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Identification of Active Species in Photodegradation of Aqueous Imidacloprid over g-C₃N₄/TiO₂ Nanocomposites

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Abstract: In this work, g-C₃N₄/TiO₂ composites were fabricated through a hydrothermal method for the efficient photocatalytic degradation of imidacloprid (IMI) pesticide. The composites were fabricated at varying loading of sonochemically exfoliated g-C₃N₄ (denoted as CNS). Complementary characterization results indicate that the heterojunction between the CNS and TiO₂ formed. Among the composites, the 0.5CNS/TiO₂ material gave the highest photocatalytic activity (93% IMI removal efficiency) under UV-Vis light irradiation, which was 2.2 times over the pristine g-C₃N₄. The high photocatalytic activity of the g-C₃N₄/TiO₂ composites could be ascribed to the band gap energy reduction and suppression of photo-induced charge carrier recombination on both TiO₂ and CNS surfaces. In addition, it was found that the active species involved in the photodegradation process are OH• and holes, and a possible mechanism was proposed. The g-C₃N₄/TiO₂ photocatalysts exhibited stable photocatalytic performance after regeneration, which shows that g-C₃N₄/TiO₂ is a promising material for the photodegradation of imidacloprid pesticide in wastewater.

Keywords: imidacloprid (IMI); graphitic carbon nitride (g-C₃N₄); titanium dioxide (TiO₂); g-C₃N₄/TiO₂ composite; photocatalytic activity

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1. Introduction

Imidacloprid (IMI), which is the most widely used pesticide in the group of neonicotinoids, is a pesticide that is used in agriculture such as in crop protection against aphids, leafhoppers, psyllids beetles, etc. [1], and parasite management [2]. The use of neonicotinoids has been registered in approximately 120 countries worldwide [3], and IMI is one of the top ten global agrochemicals used as a pesticide worldwide [4]. It acts as a nicotinic acetylcholine receptor (nAChR) agonist that interferes with the transmission in the central nervous system of insects and results in paralysis and death [5]. With their widespread use, persistent nature, and high solubility (610 mg/L in 20 °C H₂O; log K_{ow} = 0.57), IMI can cause damage to the environment via transportation in water, soil, and air [6]. Furthermore, the use of IMI can affect human health which includes neurological effects [7,8], in addition to gastrointestinal symptoms, lethargy [9], emaciation thyroid lesions, and cardiorespiratory failure [10]. Thus, the removal of these pollutants from water is essential due to their harmful influence on human health and aquatic ecosystems. Various methods can be applied for the degradation of IMI from aqueous solutions such as microfiltration membrane [11], biological degradation [12], adsorption [13,14], and advanced oxidation processes (AOPs) [15,16]. Among the AOP methods, photocatalytic activity has been used effectively in wastewater treatment for the removal of organic pollutants due to its simplicity, high activity, low cost, and ability to reduce CO₂ [17,18].

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) has attracted significant attention as a visible photocatalyst for water purification due to its stability, high surface area, eco-friendliness, and facile synthesis [19,20]. However, the disadvantage of pure $g\text{-C}_3\text{N}_4$ is the fast recombination of photogenerated electron–hole pairs which lead to low photocatalytic efficiency [21]. Many strategies have been tried to improve the photocatalytic performance such as nanostructure design [22,23], metal and non-metal doping [24], and composite photocatalysts [25–28]. Among the various strategies, photocatalysis by coupling with other semiconductor materials is a beneficial method to improve the electron recombination process and extend the visible light absorption, which can enhance the photocatalytic performance. TiO_2 is an n-type semiconductor that has been widely used owing to the high efficiency, low cost, non-toxicity, and long-term stability of this compound. However, because of the large band gap energy of 3.2 eV of TiO_2 , this results in the ineffective utilization of visible light, low quantum efficiency, and fast recombination [29]. It is expected that coupling TiO_2 with $g\text{-C}_3\text{N}_4$ can improve electron–hole pair recombination, broaden the photo-response range, and promote oxidation and reduction processes.

Herein, $g\text{-C}_3\text{N}_4/\text{TiO}_2$ photocatalysts were synthesized by a simple hydrothermal method. The phase structure, chemical composition, morphology, and scavenger trapping were investigated in detail. The $g\text{-C}_3\text{N}_4/\text{TiO}_2$ photocatalysts were used to degrade imidacloprid pesticide in wastewater under UV-Vis light irradiation. The recyclability of the composite was studied. In addition, the possible photodegradation mechanism was also proposed in this study.

2. Results and Discussion

2.1. Characterization

The XRD patterns of bulk-CN, CNS, TiO_2 , and $0.5\text{TiO}_2/g\text{-C}_3\text{N}_4$ are shown in Figure 1a. The $g\text{-C}_3\text{N}_4$ has two main diffraction peaks at 13.1° and 27.5° , which corresponds to the (001) plane caused by the arrangement of the tri-s-triazine units and the (002) plane caused by the interlayer stacking of the conjugated aromatic ring (JCPDS 87-1526) [29]. After the exfoliation of the bulk-CN, the decrease of CNS intensity (002) peak indicated that the interlayer structure was partially destroyed [30,31], and the slight shift of the (002) peak is attributed to the decreased distance of the basic sheets in the nanosheets [32]. The peaks of pure TiO_2 at 25.3° , 37.8° , 48.0° , 53.9° , 62.7° , 68.8° , 70.3° , 75.0° , and 82.6° correspond to the (101), (004), (200), (211), (204), (116), (220), (215), and (224) crystal planes of anatase TiO_2 (JCPDS 21-1272) [33]. Hydrothermally synthesized $g\text{-C}_3\text{N}_4/\text{TiO}_2$ photocatalysts showed the patterns related to both pure $g\text{-C}_3\text{N}_4$ and TiO_2 . In addition, there is no obvious change in the peaks of TiO_2 in the composites, indicating that coupling with $g\text{-C}_3\text{N}_4$ did not influence the phase structure of TiO_2 .

The Raman spectra of $g\text{-C}_3\text{N}_4$, TiO_2 , and $g\text{-C}_3\text{N}_4/\text{TiO}_2$ composites are shown in Figure 1b. The characteristic peaks of $g\text{-C}_3\text{N}_4$ appeared at 707 cm^{-1} and 1230 cm^{-1} which were assigned to the breathing modes of the tri-s-triazine ring and C-N heterocycles, respectively [34]. Moreover, all the Raman bands observed for bulk-CN can be found in the CNS. The Raman spectrum of pure TiO_2 exhibited peaks at 148 , 395 , 510 , and 640 cm^{-1} corresponding to anatase-phase TiO_2 [35]. $15\text{CNS}/\text{TiO}_2$ showed a combination peak of $g\text{-C}_3\text{N}_4$ and TiO_2 which confirms the formation of composites. No peak shifts were observed, which means no structural changes occurred during the preparation of the composites with pure TiO_2 and $g\text{-C}_3\text{N}_4$.

Figure 1. (a) Powder XRD patterns of bulk-CN, CNS, TiO₂, and 0.5CNS/TiO₂. (b) Raman spectra of bulk-CN, CNS, TiO₂, and 15CNS/TiO₂. Figure S1 shows the PXRD of the rest of nanocomposites.

The chemical binding states of g-C₃N₄, TiO₂, and composites were studied through XPS analysis. Figure 2a displays the survey scan of bulk-CN, CNS, TiO₂, and g-C₃N₄/TiO₂ in various weight ratios which confirmed the presence of C, N, Ti, and O atoms in the composites. Figure 2b shows three high-resolution C 1s spectrums at binding energies of 285.0, 288.3, and 289.2 eV, assigned as C-C, N-C=N, and sp² hybridized carbon in the tri-s-triazine ring (N₂-C=N) for g-C₃N₄.

Four binding energies in N 1s spectra (Figure 2c) can be observed, which can be classified into to sp² hybridized nitrogen C-N=C (398.8 eV), tertiary nitrogen N-(C)₃ (399.2 eV), amino functional groups N-H (400.3 eV), and π-excitation (401.2 eV), respectively [36–38]. The C 1s and N 1s spectra are slightly shifted from primitive g-C₃N₄ which suggests that there is a chemical bond connection between g-C₃N₄ and TiO₂ [39]. The C/N ratio of g-C₃N₄ is 0.90, indicating the presence of nitrogen vacancies that probably occurred during the thermal reduction process [40]. EPR spectra can provide evidence for probing the surface vacancies in photocatalysts. As shown in Figure 2f, the EPR intensity signal of CNS is significantly enhanced, revealing the increase of nitrogen vacancies generated in g-C₃N₄ [41]. Figure 2d shows the high-resolution Ti 2p spectrum. The binding energy peaks of Ti 2p^{3/2} and Ti 2p^{1/2} appeared at 459.3 and 465.0 eV, which represent Ti⁴⁺ species in the form of TiO₂ clusters [42]. In addition, there might be another Ti species in the material due to the poor XPS peak fitting for the Ti⁴⁺ alone. A better XPS profile fitting was later obtained by including a peak at 460.2 eV, being assigned as the Ti³⁺ defects on the composite surface [43,44]. The O 1s spectrum in Figure 2e can be devised into three peaks in TiO₂ with the binding energy of 530.5, 531.9, and 533.2 eV which can be assigned to (Ti-O), oxygen vacancy (V_o), and water molecules adsorbed on the surface of TiO₂, respectively [45]. Figure 2f shows the result of the solid ESR measurement which was used to confirm the presence of Ti³⁺. A strong EPR signal of TiO₂ and the composites was observed with g of 1.997, which corresponds with Ti³⁺ defect (3d¹, S = 1/2) and oxygen vacancy (V_o) [46]. It is possible that Ti⁴⁺ was reduced to Ti³⁺ by the loss of oxygen from the surface of TiO₂ because of the hydrothermal treatment at a high temperature [47].

Figure 2. (a) The survey scan of all samples. (b) The C1s spectra. (c) The N1s spectra. (d) The Ti 2p spectra. (e) The O1s spectra. (f) Solid EPR spectra of $g\text{-C}_3\text{N}_4$, TiO_2 , and $g\text{-C}_3\text{N}_4/\text{TiO}_2$.

2.2. Morphology Study

The morphologies of bulk-CN, CNS, TiO_2 , and $0.5\text{CNS}/\text{TiO}_2$ composites were examined by SEM as shown in Figure 3. We can see that bulk-CN presents in the form of bulk morphology with a layered structure (Figure 3a) [48]. CNS revealed smaller particles like the nanosheet structure after thermal exfoliation with HNO_3^- (Figure 3b). The BET surface area of bulk-CN and CNS were calculated to be 68.26 and $91.61 \text{ m}^2\text{g}^{-1}$, respectively. It is possible that the van der Waals forces and hydrogen bonds of $g\text{-C}_3\text{N}_4$ might be destroyed

with thermal treatment which results in the separation of $g\text{-C}_3\text{N}_4$ into small layers [49,50]. In addition, nitric acid might be intercalated into interlayers of bulk-CN which caused the expansion of their interlayer space and reduction of the layer thickness and hence increased its surface area [51,52]. The obtained TiO_2 showed spherical-like morphology with a particle size around 10 nm. From Figure 3d, it can be seen that the CNS particles having thin-layered structures are well distributed on the surface of TiO_2 particles, which is consistent with the presence of the peaks of $g\text{-C}_3\text{N}_4$ in XRD, XPS, and Raman spectra.

Figure 3. (a) SEM images of (a) bulk-CN, (b) CNS, (c) TiO_2 , and (d) 0.5CNS/ TiO_2 .

2.3. Optical Study

Figure 4a shows the UV-Vis diffuse reflectance spectra of $g\text{-C}_3\text{N}_4$, TiO_2 , and $g\text{-C}_3\text{N}_4/\text{TiO}_2$ composites. The exfoliated $g\text{-C}_3\text{N}_4$ nanosheets show an absorption edge at 470 nm with a band gap of 2.93 eV, which was in agreement with previous reports [53]. The absorption spectra of the TiO_2 shows an absorption edge at around 400 nm with a band gap of 3.20 eV. The presence of $g\text{-C}_3\text{N}_4$ resulted in the red shift of the absorption edge in all composites, revealing that the composites can be applied to visible-light photocatalysis. In addition, the presence of $\text{Ti}^{3+}\text{-TiO}_2$ can narrow the wide band gap of TiO_2 for harvesting visible light and can provide an increase in electronic conductivity [54].

Figure 4. (a,b) UV-Vis DRS spectra and Tauc plot of g-C₃N₄, TiO₂, and g-C₃N₄/TiO₂ photocatalysts, (c) photoluminescence spectra of the as-synthesized g-C₃N₄, TiO₂, and g-C₃N₄/TiO₂.

The band gap energy was calculated using the Tauc plot in Equation (1) and is shown in Figure 4b [55].

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (1)$$

where α is the optical absorption coefficient, h is Planck's constant, ν is photon frequency, A is constant, and E_g is band gap.

The band gaps of pure g-C₃N₄, TiO₂, and 0.5CNS/TiO₂ were calculated to be 2.93, 3.20, and 3.17 eV, respectively.

Photoluminescence analysis was performed in order to determine the electron–hole recombination which is shown in Figure 4c. Under excitation at 320 nm, the emission peak of g-C₃N₄ appears at around 457 nm. The bulk-CN and CNS showed high PL intensity because of the fast recombination of electron–hole pairs, whereas TiO₂ showed a broad emission peak at 410 nm and a lower maximum peak than that of the g-C₃N₄ system. After the hybridization of g-C₃N₄ and TiO₂, the composite showed a much weaker emission peak, implying that the recombination of charge carriers may be effectively inhibited.

2.4. Photocatalytic Study

The photocatalytic performance of g-C₃N₄, TiO₂, and composites was evaluated for IMI degradation under UV-Vis light irradiation in Figure 5. Photolysis of IMI degradation was carried out under the same conditions, as can be seen from Figure S2. It was found that the photolysis is not the main cause of effective degradation of IMI. On the other hand, the treatments of IMI with catalysts are less effective in dark conditions. From this result, the g-C₃N₄ system exhibited low photocatalytic efficiency in the degradation of IMI. This could be because of the fast recombination of electron–hole pairs, as evidenced by PL spectra (Figure 4c). However, it was found that exfoliated g-C₃N₄ showed higher photocatalytic activity than bulk-g-C₃N₄. It could be explained as the effects of a larger specific surface area, narrow band gap, and nitrogen defects which improved photogenerated charge separation and transfer [56]. In addition, the incorporation of TiO₂ clearly enhances the photocatalytic activity of g-C₃N₄. Specifically, 0.5CNS/TiO₂ and 1CNS/TiO₂ exhibited excellent photocatalytic activity, and photocatalysts were able to degrade 93.1% and 88.3% of IMI within 150 min, while pure TiO₂ and g-C₃N₄ only degraded IMI by 79.7% and 51.8%, respectively. It is reasonable that there might have been a synergetic effect between TiO₂ and g-C₃N₄. g-C₃N₄ can narrow the band gap energy and increase solar absorption efficiency. In addition, Ti³⁺ and oxygen vacancies (Ov) in TiO₂ can suppress the recombination of photogenerated electron–hole pairs and promote charge separation [57] which led to high photocatalytic degradation of IMI. As seen in Figure 4c, CNS gave a very broad PL spectrum having a very high intensity. In addition, the PL intensity from 0.5CNS/TiO₂ was found just slightly higher than that from the TiO₂ material (much weaker than that of CNS). Several works [58,59] related the intensity of PL spectra to the oxidation–reduction potential between the conduction band and the valence band. PL spectra with lower intensity described a low probability of photogenerated electron–hole recombination. Although PL results suggest a slightly faster recombination rate on the 0.5CNS/TiO₂, its relatively narrow band gap (compared with TiO₂) promoted superior IMI removal efficiencies (Figure 5). It should be noted that the loading level of g-C₃N₄ played an important role in improving the IMI photodegradation. It was found that the photocatalytic rate of activity slightly decreased after 90 min irradiation time when the loading of g-C₃N₄ was increased from 4% to 15%. This might be due to the fast recombination of the electron–hole pair in g-C₃N₄. Furthermore, from Figure 5, 0.5CNS/TiO₂ gave a higher IMI degradation rate than that of 1CNS/TiO₂, as seen from the slope. However, the IMI removal efficiencies obtained from the 4CNS/TiO₂ treatment were higher during 0–120 min. Effective photodegradation of organic compounds requires a suitable amount of stable radical species in the aqueous media. Too-high concentrations of radical species may cause termination of the radical reaction pathway, while insufficient radical concentrations resulted in slow degradation rates and low removal efficiencies. We could explain the removal efficiencies by the varied concentrations of radicals over time. Hence, after 150 min, three samples (i.e., 0.5CNS/TiO₂, 1CNS/TiO₂, and TiO₂) gave % IMI removal efficiencies of 80% and above, likely due to the suitable amount of stable radical species in the aqueous media through the prolonged degradation process.

Figure 5. (a) Photocatalytic degradation of imidacloprid when treated with g-C₃N₄, TiO₂, and g-C₃N₄/TiO₂ composites under UV-Vis light irradiation (10 ppm of pesticide and 1g/L of catalyst loading), and (b) the first-order kinetic fitting curve of the photocatalytic IMI degradation during 30 min irradiation time.

The initial rate constants, derived from the first-order kinetic fitting curve (Figure 5b), for the photodegradation of IMI from the highest to the lowest, are given in the order of 4CN/TiO₂ ($1.50 \times 10^{-2} \text{ min}^{-1}$), 10CNS/TiO₂ ($9.96 \times 10^{-3} \text{ min}^{-1}$), 0.5CNS/TiO₂ ($9.70 \times 10^{-3} \text{ min}^{-1}$), 15CNS/TiO₂ (8.26×10^{-3}), CNS ($8.00 \times 10^{-3} \text{ min}^{-1}$), TiO₂ ($7.60 \times 10^{-3} \text{ min}^{-1}$), bulk-CN ($6.13 \times 10^{-3} \text{ min}^{-1}$), and 1CNS/TiO₂ ($1.88 \times 10^{-3} \text{ min}^{-1}$) catalysts. As a result, the initial rate constants are poorly correlated with the IMP removal efficiencies after 180 min of irradiation time, possibly due to the stability of radical species as a function of time discussed earlier.

2.5. Reusability and Regeneration

The stability of the photocatalysts was evaluated over multiple cycles of IMI degradation. As shown in Figure 6a, the IMI removal efficiency of 0.5CN/TiO₂ decreased significantly in the fourth cycle. The SEM image (Figure 6b,c) shows that the sheet-like morphology of the photocatalyst remained. However, the surface of the catalysts could be covered either by reactants or products that hindered photocatalytic performance. A regeneration experiment was carried out. After the photocatalysis experiment, the catalyst was separated from the reaction mixture by centrifugation. The used photocatalyst was regenerated by stirring in water (dark) for 1 h and irradiated for 2.5 h before using it in the next cycle. It was found that the 0.5CN/TiO₂ composite still kept ~91% regeneration efficiency at the end of the fourth cycle, indicating a relatively high regeneration potential of the nanocomposite.

From this work, the bulk carbon nitride is less suitable than the exfoliated material to be incorporated with TiO₂ for photocatalytic applications. The IMI removal efficiencies obtained from the 4CNS/TiO₂ treatment are significantly higher (ca. 30%) than those obtained from 4CN/TiO₂ (Figure S1, Supplementary Data). The photocatalytic performance of several carbon nitride based composites in the degradation of imidacloprid is given in Table 1.

Figure 6. (a) Reusability and regeneration performance test of 0.5CN/TiO₂ for imidacloprid degradation, SEM images of (b) fresh and (c) spent 0.5CN/TiO₂ photocatalyst

Table 1. Comparative photocatalytic degradation of imidacloprid pesticide at varying conditions, over various carbon nitride based materials.

Photocatalyst	Light Source	Cat. Loading (g/L)	Initial (IMI) (ppm)	Irradiation Time (h)	Best Removal Eff. (%)	Ref.
g-C ₃ N ₄ (urea)	$\lambda > 400$ nm (8 W)	0.5	20	5.0	90	[60]
g-C ₃ N ₄ (melamine)		1.0			43	
Ag ₂ O/g-C ₃ N ₄	Infrared lamp (250 W)	1.0	10	2.0	80	[61]
g-C ₃ N ₄	LED lamp (35 W)	0.6	26	9.0	60	[62]
P doped g-C ₃ N ₄ (PCN)					72	
0.04C ₆₀ /PCN					95	
g-C ₃ N ₄	LED lamp (35 W)	0.5	26	8.0	65	[63]
Ag-Bi ₂ O ₃ /g-C ₃ N ₄					98	
Bi ₂ WO ₆ : NH ₂ -MOF	Xe lamp	0.4	10	3.0	84	[64]
Ag ₄ V ₂ O ₇ /g-C ₃ N ₄	Xe lamp (300 W)	1.0	10	4.0	38	[65]
g-C ₃ N ₄ (urea)	W lamp (300 W)	1.0	10	2.5	42	This work
CNS					51	
0.5CNS/TiO ₂					93	

As seen in Table 1, a quite prolonged reaction time (5 h) was required in order to achieve high IMI removal efficiencies in the photocatalytic treatments of IMI (aq) over the g-C₃N₄ materials, and the photocatalytic performance of g-C₃N₄ is precursor-dependent. Direct comparison of the catalytic performance of the reported photocatalysts and those developed in this work could not be entirely appropriate as each report utilized specific performance testing setups and conditions (initial concentration, catalyst loading, and reaction time). Nevertheless, a greater number of steps and expensive chemicals would be required to prepare several functional photocatalysts (0.04C₆₀/PCN, Ag-Bi₂O₃/g-C₃N₄, Bi₂WO₆: NH₂-MOF, Ag₄V₂O₇/g-C₃N₄), compared to this work.

2.6. Photocatalytic Mechanism

To find out the major active species for the photocatalytic oxidation, several scavengers were added to the photocatalytic system individually to trap and remove active species

(Figure 7). Ammonium oxalate (AO), isopropanol (IPA), and benzoquinone (BQ) act as scavengers to holes (h^+), hydroxyl radical ($\bullet OH$), and superoxide radical ($\bullet O_2^-$), respectively. The addition of p-benzoquinone had a little effect on the photocatalytic degradation of IMI, implying that $\bullet O_2^-$ has a minor role in the reaction as an oxidative species. In contrast, the photocatalytic degradation activity of the 0.5CNS/TiO₂ had a dramatic decrease with the addition of IPA and AO, suggesting that both OH^- and holes are the main oxidative species in this system.

Figure 7. Effects of different scavengers on the photocatalytic degradation of IMI.

In order to describe the photocatalytic mechanism of 0.5CNS/TiO₂ for the degradation of IMI, the CB and VB edge potentials of g-C₃N₄ and TiO₂ were calculated from Equations (2) and (3) [66].

$$E_{CB} = X - E_c - 1/2E_g \quad (2)$$

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

where X is the absolute electronegativity of the atom semiconductor, and the X values of TiO₂ and g-C₃N₄ are 5.8 eV and 4.73 eV, respectively [66]. E_c is the energy of free electrons of the hydrogen scale (4.5 eV). E_g is the band gap of the semiconductor which is 2.93 and 3.20 eV for g-C₃N₄ and TiO₂, respectively. Therefore, the reductive potentials of the conduction band (CB) are -0.30 and -1.23 V for TiO₂ and g-C₃N₄, and the oxidizing potentials of the valence band (VB) of TiO₂ and g-C₃N₄ are $+2.90$ and $+1.70$ V, respectively.

Based on the above results, the possible Z-scheme photocatalytic mechanism of g-C₃N₄/TiO₂ was proposed as shown in Figure 8. Under UV-Vis irradiation, TiO₂ absorbed photon energy, and then electrons were excited from the VB to the CB. The photogenerated holes tended to stay in the VB of TiO₂, whereas photogenerated electrons on the CB of TiO₂ can be directly transferred into the VB of g-C₃N₄ due to their proximity to each other. Then, the electrons in the VB of g-C₃N₄ are further excited into the CB. This resulted in an efficient charge separation of the photo-induced electron–hole pair and an enhancement in their oxidation–reduction ability. Specifically, the presence of Ti³⁺ and oxygen vacancy could be an important reason for the hindrance of the electron–hole recombination. It was found that the photogenerated holes (h^+) in the VB of TiO₂ ($E_{VB} = 2.90$ V vs. NHE) have the ability to oxidize H₂O or hydroxyl ions (OH^-) to hydroxyl radicals ($\bullet OH$), while the photogenerated h^+ in the VB of g-C₃N₄ ($E_{VB} = 1.70$ V vs. NHE) is not sufficient for the oxidation of H₂O to hydroxyl radicals. In addition, the photogenerated electron in the CB of g-C₃N₄ was

trapped on the surface to form reactive superoxide radical ions ($\bullet\text{O}_2^-$). The photocatalytic mechanism was consistent with the scavenger experiments in which the hydroxyl radical and holes were the principal reactive species for the IMI degradation, whereas the superoxide radical had a minor role. The Z-scheme photocatalyst was suggested since the photogenerated h^+ on the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ composite has a sufficient oxidation potential for producing $\bullet\text{OH}$ radicals [67]. Evaluated by using Equations (2) and (3), the reduction potential of $\text{g-C}_3\text{N}_4$ (+1.70 V) is less positive to oxidize H_2O to $\bullet\text{OH}$ (+1.99 V). Thus, the holes in the VB of $\text{g-C}_3\text{N}_4$ cannot adsorb water molecules near the surface of $\text{g-C}_3\text{N}_4$ to generate hydroxyl radicals ($\bullet\text{OH}$). Note that $\bullet\text{OH}$ radicals can be produced on semiconductors with an oxidation potential of 2.4 V (and above) versus NHE. The scavenging testing indicated that $\bullet\text{OH}$ radicals are the key radicals promoting effective IMI degradation. The Z-scheme $\text{g-C}_3\text{N}_4/\text{TiO}_2$ composites showed better photocatalytic performance than TiO_2 or $\text{g-C}_3\text{N}_4$ alone. However, with the content of $\text{g-C}_3\text{N}_4$ in $\text{g-C}_3\text{N}_4/\text{TiO}_2$ being in excess, numerous photo-induced electrons and holes would recombine easily. Therefore, the 0.5CNS/ TiO_2 sample displayed the best photocatalytic performance among these different $\text{g-C}_3\text{N}_4/\text{TiO}_2$ photocatalysts.

Figure 8. Photocatalytic mechanism of 0.5CNS/ TiO_2 for degradation of imidacloprid.

3. Materials and Methods

3.1. Chemicals

Urea ($\text{CH}_4\text{N}_2\text{O}$) was obtained from Kemaus, Australia. Ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4$), nitric acid (HNO_3), and methanol (CH_3OH) were purchased from Merck, Darmstadt, Germany. Benzoquinone, isopropyl alcohol, titanium (IV) oxysulfate (TiOSO_4) and imidacloprid were obtained from Sigma-Aldrich, USA. All reagents were of analytical grade and were used without further purification. Deionized water was used in preparing all aqueous solutions.

3.2. Characterization

The sample was determined using powder X-ray diffraction (Bruker AXS, D8 advance, Germany) with CuK α radiation ($\lambda = 1.54 \text{ \AA}$) and was collected in 2θ range from 10° to 90° . The X-ray photoelectron spectroscopy (XPS) was carried out to determine the surface electronic state of the samples with a monochromatized Al K α radiation source (AXIS Ultra DLD, Japan). The Raman spectra were recorded using Raman microscope at laser wavelength of 785 nm (Horiba, XploRA Plus, France). The electron paramagnetic resonance (EPR) signals of free radicals were recorded at ambient temperature (Bruker; Eleksys 500, Germany). The morphologies and elemental composites of the samples were examined by a scanning electron microscope (JEOL, JSM-IT500, Japan) and Field emission scanning electron microscope (FE-SEM, JEOL, JSM-7610FPlus, Japan). Photoluminescence (PL) spectrum was performed with excitation at 320 nm (Horiba, FluoroMax, France). The band gap energy of the prepared samples was carried out by UV-Vis NIR spectrophotometer (Shimadzu, UV3600 plus, Tokyo, Japan). The degradation of IMI was monitored by measuring the absorbance at 268 nm with a UV-Vis spectrophotometer (Perkin Elmer, Lambda 800, MA, USA).

3.3. Synthesis of $g\text{-C}_3\text{N}_4$

Bulk- $g\text{-C}_3\text{N}_4$ was prepared by direct pyrolysis of urea according to a reported procedure with modification [68]. In detail, 125 g of urea was put into an alumina crucible with a cover and heated with a heating rate of $10^\circ\text{C}/\text{min}$ to 600°C for 4 h. After being cooled to room temperature, the pale yellow of bulk- $g\text{-C}_3\text{N}_4$ (CN) was obtained. The bulk-CN was exfoliated into a nanosheet structure by thermal exfoliation in the presence of acid, and 2.5 g of bulk-CN was stirred in 65 % of HNO_3 solution (100 mL) for 12 h. The dispersion was filtrated and washed several times with D.I. water, followed by annealing at 500°C for 4 h to obtain $g\text{-C}_3\text{N}_4$ nanosheet (CNS).

3.4. Synthesis of $g\text{-C}_3\text{N}_4/\text{TiO}_2$ Composites

$g\text{-C}_3\text{N}_4/\text{TiO}_2$ composites were prepared by a hydrothermal method. Firstly, TiOSO_4 suspensions were obtained by sonication for 35 min in D.I. water. After dispersing, CNS was added into the solution and was sonicated continuously for 30 min. The solution was transferred to a Teflon-lined autoclave which was then further heated at 180°C for 4 h. The obtained solution was centrifuged, washed with D.I. water, and dried at 65°C for 24 h. According to the above method, different weight ratios of $g\text{-C}_3\text{N}_4$ to TiO_2 at 0.5%, 1%, 4%, 10%, and 15% were synthesized and labeled as 0.5CNS/ TiO_2 , 1CNS/ TiO_2 , 4CNS/ TiO_2 , 10CNS/ TiO_2 , and 15CNS/ TiO_2 , respectively. TiO_2 was also prepared by the same procedure without adding $g\text{-C}_3\text{N}_4$.

3.5. Photocatalytic Activity

The photocatalytic behavior of the catalyst was evaluated by the photodegradation of imidacloprid in an aqueous solution with an initial concentration of 10 mg/L under 300 watts of W lamp. First, 10 mg of photocatalyst was added to 10 mL of IMI solution. The suspension was stirred using a magnetic stirrer in the dark at room temperature for 1 h before irradiation. The solution was collected every 30 min to 150 min using a syringe with a microspore filter ($0.45 \mu\text{m}$). The concentration of IMI was analyzed by UV-Vis spectrophotometry at 268 nm, and the removal efficiency was calculated via Equation (4) [69].

Where C_0 is the initial concentration of IMI, and C_t is the concentration of IMI after t minutes.

To study the reaction kinetic, the obtained data were fitted by a first-order kinetic model which is shown in Equation (2).

$$\ln(C_0/C) = kt \quad (4)$$

where k is the pseudo-first-order rate constant, C_0 is the initial IMI concentration, and C is imidacloprid equilibrium concentration in aqueous solution at time t .

3.6. Scavenger Activity

Active species capture experiments were used to study the photocatalysis mechanism. First, isopropyl alcohol (IPA; 0.5 mM) was used as the hydroxyl scavenger ($\bullet\text{OH}$), benzoquinone (BQ; 0.5 mM) was employed as the superoxide scavenger ($\bullet\text{O}_2^-$), and ammonium oxalate (AO; 0.5 mM) was used as the hole scavenger (h^+) [70]. Different scavengers were used in the trapping experiments to check the inhibitory effect of scavengers during the photocatalytic reaction under analogous irradiation experimental conditions.

4. Conclusions

In this work, g-C₃N₄ nanosheets were exfoliated from bulk-g-C₃N₄ by thermal exfoliation in the presence of HNO₃. The exfoliated g-C₃N₄ resulted in nanosheets with a large specific surface area and N vacancy defects, which can be prepared and further used in the fabrication of TiO₂ base composites having superior photocatalytic activity, under UV-Vis light irradiation, to bulk the g-C₃N₄ and g-C₃N₄/TiO₂ composites. Results show that the g-C₃N₄/TiO₂ photocatalyst exhibited higher removal efficiency for IMI than g-C₃N₄ and TiO₂, indicating that a synergistic effect exists between Ti³⁺-TiO₂ and g-C₃N₄. With the increase of g-C₃N₄ loading, the photocatalytic activity of g-C₃N₄/TiO₂ composites may also decrease the photocatalytic activity of g-C₃N₄. The sample of 0.5CNS/TiO₂ showed the highest photocatalytic activity with 93% removal efficiency within 150 min. The enhanced photocatalytic performance of the g-C₃N₄/TiO₂ composites could be due to the generation of reactive oxidation species induced by photogenerated electrons and the effective suppression of the recombination of the charge carriers. In addition, the g-C₃N₄/TiO₂ photocatalyst showed good stability for multiple recycling. Thus, the g-C₃N₄/TiO₂ could be effectively used as material for the photodegradation of imidacloprid pesticide in wastewater. Comprehensive photoelectrochemical analysis of the g-C₃N₄/TiO₂ materials should be further studied to obtain the photogenerated charge recombination rates in detail.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12020120/s1>, Figure S1: Powder XRD patterns of 1CNS/TiO₂, 4CNS/TiO₂, 10CNS/TiO₂, and 15CNS/TiO₂, Figure S2: Photolysis of imidacloprid.

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