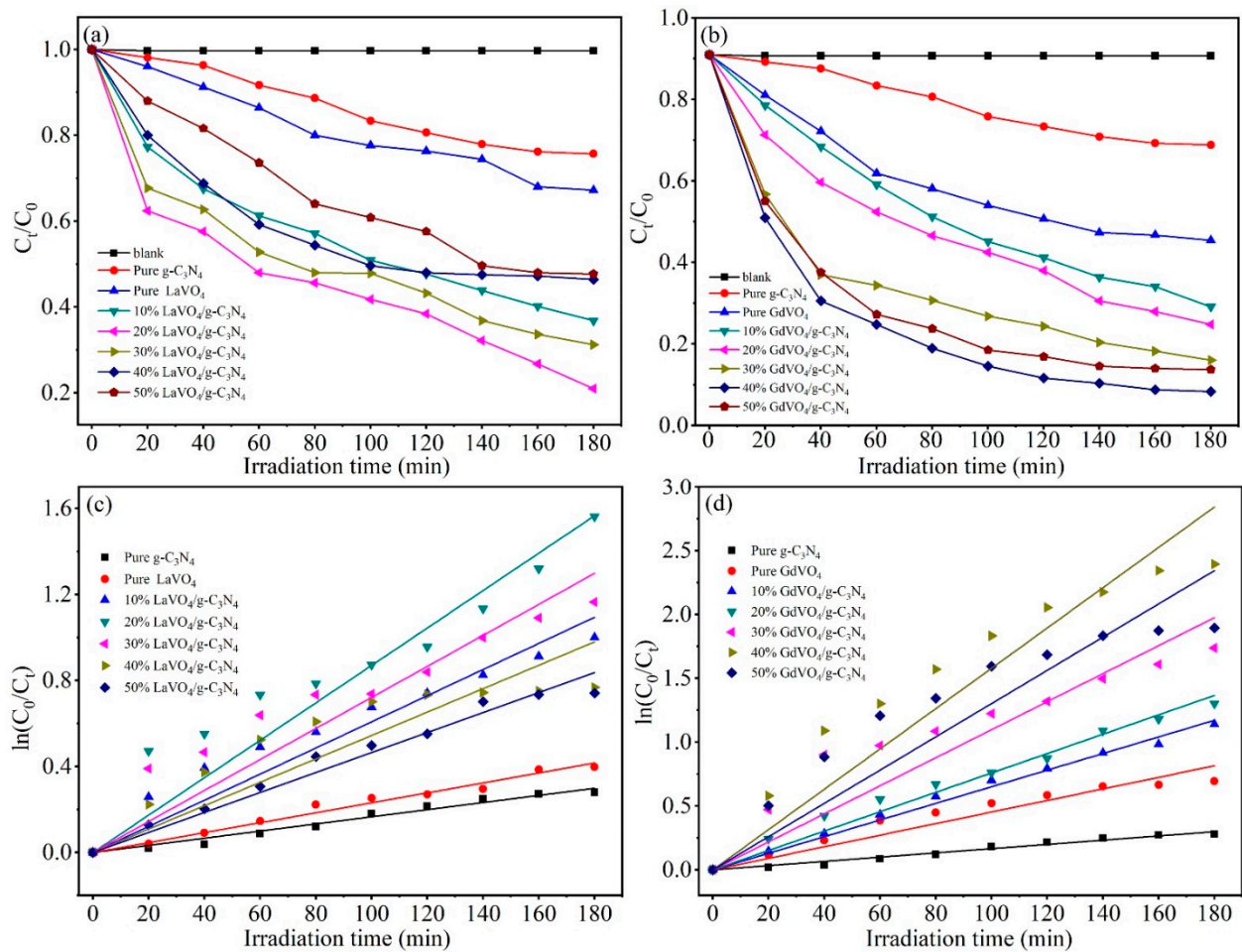


Figure 7. Photocatalytic performance of (a) $g\text{-C}_3\text{N}_4$, LaVO_4 , and 10–50% $\text{LaVO}_4/g\text{-C}_3\text{N}_4$, (b) $g\text{-C}_3\text{N}_4$, GdVO_4 , and 10–50% $\text{GdVO}_4/g\text{-C}_3\text{N}_4$ and kinetic curves of (c) $g\text{-C}_3\text{N}_4$, LaVO_4 , and 10–50% $\text{LaVO}_4/g\text{-C}_3\text{N}_4$, (d) $g\text{-C}_3\text{N}_4$, GdVO_4 , and 10–50% $\text{GdVO}_4/g\text{-C}_3\text{N}_4$.

Table 1. Photocatalytic results of all samples.

Sample Name	Degradation (%)	K (min^{-1})	R ²
$g\text{-C}_3\text{N}_4$	25.3%	0.00 166	0.99 093
LaVO_4	32.8%	0.00 225	0.97 831
GdVO_4	51.0%	0.00 453	0.97 748
10% $\text{LaVO}_4/g\text{-C}_3\text{N}_4$	63.2%	0.00 503	0.96 199
20% $\text{LaVO}_4/g\text{-C}_3\text{N}_4$	79.1%	0.00 717	0.94 071
30% $\text{LaVO}_4/g\text{-C}_3\text{N}_4$	69.8%	0.00 565	0.93 048
40% $\text{LaVO}_4/g\text{-C}_3\text{N}_4$	53.6%	0.00 399	0.82 037
50% $\text{LaVO}_4/g\text{-C}_3\text{N}_4$	52.4%	0.00 430	0.97 268
10% $\text{GdVO}_4/g\text{-C}_3\text{N}_4$	68.0%	0.00 651	0.99 711
20% $\text{GdVO}_4/g\text{-C}_3\text{N}_4$	73.4%	0.00 759	0.99 278
30% $\text{GdVO}_4/g\text{-C}_3\text{N}_4$	82.4%	0.01 097	0.95 985
40% $\text{GdVO}_4/g\text{-C}_3\text{N}_4$	91.0%	0.01 578	0.96 861
50% $\text{GdVO}_4/g\text{-C}_3\text{N}_4$	84.9%	0.01 302	0.95 533

3.3. Photodegradation Mechanism

We further explored the possible mechanism of $\text{GdVO}_4/g\text{-C}_3\text{N}_4$ photodegradation of TC, which was shown in Figure 8. According to the DRS analysis of all the samples, the edge of the corresponding band energies (E_g) of pure $g\text{-C}_3\text{N}_4$ and pristine GdVO_4 were

approximately 2.86 eV and 3.54 eV. The valence band (VB) and conduction band (CB) of samples were calculated by following formula:

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

$$E_{CB} = E_{VB} - E_g \quad (3)$$

where X is the absolute electronegativity of semiconductors [30], E_e is the energy of free electrons compared to hydrogen (4.5 eV), and E_g is the bandgap of materials. It was calculated that the E_{CB} and E_{VB} of $g\text{-C}_3\text{N}_4$ were -1.11 eV and 1.75 eV, and of GdVO_4 were -0.34 eV and 3.20 eV. The semiconductor coupling effect between GdVO_4 and $g\text{-C}_3\text{N}_4$ induces electron migration from the $g\text{-C}_3\text{N}_4$ conduction band to the GdVO_4 conduction band, and hole migration from the GdVO_4 valence band to $g\text{-C}_3\text{N}_4$ valence band. Specifically, the photoexcited electrons on the CB of $g\text{-C}_3\text{N}_4$ can react with O_2 to generate the $\cdot\text{O}_2^-$ because their CB potential values were lower than $\text{O}_2/\cdot\text{O}_2^-$ potential values (-0.33 eV vs. NHE), while the holes on the VB of LaVO_4 can react with H_2O and OH^- to form $\cdot\text{OH}$ on account of the fact that the VB potential of GdVO_4 was higher than $\cdot\text{OH}/\text{OH}^-$ potential (1.99 eV vs. NHE) [18]. Then, $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ participated in the degradation of TC. Furthermore, the possible degradation process is displayed in the following equations:

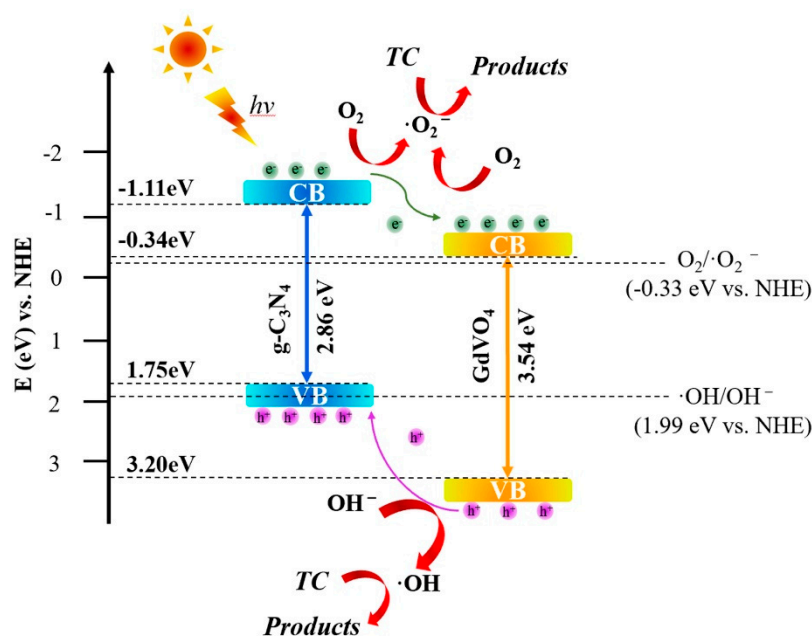
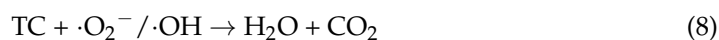
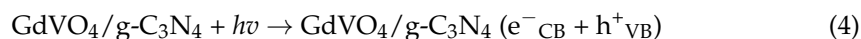


Figure 8. The possible degradation mechanism of $\text{GdVO}_4/g\text{-C}_3\text{N}_4$ composite.

4. Conclusions

In conclusion, a novel $\text{MVO}_4/g\text{-C}_3\text{N}_4$ ($M = \text{La}, \text{Gd}$) nanocomposite material was prepared by a facile hydrothermal method. This novel photocatalyst has the activity of initiating the decomposition of TC under visible light illuminate. As shown in XRD and FT-IR results, there were no impurity diffraction peaks observed, which confirmed

the successful synthesis of $\text{MVO}_4/\text{g-C}_3\text{N}_4$. We also observed that, in the SEM and TEM results, both the pin-like LaVO_4 and coral-like GdVO_4 were successful in loading on the sheet $\text{g-C}_3\text{N}_4$, respectively. And the results of DRS and PL characterization showed that MVO has more efficient visible light response ability. In addition, it also exhibits excellent photocatalytic performance under ultraviolet light irradiation. The enhanced photocatalytic performance of $\text{GdVO}_4/\text{g-C}_3\text{N}_4$ is not only related to the energy band potential of GdVO_4 and $\text{g-C}_3\text{N}_4$, but also related to the interconnected nanocrystalline heterojunction of $\text{g-C}_3\text{N}_4$. This study may provide an important strategy for the designation and preparation of high-performance photocatalysts induced by visible light.

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