Facile Synthesis with TiO$_2$ Xerogel and Urea Enhanced Aniline Aerofloat Degradation Performance of Direct Z-Scheme Heterojunction TiO$_2$/g-C$_3$N$_4$ Composite

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1. Introduction

Aniline Aerofloat (dianilinodithiophosphoric acid, AAF, (C$_6$H$_5$NH)$_2$PSSH) has been used frequently as an efficient flotation collecting agent for lead-zinc sulfide ore in China [1]. It was discharged with flotation wastewater into nature although it is highly toxic and contains dithiophosphate and aniline groups [2–4]. Moreover, AAF has been hard to degrade thoroughly so far. Some degradation methods have been researched such as sodium hypochlorite oxidation [5], vacuum ultraviolet/ozone [6], chelate precipitation [7], and so on. Thereinto, photocatalytic degradation has great potential to degrade AAF quickly, easily, and effectively.

In the photocatalytic degradation of organic pollution, titanium dioxide (TiO$_2$) has been researched extensively in dyes, endocrine disrupters, pesticides, etc., as a photocatalyst [8–10]. It deserves more attention even as a commercialized attribute to safety, non-toxicity, stability, high-performance, and low cost [11–13]. However, TiO$_2$ was limited in practical applications due to its wide bandgap (3.2 eV) and the rapid recombination of electron (e$^-$) and hole (h$^+$). The construction of TiO$_2$/semiconductor heterojunction is an effective method in many ways. Graphene carbon nitride (g-C$_3$N$_4$) has a narrow bandgap (2.7 eV) with an electronic structure, excellent visible light responding and is easy to prepare in the meantime [14,15]. Therefore, g-C$_3$N$_4$ was identified as an appropriate and complementary semiconductor to composite TiO$_2$/semiconductor heterojunction [16–18]. For example, Tan et al. prepared Ti$^{3+}$ self-doped TiO$_2$/g-C$_3$N$_4$ heterojunctions via solid-state...
The next step is adding solution A to solution B at a speed of 0.1 mL. TiO$_2$ prepared with a simple pyrolysis process. Urea (20 g) and TiO$_2$ composite catalyst. Synthesis conditions including the mass ratio of TiO$_2$ to C$_3$N$_4$, which attribute to the O–Ti–N bond interface heterojunction between TiO$_2$ and g-C$_3$N$_4$ separated and transferred charge carriers efficiently [21]. To enhance TiO$_2$ light response, a uniform mesopore TiO$_2$/g-C$_3$N$_4$ composite with core/shell heterojunction structure was prepared by Xia et al., and the uniform mesoporous g-C$_3$N$_4$ nanosheets were used to decorate TiO$_2$ spheres [22].

The TiO$_2$/g-C$_3$N$_4$ composite was studied deeply by lots of specialists and multitudinous synthesis methods and raw materials were exploited. In the synthesis process of TiO$_2$/g-C$_3$N$_4$, there are many ways to prepare such as adding g-C$_3$N$_4$ powder in a precursor solution of TiO$_2$, depositing TiCl$_4$ precursor onto the surface of the g-C$_3$N$_4$ powder, mixing TiO$_2$ powder with melamine in solution, and so on [23–26].

To our knowledge, even though so many methods were adopted to prepare TiO$_2$/g-C$_3$N$_4$ composite, TiO$_2$ xerogel has not been directly mixed with urea as raw materials to synthesize the composite. TiO$_2$ xerogel was used rather than commercial TiO$_2$ (P25), which could compose better with g-C$_3$N$_4$ during TiO$_2$ catalyst forming. In this work, TiO$_2$/g-C$_3$N$_4$ composite was synthesized by simple pyrolysis with urea and TiO$_2$ xerogel, and AAF was selected as the potential pollutant to detect the photocatalytic activities of the prepared composite catalyst. Synthesis conditions including the mass ratio of TiO$_2$ to C$_3$N$_4$, calcination temperature, calcination time, and heating rate were studied detailed. X-ray diffraction, scanning electron microscope, transmission electron microscope, ultraviolet-visible diffuse reflectance spectrum, X-ray photoelectron spectroscopy N$_2$-adsorption isotherms and electrochemical impedance spectroscopy were all characterized to analyze the heterojunction structure and physicochemical properties of TiO$_2$/g-C$_3$N$_4$. Furthermore, the stability and mechanism of TiO$_2$/g-C$_3$N$_4$ were also deduced.

2. Materials and Methods
2.1. Materials

- Aniline Aerofloat (AAF, (C$_6$H$_5$NH)$_2$PSSH, 99.5%): Hunan Mingzhu Flotation Reagents Limited Company, Hunan, China.
- Ethylene glycol (CH$_3$CH$_2$OH, 99.7%): Tianjin Guangfu Science and Technology Development Co., Ltd., Tianjin, China.
- Glacial acetic acid (CH$_3$COOH, 99.5%): Xilong Scientific Co., Ltd., Guangdong, China.
- Ammonium oxalate ((NH$_4$)$_2$C$_2$O$_4$, 99.8%): Damao Chemical Reagent Factory, Tianjin, China.
- Methanol (CH$_3$OH, 99.9%), tetrabutyl titanate (Ti(OCH$_3$)$_4$, 98.0%), isopropanol (C$_3$H$_8$O, 99.7%) and urea ((NH$_2$)$_2$CO, 99.0%): Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

2.2. Synthesis of Photocatalysts
2.2.1. Synthesis of TiO$_2$ Xerogel

The TiO$_2$ xerogel was prepared by the sol-gel method [27,28]. In preparing solutions A and B, respectively, solution A was the mixture consisting of 10 mL ethyl alcohol and 2 mL glacial acetic acid; solution B could be obtained when the 10 mL tetrabutyl titanate was dripped into 15 mL ethyl alcohol slowly at a speed of 0.1 mL·s$^{-1}$ with magnetic stirring. The next step is adding solution A to solution B at a speed of 0.1 mL·s$^{-1}$, the transparent colloid was obtained after 30 min. The transparent colloid was naturally aged for 48 h and dried in the oven at 90 °C for 24 h. Finally, xerogel powder was collected after ground.

2.2.2. Synthesis of TiO$_2$/g-C$_3$N$_4$

According to previous reports [29–32], TiO$_2$/g-C$_3$N$_4$ composite photocatalysts were prepared with a simple pyrolysis process. Urea (20 g) and TiO$_2$ xerogel powder (2, 1, 0.67, 0.5, 0.4 g) were mixed and vibrated for 30 min with ultrasonic (KQ5200E, 40 KHz, Kunshan Ultrasonic Instruments Co., Ltd., Kunshan, China). The solid mixture was placed into
the ceramic crucible with a cover and calcined at different temperatures for several hours at a heating rate with the muffle furnace. The details are illustrated in Scheme 1. The resultant powder which was ground and collected after cooling to an ambient temperature was TiO$_2$/$g$-C$_3$N$_4$ composite denoted as TCN. TiO$_2$/$g$-C$_3$N$_4$ composite with a doping mass ratio of x and a heating rate of 5 °C·min$^{-1}$, 550 °C for 6 h is denoted as TCN-U$_x$. TiO$_2$/$g$-C$_3$N$_4$ composite with a doping mass ratio of 20 and a heating rate of 10 °C·min$^{-1}$, y °C for 6 h is denoted as TCN-T$_y$. TiO$_2$/$g$-C$_3$N$_4$ composite with a doping mass ratio of 20 and a heating rate of z °C·min$^{-1}$, 550 °C for 6 h is denoted as TCN-R$_z$. TiO$_2$/$g$-C$_3$N$_4$ composite with a doping mass ratio of 20 and a heating rate of 10 °C·min$^{-1}$, 550 °C for n h is denoted as TCN-H$_n$ (x = urea, $m_{xerogel}$ = 10, 20, 30, 40, 50; y = 450, 500, 550, 600, 650; z = 5, 10, 15, 20, 25; n = 2, 3, 4, 5, 6, 7).

Scheme 1. The synthesis of simple TiO$_2$/$g$-C$_3$N$_4$ by pyrolysis process.

2.3. Characterization

X’TRA rotating anode powder X-ray diffraction (XRD, PANalytical B.V., X’Pert powder) with Cu Kα radiation (λ = 0.154056 nm) in the diffraction angle range of 2θ = 10~90° with 0.02° interval. The sample’s phase and composition were identified by it. The morphology of TCN was exhibited by scanning electron microscope (FE SEM, Tescan, Brno, Czech Republic, MIRA3 LMH). Crystal and element imaging of samples were shown via transmission electron microscope (TEM, FEI, Tecnai Hillsboro, USA, G2-20) connected with a CCD camera from Gatan Company (Pleasanton, CA, USA) and X-ray energy dispersive spectrometer from EDAX Company. Ultraviolet-visible diffuse reflectance spectrum (UV-Vis DRS, Shimadzu, Kyoto, Japan, UV-2600PC) was employed in the range of 200~800 nm with 1 nm interval to obtain the optical absorption spectra of materials, and BaSO$_4$ was used as the reference. The Brunauer–Emmett–Teller (BET) surface area and Barrett–Joyner–Halenda (BJH) pore width were analyzed by Micromeritics ASAP 2460 nitrogen adsorption apparatus. X-ray photoelectron spectroscopy (XPS, Thermo, Waltham, MA, USA, ESCALAB 250Xi) spectra were operated with a monochromatic Al Kα radiation source (1486.6 eV) and the binding energies were adjusted with C1s (284.8 eV). Electrochemical impedance spectroscopy (EIS) was analyzed by three-electrode cell electrochemical workstation (CHI-660E, Chinstruments, Shanghai, China) with Pt and saturated calomel electrode as the counter and reference electrode, and 0.1 mol·L$^{-1}$ Na$_2$SO$_4$ aqueous solution as electrolyte. The sample (10 mg) was dispersed in 1 mL ethylalcohol with ultrasonic for 30 min, and then the mixture was dispersed uniformly on the indium tin oxide (ITO) glass as a working electrode within a 1.0 cm$^2$ area.

2.4. Photocatalytic Degradation and Analysis

The photocatalytic activity of TCN was explored by degradation of AAF under ultraviolet light provided by a 300 W mercury lamp. All photocatalysis experiments were implemented with the rotary photochemical reaction instrument (XPA-7, Xujiang Electromechanical Plant, Nanjing, China). The catalyst of TCN (30 mg) was dispersed in the AAF solution (50 mL, 100 mg·L$^{-1}$) contained in the quartz tube. The first 30 min of the reaction were in the dark to reach absorption equilibrium, and then they were illuminated for 180 min. After every given time interval, 5 mL of solution was obtained and filtered through a 0.45 μm water filtration membrane to be analyzed by high-performance liquid chromatography (HPLC, 1260 infinity, Agilent, Santa Clara, CA, USA).
The concentration of AAF was tested by HPLC, equipped with eclipse plus C18 (3.5 µm, 4.6 mm × 150 mm) and the temperature of the chromatograph column was 30 °C. The measured wavelength was set as 230 nm according to the full wavelength scanning by ultraviolet-visible spectrophotometer (T6 New century, Beijing Persee General Co., Ltd., Beijing, China). The mobile phase consists of water and methanol (v/v = 60:40) and flows at 1 mL·min⁻¹. The degradation efficiency was calculated by \( \frac{C_t}{C_0} \), in which \( C_0 \) and \( C_t \) were the concentration of AAF at the beginning and a certain time.

At the same time, the catalyst was reused 4 times under the same conditions to investigate the stability and the prospects for practicality in industrial. Reactive active species hole (h⁺) and hydroxyl radical (-OH) in the photocatalytic degradation process were analyzed by quenching agent ammonium oxalate and isopropanol experiments.

3. Results and Discussion

3.1. Morphology Analysis

SEM images of pure TiO₂, g-C₃N₄, TCN-U₂₀ and TCN-Tₐ shown in Figures 1a–c and S1 provided that TiO₂ and g-C₃N₄ were composed successfully. As we can see, the TCN composite combined with the structure of the lamellae g-C₃N₄ stack on bulk TiO₂. The thickness and density of g-C₃N₄ lamellae increase, respectively, which made the poriness and active positions more with the doping ratio and calcination temperature higher. Nevertheless, overmuch g-C₃N₄ lamellae would impede UV-light absorption of TiO₂ which was covered and thus weaken the photocatalytic activity of CNT. Meanwhile, the TEM image of TCN-U₂₀ shown in Figure 1d suggested the lattice spaces of 0.350 nm and 0.320 nm correspond to the plane (101) of TiO₂ and the plane (002) of the g-C₃N₄ [33,34]. The results of mapping images and EDS spectrum in Figure 1e showed the percent of C, N, O and Ti. The atom percent of C and N is approximately 0.73~0.89 conforming to 0.75 that the ratio of C and N in g-C₃N₄. Because of the oxygen in the air, the atom percent of Ti and O is approximately 0.30~0.31, which is far less than 0.5 that the ratio of Ti and O in TiO₂. The results suggested doping of g-C₃N₄ is successful and the formation of the heterojunction between TiO₂ and g-C₃N₄.

![Figure 1. SEM images of (a) pure TiO₂, (b) g-C₃N₄, and (c) TCN-U₂₀; (d) TEM image, (e) mapping images of TCN-U₂₀.](image-url)
3.2. XRD Analysis

The crystal phases of TCN, pure g-C$_3$N$_4$ and TiO$_2$ are exhibited in Figures 2a and S2. Diffraction peaks at 25.3°, 37.8° and 48.0° were pointed to (101), (004) and (200) of anatase TiO$_2$ (JCPDS 21-1272). Peaks at 27.4°, 36.1°, 41.2° and 54.3° are pointed to (110), (101), (111) and (211) of rutile TiO$_2$ (JCPDS 21-1276), and peaks at 12.9° and 27.7° correspond to (100) in the in-plane repetitive unit of tri-s-triazine and (002) attributed to interlayer stacking of g-C$_3$N$_4$ (JCPDS 87-1526) [35–37]. Almost all TCN samples were mixed with the rutile phase and anatase phase of TiO$_2$. Observing all XRD patterns of TCN, it is indistinguishable if the peak at 27.7° belongs to the phase of g-C$_3$N$_4$ due to low loading and overlapped peaks [38]. The calculated crystalline phase ratio and cell parameters of TCN are shown in Tables 1 and S1. The growth of the TiO$_2$ rutile phase was suppressed with the doping of g-C$_3$N$_4$, and the ratio was lowest when the doping ratio was 20. Similarly, the other results can be seen in Table S1. The growth of the TiO$_2$ rutile phase was also suppressed with the heating rate, and the ratio was lowest when the heating rate was 10, and the growths of the TiO$_2$ rutile phase were both always promoted with the temperature and heat preservation hour. Suggesting the changes of diffraction peaks were caused by the transformation between TiO$_2$ anatase and rutile and the growth of crystal particles. Excellent mixed ratios of TiO$_2$ anatase and rutile when the weight percent of the anatase phase was 76.8 or 73.8 and the rutile phase was 23.2 or 26.2 demonstrated excellent photocatalytic activity [39,40]. The change in lattice size was caused by the formation of a heterojunction between g-C$_3$N$_4$ and TiO$_2$ [33]. Obviously, the crystal phase ratio of TiO$_2$ anatase and rutile changed with TCN preparation conditions. To clear the relationship between TCN degradation efficiency of AAF and the ratio of TiO$_2$ anatase, the degradation efficiency plots were fitted with a curve as shown in Figure 2b. The fitted curve was obtained by the power function with six and the correlation coefficient R-square is 0.618. So, the change of crystal phase ratio not only decided cell size but also affected the photocatalytic activity significantly [41].

![Figure 2. (a) XRD patterns of pure TiO$_2$, g-C$_3$N$_4$ and TCN-U$_x$ and (b) fitted curve between photocatalytic degradation efficiency of AAF and ratio of TiO$_2$ anatase.](image)

| Sample  | Anatase/wt% | Rutile/wt% | $a = b/\text{nm}$ | $c/\text{nm}$ |
|---------|-------------|------------|-----------------|---------------|
| Pure TiO$_2$ | 5.6 | 94.4 | 1.42442 | 2.08097 |
| 10:1 | 30.3 | 69.7 | 1.30545 | 1.99599 |
| 20:1 | 76.8 | 23.2 | 0.80742 | 1.74158 |
| 30:1 | 23.7 | 76.3 | 1.05978 | 2.33788 |
| 40:1 | 26.8 | 73.2 | 1.19316 | 2.29493 |
| 50:1 | 48.9 | 51.1 | 1.10269 | 2.11718 |
3.3. UV-Vis DRS Analysis

The ultraviolet light absorption intensity of all TCN samples was much stronger than pure g-C₃N₄ and TiO₂ as shown in Figures 3a and S3a–c suggested the doped of g-C₃N₄ enhanced the UV-light absorption intensity significantly. Furthermore, the bandgap was calculated by the Kubelka–Munk function Equation (1) as follows:

\[ \alpha h \nu = A (h \nu - E_g)^2 \]  

where \( \alpha \), \( h \), \( \nu \), \( A \), and \( E_g \) was absorption coefficient, Planck constant, light frequency, a constant, and optical bandgap energy, respectively. The bandgap calculation spectra shown in Figures 3b and S3d–f and the results indicated that different preparation conditions influenced the bandgaps to different degrees. Combined with the XRD results, it can be inferred that the change in UV-light absorption intensity and bandgap were related to the formation of the TiO₂/g-C₃N₄ heterojunction and TiO₂ phase transformation between anatase and rutile [42–44].

![Figure 3. UV-Vis DRS spectra (a) and bandgap calculation spectra (b) of pure TiO₂, g-C₃N₄ and TCN-Uₓ.](image)

3.4. S BET and Porosity Analysis

\( \text{N}_2 \) adsorption-desorption isotherms and pore size distribution of TCN-Uₓ and pure TiO₂ showed in Figure 4. The BET fitted curve and specific surface area data of TCN-Uₓ are exhibited in Figure S4, Tables 2 and S2. Compared with pure TiO₂, \( S_{\text{BET}} \) of TCN increased 3–7 times after g-C₃N₄ doping. All samples showed the typical IV isotherm with H1 hysteresis loops reflecting the existence of homogeneous mesoporous. The hysteresis loops were caused by capillary condensation in the relative pressure (\( P/P_0 \)) range of about 0.5–1.0. The results suggested that TCN has a bigger specific surface area and smaller pore size than pure TiO₂. TCN performed high photocatalytic activity demonstrated by a bigger specific surface area, more abundant mesoporous structure, and more adsorption sites [39]. The increase of \( S_{\text{BET}} \) was attributed to covered g-C₃N₄ increased with doping ratio, and growth of TiO₂ anatase with heating rate sped within range of 10 °C/min. The decrease of SBET was due to the growth of TiO₂ rutile with a heating rate speed from 10 to 25 °C/min, calcination temperature raised from 450 to 650 °C, and heating preservation hour increasing from 2 to 7 h. The results were consistent with the XRD and SEM characterization of the samples.
Figure 4. N₂ adsorption-desorption isotherms (a) and pore size distribution (b) of pure TiO₂, g-C₃N₄ and TCN-Uₓ.

Table 2. Specific surface area of pure TiO₂ and UₓT₅₅₀R₅H₆-TCN.

| Sample   | g-C₃N₄ | Pure TiO₂ | 10:1 | 20:1 | 30:1 | 40:1 | 50:1 |
|----------|--------|-----------|------|------|------|------|------|
| Surface area (m²·g⁻¹) | 121.0  | 2.5       | 7.3  | 9.7  | 11.7 | 13.1 | 18.1 |

3.5. Photodegradation Experiment

The photocatalytic degradation of AAF by TCN (Figure 5) was always higher than by commercial TiO₂ (P25) and pure TiO₂ prepared, which might be attributed to the formation of the TiO₂/g-C₃N₄ heterojunction [29,44–47]. The TCN samples with a 20 doping ratio, 10 °C·min⁻¹, 550 °C, 6 h in the same three other conditions showed the optimum photocatalytic degradation efficiency.

The performance of photocatalytic degradation could be attributed to these reasons as results of characterization showed: the bigger specific surface area and more active positions with the doping ratio of g-C₃N₄ compared with pure TiO₂, transforming from urea to g-C₃N₄ smoother with the heating rate, completeness, and crystallinity of TiO₂/g-C₃N₄ composite better with the calcination temperature and heating preservation hour. However, the excessive g-C₃N₄ would obstruct the UV-light absorption to TiO₂ with the further increase of doping ratio. The transformation process was too fast to attach uniformly to the TiO₂ surface resulting in stacking, and TCN got heavily agglomerated with the further rise in calcination temperature. Moreover, a suitable ratio of TiO₂ rutile phases and anatase phases is a vital contribution to promoting photocatalytic degradation efficiency [40,41,48].

On the whole, the calcination temperature has the greatest influence on the photocatalytic activity of aniline aerofloat degradation, followed by the doping ratio, heat preservation hour and heating rate have the least influence in a certain range.

The stability of the photocatalyst is an important index to estimate the photocatalytic activity so it is significant to study the recycling of the TiO₂/g-C₃N₄ composite. At room temperature, TCN-T₅₅₀ (30 mg) was added to a 50 mL AAF solution (100 mg·L⁻¹). The catalyst used was collected and reused in the next degradation experiment. The results of reusing catalyst photocatalytic activity were showed in Figure 6. After four times of recycling, the TiO₂/g-C₃N₄ composite photocatalytic degradation efficiency of AAF was always steadily high, indicating that the TiO₂/g-C₃N₄ composite is a kind of potential photocatalyst for practical engineering application.
Figure 5. Activity of (a) TCN-U, (b) TCN-R, (c) TCN-T, (d) TCN-H on the photocatalytic degradation of AAF.

Figure 6. Activity of recycling test of TCN-T for photocatalytic degradation of AAF.

3.6 XPS Analysis

The surface chemical compositions of TCN-T were tested by XPS and the results shown in Figure 7 show survey, C1s, N1s, O1s and Ti2p scans. The peaks at 284.6 eV, 285.3 eV, and 288.6 eV shown in Figure 7b correspond to the $sp^2$ C−C, C=, N−C=N bonds [49]. Meanwhile, the binding energies of 399.3 eV and 400.6 eV shown in Figure 7c
correspond to the sp$^3$ N-(C)$_3$ and interstitial N, which indicated the existence of g-C$_3$N$_4$ and composite structure [8,50]. Binding energies in 529.8 eV and 530.6 eV shown in Figure 7d corresponds to Ti–O band and surface absorbed –OH [44], and binding energies in 458.6 eV and 464.3 eV shown in Figure 7e were attributed to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ [51], which directly testified TiO$_2$. Furthermore, there no peaks of C–O, N–O, Ti–C, or Ti–N observed indicating that TiO$_2$ and g-C$_3$N$_4$ were composed with molecule doping rather than lattice replace.

Figure 7. XPS of survey (a), C1s (b), N1s (c), O1s (d) and Ti2p (e) scans of TCN-T$_{550}$. 
3.7. Electrochemical Analysis

The electrochemical impedance spectroscopy (EIS) of pure TiO$_2$ and TCN-T$_{550}$ shown in Figure 8 indicated that e$^-$-h$^+$ pair separation-effective of TCN-T$_{550}$ is more efficient than TiO$_2$ [49].

![EIS of pure TiO$_2$ and TCN-T$_{550}$](image)

**Figure 8.** The EIS of pure TiO$_2$ and TCN-T$_{550}$.

3.8. Mechanism of Composite

3.8.1. Reactive Active Species of Photocatalyst

Research of photocatalysts’ reactive active species in the photocatalytic degradation process is the fundamental research of photocatalytic mechanism. As we all know, ammonium oxalate is the quenching agent of hole (h$^+$), and isopropanol is the quenching agent of hydroxyl radical (·OH). The results are shown in Figure 9.

![Effect of TCN-T$_{550}$ for photocatalytic of AAF degradation with different concentration quenching agents](image)

**Figure 9.** Effect of TCN-T$_{550}$ for photocatalytic of AAF degradation with different concentration quenching agents: (a) ammonium oxalate, (b) isopropanol.

The photocatalytic degradation of AAF efficiency declined gradually with the increasing concentration of ammonium oxalate and isopropanol shown in Figure 9. The result illustrates the oxidation action of h$^+$ and -OH in the photocatalytic degradation process. Meanwhile, the effect of ammonium oxalate and isopropanol on the photocatalytic degradation efficiency is similarly judged from the degradation efficiency decrement. In conclusion, the h$^+$ and -OH, which were both photocatalysts reactive active species in the photocatalytic degradation process, react synergistically in the photocatalytic reaction system.
3.8.2. Mechanism Conjecture of Photodegradation

The bandgap energy of TiO$_2$ and g-C$_3$N$_4$ were 3.04 eV and 2.98 eV, which is based on UV-Vis DRS results. The valence band (VB) and conduction band (CB) edge potentials were calculated by the following Equations (2) and (3) [52]:

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

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

where $E_{VB}$, $E_{CB}$, $\chi$, $E_e$ and $E_g$ were the VB edge potential, the CB edge potential, the geometric mean of Mulliken electronegativity [53], and the energy of electrons on the hydrogen scale (~4.5 eV vs. NHE) and optical bandgap energy. The value of $\chi$ of TiO$_2$ and g-C$_3$N$_4$ were 5.81 eV [54] and 4.73 eV [55]. The $E_{VB}$ of TiO$_2$ and g-C$_3$N$_4$ were 2.83 eV and 1.72 eV, and the $E_{CB}$ of TiO$_2$ and g-C$_3$N$_4$ were calculated as ~0.21 eV and ~1.26 eV, respectively. The VB potential of TiO$_2$ (2.83 eV) is more positive than H$_2$O/·OH (+1.99 eV vs. NHE), and the CB potential of g-C$_3$N$_4$ is more negative than O$_2$/·O$_2^-$ (~0.33 eV vs. NHE) [56], so there was an oxidation reaction in the VB of TiO$_2$ and a reduction reaction in the CB of g-C$_3$N$_4$. This result and the results of photocatalysts reactive active species confirmed each other. TiO$_2$ and g-C$_3$N$_4$ might form type-II or direct Z-scheme heterojunction. If it belongs to type-II heterojunction, e$^-$ on the CB of g-C$_3$N$_4$ would transfer to the CB of TiO$_2$ and h$^+$ on the VB of TiO$_2$ would transfer to the VB of g-C$_3$N$_4$. However, the VB potential of g-C$_3$N$_4$ (1.72 eV) is more negative than H$_2$O/·OH (+1.99 eV vs. NHE) and cannot produce ·OH which was the active species. The conclusion is contradictory to the result of the quenching experiment. So, the possible photodegradation mechanism process was conjectured as a direct Z-scheme heterojunction shown in Figure 10 [57] and following Equations (4)–(8):

$$\text{TiO}_2/\text{g-C}_3\text{N}_4 + h\nu \rightarrow \text{TiO}_2 (e^-, h^+)/\text{g-C}_3\text{N}_4 (e^-, h^+)$$  \hspace{1cm} (4)

$$\text{TiO}_2 (e^-, h^+)/\text{g-C}_3\text{N}_4 (e^-, h^+) \rightarrow \text{TiO}_2 (h^+) + \text{g-C}_3\text{N}_4 (e^-)$$  \hspace{1cm} (5)

$$\text{TiO}_2 (h^+) + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}.$$  \hspace{1cm} (6)

$$\text{g-C}_3\text{N}_4 (e^-) + \text{O}_2 \rightarrow \cdot\text{O}_2^-$$  \hspace{1cm} (7)

$$\cdot\text{OH}/\text{TiO}_2 (h^+)/\cdot\text{O}_2^- + \text{Aniline Aerofloat} \rightarrow \text{products}$$  \hspace{1cm} (8)

**Figure 10.** The possible photodegradation mechanism process of TiO$_2$/g-C$_3$N$_4$.

Under light irradiation excitation, e$^-$ in transfers from CB to VB of TiO$_2$ and g-C$_3$N$_4$ severally, and there is h$^+$ left in CB. Meanwhile, e$^-$ of TiO$_2$ combines with h$^+$ of g-C$_3$N$_4$ on the VB of g-C$_3$N$_4$. Next h$^+$ of TiO$_2$ oxidizes the H$_2$O molecule into ·OH and H· and
e− of g-C₃N₄ reduces the O₂ molecule into ·O₂⁻. Then, ·OH, h+ and ·O₂⁻, which all have oxidizability, can oxidize the Aniline Aerofloat molecule into degraded products.

4. Conclusions

TiO₂/g-C₃N₄ composites with different doping ratios, heating rates, calcination temperatures and heating preservation hours were synthesized successfully by a simple pyrolysis method with the raw material of TiO₂ xerogel and urea. TCN samples with a 20 doping ratio, 10 °C·min⁻¹, 550 °C, 6 h in the same three other conditions showed the optimum photocatalytic degradation efficiency. The excellent activity was attributed to the appropriate crystal phase ratio of TiO₂ rutile phases and anatase phases, high UV-light absorption intensity, big specific surface area, and formation of the TiO₂/g-C₃N₄ heterojunction. In addition, the TiO₂/g-C₃N₄ heterojunction could postpone the recombination of h+ and e− to extend the reaction time and enhance the photodegradation efficiency. Furthermore, TiO₂/g-C₃N₄ composites have great photodegradation stability for AAF after four times.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ma15103613/s1, Figure S1: SEM images at 20,000 times of TCN-Ty: (a) T₄50; (b) T₅00; (c) T₅50; (d) T₆00; (e) T₆50 and (f) EDS spectrum of TCN-U₂0; Figure S2: XRD patterns of TCN: (a) TCN-Rz, (b) TCN-Ty, (c) TCN-H₄; Figure S3: UV-Vis DRS spectra of U₂0₅T₅50R₁H₄-CNT (a,d), TCN-Ty (b,e), and TCN-H₄ (c,f); Figure S4: Fitted curve of BET of TCN-Ux; Table S1: Crystalline phase ratio and cell parameters of TCN-Ty, TCN-Rz and TCN-H₄; Table S2: Specific surface area of CNT-Ty, TCN-Rz and TCN-H₄.

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References
1. He, M.F. Research on Key Technology in the Beneficiation of Sn-Bearing Refractory Lead-zine Mine in Southeast Yunnan. Ph.D. Thesis, Central South University, Changsha, China, 2012.
2. Xiang, L.; Xiao, T.; Mo, C.-H.; Zhao, H.M.; Li, Y.W.; Li, H.; Cai, Q.Y.; Zhou, D.M.; Wong, M.H. Sorption kinetics, isotherms, and mechanism of aniline aerofloat to agricultural soils with various physicochemical properties. Ecotoxicol. Environ. Saf. 2018, 154, 84–91. [CrossRef] [PubMed]
3. Fu, P.; Ma, Y.; Lei, B.; Li, G.; Lin, X. Decomposition of refractory aniline aerofloat collector in aqueous solution by an ozone/uv-curing process. Environ. Technol. 2021, 42, 659–670. [CrossRef] [PubMed]
4. Fu, P.; Wang, L.; Li, G.; Hou, Z.; Ma, Y. Homogenous catalytic ozonation of aniline aerofloat collector by coexisted transition metallic ions in flotation wastewaters. J. Environ. Chem. Eng. 2020, 8, 103714. [CrossRef]
5. Lin, W.; Tian, J.; Ren, J.; Xu, P.T.; Dai, Y.K.; Sun, S.Y.; Wu, C. Oxidation of aniline aerofloat in flotation wastewater by sodium hypochlorite solution. Environ. Sci. Pollut. Res. 2016, 23, 785–792. [CrossRef]
6. Deng, X.; Zhang, D.; Wu, M.; Antwi, P.; Su, H.; Lai, C. Enhanced removal of refractory pollutant from aniline aerofloat wastewater using combined vacuum ultraviolet and ozone (VUV/O₃) process. Water Sci. Technol. 2019, 80, 2250–2259. [CrossRef]
7. Jie, X.; Wang, H.; Chen, Y. Removal of dianiline dithiophosphoric acid from wastewater by chelate precipitation. Desalin. Water Treat. 2016, 57, 5100–5107. [CrossRef]
8. Liu, H.; Yu, D.; Sun, T.; Du, H.; Jiang, W.; Muhammad, Y.; Huang, L. Fabrication of surface alkalinized g-C₃N₄ and TiO₂ composite for the synergistic adsorption-photocatalytic degradation of methylene blue. *Appl. Surf. Sci.* 2019, 473, 855–863. [CrossRef]

9. Rashid, J.; Abbas, A.; Chang, L.C.; Iqbal, A.; Haq, I.U.; Rehman, A.; Awan, S.U.; Arshad, M.; Rafique, M.; Barakat, M.A. Butterfly cluster like lamellar BiOBr/TiO₂ nanocomposite for enhanced sunlight photocatalytic mineralization of aqueous ciprofloxacin. *Sci. Total Environ.* 2019, 665, 668–677. [CrossRef]

10. Pang, N.N.; Lin, H.F.; Hu, J.Y. Photodegradation of fluazindolizine in aqueous solution with graphitic carbon nitride nanosheets under simulated sunlight illumination. *Ecotoxicol. Environ. Saf.* 2019, 170, 33–38. [CrossRef]

11. Zheng, X.; Liu, Y.; Liu, X.; Li, Q.; Zheng, Y. A novel PVDF-TiO₂@g-C₃N₄ composite electrospun fiber for efficient photocatalytic degradation of tetracycline under visible light irradiation. *Ecotoxicol. Environ. Saf.* 2021, 210, 118166. [CrossRef]

12. Balu, S.; Chen, Y.-L.; Yang, T.C.K.; Chen, J.-N.; Chen, S.-W. Effect of ultrasound-induced hydroxylation and exfoliation on P90-TiO₂@g-C₃N₄ hybrids with enhanced optoelectronic properties for visible-light photocatalysis and electrochemical sensing. *Ceram. Int.* 2020, 46, 18002–18018. [CrossRef]

13. Wu, Z.; Liang, Y.; Yuan, X.; Zou, D.; Fang, J.; Jiang, L.; Zhang, J.; Yang, H.; Xiao, Z. MXene Ti₃C₂ derived Z-scheme photocatalyst of graphene layers anchored TiO₂-g-C₃N₄ for visible light photocatalytic degradation of refractory organic pollutants. *Chem. Eng. J.* 2020, 394, 124921. [CrossRef]

14. Du, X.; Bai, X.; Xu, L.; Yang, L.; Jin, P. Visible-light activation of persulfate by TiO₂/g-C₃N₄ photocatalyst toward efficient degradation of micropollutants. *Chem. Eng. J.* 2020, 384, 123245. [CrossRef]

15. Zhang, Y.; Xu, J.; Mei, J.; Sarina, S.; Wu, Z.; Liao, T.; Yan, C.; Sun, Z. Strongly interfacial-coupled 2D-2D TiO₂/g-C₃N₄ heterostructure for enhanced visible-light induced synthesis and conversion. *J. Hazard. Mater.* 2020, 394, 122529. [CrossRef]

16. Wang, J.; Ma, J.; Zhang, Q.; Chen, Y.; Hong, L.; Wang, B.; Chen, J.; Jing, H. New heterojunctions of CN/TiO₂ with different band structure as highly efficient catalysts for artificial photosynthesis. *Appl. Catal. B Environ.* 2021, 265, 119781. [CrossRef]

17. Zhou, P.; Shen, Y.; Zhao, S.; Li, G.; Cui, B.; Wei, D.; Shen, Y. Synthesis of clinoptilolite-supported BiOCl/TiO₂ heterojunction nanocomposites with highly-enhanced photocatalytic activity for the complete degradation of xanthates under visible light. *Chem. Eng. J.* 2021, 407, 126697. [CrossRef]

18. Iqbal, A.; Kafizas, A.; Sotelo-Vazquez, C.; Wilson, R.; Ling, M.; Taylor, A.; Blackman, C.; Bevan, K.; Parkin, I.; Quesada-Cabrera, R. Charge Transport Phenomena in Heterojunction Photocatalysts: The WO₃/TiO₂ System as an Archetypical Model. *ACS Appl. Mater. Interfaces* 2021, 13, 9781–9793. [CrossRef]

19. Xiu, Z.; Xing, Z.; Li, Z.; Wu, X.; Yan, X.; Hu, M.; Cao, Y.; Yang, S.; Zhou, W. Ti³⁺-TiO₂/Ce³⁺-CeO₂ Nanosheet heterojunctions as efficient visible-light-driven photocatalysts. *Mater. Res. Bull.* 2018, 100, 191–197. [CrossRef]

20. Wei, H.; McMaster, W.A.; Tan, J.Z.Y.; Chen, D.; Caruso, R.A. Tricomponent brookite/anatase TiO₂/g-C₃N₄ heterojunction in mesoporous hollow microspheres for enhanced visible-light photocatalysis. *J. Mater. Chem. A* 2018, 6, 7236–7245. [CrossRef]

21. Zhang, R.; Yu, Y.; Wang, H.; Du, J. Mesoporous TiO₂/g-C₃N₄ composites with O-Ti-N bridge for improved visible-light photodegradation of enrofloxacin. *Sci. Total Environ.* 2020, 724, 138280. [CrossRef]

22. Xia, Y.; Xu, L.; Peng, J.; Han, J.; Guo, S.; Zhang, L.; Han, Z.; Komarneni, S. TiO₂@g-C₃N₄ core/shell spheres with uniform mesoporous structures for high performance visible-light photocatalytic application. *Ceram. Int.* 2019, 45, 18844–18851. [CrossRef]

23. Zi, T-Q.; Zhao, X-R.; Liu, C.; Cao, Y-Q.; Li, A-D. A facile route to prepare TiO₂/g-C₃N₄ nanocomposite photocatalysts by atomic layer deposition. *J. Alloy. Compd.* 2021, 855, 157446. [CrossRef]

24. Sun, S.; Ding, H.; Mei, L.; Chen, Y.; Hao, Q.; Chen, W.; Xu, Z.; Chen, D. Construction of SiO₂-TiO₂/g-C₃N₄ composite photocatalyst for hydrogen production and pollutant degradation: Insight into the effect of SiO₂. *Chin. Chem. Lett.* 2020, 31, 2287–2294. [CrossRef]

25. Song, J.; Huang, M.; Jiang, N.; Zheng, S.; Mu, T.; Meng, L.; Liu, Y.; Liu, J.; Chen, G. Ultrasensitive detection of amoxicillin by TiO₂-g-C₃N₄@AuNPs impedimetric aptasensor: Fabrication, optimization, and mechanism. *J. Hazard. Mater.* 2020, 391, 122024. [CrossRef]

26. Meng, Z.; Zhou, B.; Xu, J.; Li, Y.; Hu, X.; Tian, H. Heterostructured Nitrogen and Sulfur Co-doped Black TiO₂/g-C₃N₄ Photocatalyst with Enhanced Photocatalytic Activity. *Chem. Res. Chin. Uni.* 2020, 36, 1045–1052. [CrossRef]

27. Zhu, S.P.; Wang, C.Y.; Luo, X.P. Preparation and degradation activity for benzohydroxamic acid of Gd-doped anatase TiO₂ photocatalysts. *J. Chin. Ceram. Soc.* 2017, 45, 1523–1530. [CrossRef]

28. Zhu, S.P.; Wang, C.Y.; Wei, Z.Y.; Chen, Z.Y.; Wu, C.T.; Luo, X.P. Degradation activity for aniline aerofloat of Sm-doped TiO₂ photocatalysts. *J. Chin. Ceram. Soc.* 2018, 46, 1632–1638. [CrossRef]

29. Tan, Y.G.; Shu, Z.; Zhou, J.; Li, T.; Wang, W.; Zhao, Z. One-step synthesis of nanostructured g-C₃N₄/TiO₂ composite for highly enhanced visible-light photocatalytic H₂ evolution. *Appl. Catal. B Environ.* 2018, 230, 260–268. [CrossRef]

30. Niu, P.; Zhang, L.L.; Liu, G.; Cheng, H.M. Graphene-Like Carbon Nitride Nanosheets for Improved Photocatalytic Activities. *Adv. Funct. Mater.* 2012, 22, 4763–4770. [CrossRef]

31. Tripathi, A.; Narayanan, S. Impact of TiO₂ and TiO₂/g-C₃N₄ Nanocomposite to Treat Industrial Wastewater. *Environ. Nanotechnol. Monit. Manag.* 2018, 10, 280–291. [CrossRef]

32. Youssefzadeh, S. Effect of thermal condensation temperature on electrochemical capacitive properties of g-C₃N₄ supported on reduced TiO₂ nanowires/nanotubes array. *J. Alloy. Compd.* 2019, 785, 1–6. [CrossRef]
33. Pan, J.; You, M.; Chi, C.; Dong, Z.; Wang, B.; Zhu, M.; Zhao, W.; Song, C.; Zheng, Y.; Li, C. The two dimension carbon quantum dots modified porous g-C3N4/TiO2 nano-heterojunctions for visible light hydrogen production enhancement. Int. J. Hydrogen Energy 2018, 43, 6586–6593. [CrossRef]

34. Pan, J.; Dong, Z.; Wang, B.; Jiang, Z.Y.; Zhao, C.; Wang, J.J.; Song, C.S.; Zheng, Y.Y.; Li, C.R. The enhancement of photocatalytic hydrogen production via Ti3+ self-doping black TiO2/g-C3N4 hollow core-shell nano-heterojunction. Appl. Catal. B Environ. 2019, 242, 92–99. [CrossRef]

35. Zhu, H.; Yang, X.; Zhang, M.; Li, Q.; Yang, J. Construction of 2D/2D TiO2/g-C3N4 nanosheet heterostructures with improved photocatalytic activity. Mater. Res. Bull. 2020, 125, 110765. [CrossRef]

36. Zhang, H.; Liu, Z.; Li, Y.; Zhang, C.; Wang, Y.; Zhang, W.; Wang, L.; Niu, L.; Wang, P.; Wang, C. Intimately coupled TiO2/g-C3N4 photocatalysts and in-situ cultivated biofilms enhanced nitrate reduction in water. Appl. Surf. Sci. 2020, 503, 144092. [CrossRef]

37. Zada, A.; Khan, M.; Qureshi, M.N.; Liu, S.-Y.; Wang, R. Accelerating Photocatalytic Hydrogen Production and Pollutant Degradation by Functionalizing g-C3N4 With SnO2. Front. Chem. 2020, 7, 941. [CrossRef]

38. Du, L.; Jin, C.; Cheng, Y.; Xu, L.; An, X.; Chang, W.; Zhang, Y.; Rao, X. Improvement of antibacterial activity of hydrothermal treated TiC3 substrate through an in situ grown TiO2/g-C3N4 Z-scheme heterojunction film. J. Alloy. Compd. 2020, 842, 155612. [CrossRef]

39. Sun, Q.; Hu, X.L.; Zheng, S.L.; Zhang, J.; Sheng, J.W. Effect of calcination on structure and photocatalytic property of N-TiO2/g-C3N4@diatomite hybrid photocatalyst for improving reduction of Cr(VI). Environ. Pollut. 2019, 245, 53–62. [CrossRef]

40. Wang, W.K.; Chen, J.J.; Zhang, X.; Huang, Y.X.; Li, W.W.; Yu, H.Q. Self-induced synthesis of phase-junction TiO2 with a tailored rutile to anatase ratio below phase transition temperature. Sci. Rep. 2016, 6, 20491. [CrossRef]

41. Wang, X.L.; Li, C. Roles of Phase Junction in Photocatalysis and Photoelectrocatalysis. J. Phys. Chem. C 2018, 122, 21083–21096. [CrossRef]

42. Lei, J.; Chen, B.; Lv, W.; Zhou, L.; Wang, L.; Liu, Y.; Zhang, J. An inverse opal TiO2/g-C3N4 composite with a heterojunction for enhanced visible light-driven photocatalytic activity. Dalton Trans. 2019, 48, 3486–3495. [CrossRef]

43. Fang, Y.; Huang, W.; Yang, S.; Zhou, X.; Ge, C.; Gao, Q.; Fang, Y.; Zhang, S. Facile synthesis of anatase/rutile TiO2/g-C3N4 multi-heterostructure for efficient photocatalytic overall water splitting. Int. J. Hydrogen Energy 2020, 45, 17378–17387. [CrossRef]

44. Li, G.; Wu, Y.; Zhang, M.; Chu, B.; Huang, W.; Fan, M.; Dong, L.; Li, B. Enhanced Removal of Toxic Cr(VI) in Wastewater by Synthetic TiO2/g-C3N4 Microspheres/IGO Photocatalyst under Irradiation of Visible Light. Ind. Eng. Chem. Res. 2019, 58, 8979–8989. [CrossRef]

45. Lin, X.; Sun, M.; Gao, B.; Ding, W.; Zhang, Z.; Anandan, S.; Umar, A. Hydrothermally regulating phase composition of TiO2 nanocrystals toward high catalytic activity. J. Alloy. Compd. 2021, 850, 156653. [CrossRef]

46. Zhu, Y.; Liu, Y.; Ai, Q.; Gao, G.; Yuan, L.; Fang, Q.; Tian, X.; Zhang, X.; Egap, E.; Ajayan, P.M.; et al. In Situ Synthesis of Lead-Free Halide Perovskite–COF Nanocomposites as Photocatalysts for Photoinduced Polymerization in Both Organic and Aqueous Phases. ACS Mater. Lett. 2022, 4, 464–471. [CrossRef]

47. Kipkorir, A.; Dubose, J.; Cho, J.; Kamat, P.V. CsPbBr3–CdS heterostructure: Stabilizing perovskite nanocrystals for photocatalysis. Chem. Sci. 2021, 12, 14815–14825. [CrossRef]

48. Colomer, M.T.; Campo, A.D. Preparation of nanostructured TiO2 films with high catalytic activity and their 3D spatial distribution of anatase and rutile phases. J. Mater. Sci. 2019, 54, 9414–9425. [CrossRef]

49. Jin, C.; Li, Z.; Zhang, Y.; Wang, M.; Wu, Z.; Xie, Y.; Wang, Y.; Zhu, T. The construction of g-C3N4/Sm2+ doped Bi2WO6 2D/2D Z-scheme heterojunction for improved visible-light excited photocatalytic efficiency. Sep. Purif. Technol. 2019, 224, 33–43. [CrossRef]

50. Li, J.; Li, B.; Li, Q.; Yang, J. The effect of N-doped form on visible light photocatalytic activity of Z-scheme g-C3N4/TiO2 photocatalyst. Appl. Surf. Sci. 2019, 466, 268–273. [CrossRef]

51. Li, C.; Lou, Z.; Yang, Y.; Wang, Y.; Lu, Y.; Ye, Z.; Zhu, L. Hollowsphere Nanoheterojunction of g-C3N4@g-C3N4 with High Visible Light Photocatalytic Property. Langmuir 2019, 35, 779–786. [CrossRef]

52. Nethercot, A. Prediction of Fermi Energies and Photoelectric Thresholds Based on Electronegativity Concepts. Phys. Rev. Lett. 1974, 33, 1088–1091. [CrossRef]

53. Mulliken, R.S. A New Electroaffinity Scale; Together with Data on Valence States and on Valence Ionization Potentials and Electron Affinities. J. Chem. Phys. 1934, 2, 782–793. [CrossRef]

54. Corpus-Mendoza, A.N.; Moreno-Romero, P.M.; Hu, H. Evaluation of Mulliken Electronegativity on CH3NH3PbI3 Hybrid Perovskite as a Thought-Provoking Activity. J. Chem. Educ. 2019, 96, 974–978. [CrossRef]

55. Hao, R.; Wang, G.; Tang, H.; Sun, L.; Xu, C.; Han, D. Template-free preparation of macro/mesoporous g-C3N4/TiO2 heterojunction photocatalysts with enhanced visible light photocatalytic activity. Appl. Catal. B Environ. 2016, 187, 47–58. [CrossRef]

56. Liu, Y.; Zeng, X.; Hu, X.; Hu, J.; Zhang, X. Two-dimensional nanomaterials for photocatalytic water disinfection: Recent progress and future challenges. J. Chem. Technol. Biotechnol. 2019, 94, 22–37. [CrossRef]

57. Zhu, B.C. Research on Adsorption and Photocatalytic Activity of g-C3N4: First-Principle Calculation and Experimental Study. Ph.D. Thesis. Wuhan University of Technology, Wuhan, China, 2018.