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Polymeric Carbon Nitride-CNTs-Ferric Oxide All-Solid Z-Scheme Heterojunction with Improved Photocatalytic Activity towards Organic Dye Removal

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Abstract: Polymeric carbon nitride (PCN) is a kind of polymeric semiconductor that is widely popular in photocatalysis-related energy and environmental fields. However, the photocatalytic activity is still limited due to its poor conductivity and low charge separation efficiency. In this work, benzene rings were introduced to adjust the electronic structure of PCN, and then a PCN-based all-solid Z-scheme heterojunction was fabricated by combing multiwall carbon nanotubes (CNTs) and ferric oxide through precipitation and the in situ deposit method. Upon optimizing the ratio between PCN, CNTs, and Fe2O3 (PCN: CNTs: Fe2O3 = 10:1:3 by weight), the composites expressed superior photocatalytic degradation activity towards methylene blue (MB) and crystal violet (CV) compared with pristine PCN and Fe2O3. The MB degradation percentage achieved 90% in 75 min, and the CV up to 99.6% within 50 min. The Z-scheme mechanism was verified by band alignment and metal selective deposition. The CNTs in the heterojunction played the role of an electron shuttling mediator and hence improved charge separation efficiency. This work provides ideas for the construction of polymer-inorganic all-solid Z-scheme photocatalysts for practical applications.

Keywords: PCN; α-Fe2O3; Z-scheme; heterojunction; photocatalytic degradation

1. Introduction

Environmental pollution, especially wastewater containing organic dyes, has great potential to cause harm to the human and ecological environment due to its cumulative carcinogenic toxicity [1–3]. Wastewater treatment is a time- and cost-consuming process, yet it is always a necessary process before wastewater is discharged into nature. The development of efficient, green, and sustainable treatments to clear organic dyes from water is still a research hotspot. Photocatalysis, utilizing solar energy and its photooxidation ability, represents green and advanced oxidation technology and has been successfully applied to environmental remediation, such as organics decomposition [4], heavy metal ion removal [5], and gas purification [6]. Despite this, higher requirements always exist in terms of exploiting robust photocatalysts with low cost and facile preparation.

Graphitic carbon nitride is a polymeric semiconductor composed of tri-s-triazine units, which are linked by a N-bridge [7,8]. The presence of the bridge-N atom destroys the conjugation structure and leads to poor electronic conductivity and charge separation efficiency. Co-polymerization of monomer d to tris-triazine or triazine-based carbon nitride, normally named polymeric carbon nitride (PCN), and improved the surface and electronic structure of carbon nitride, and thus the conductivity and charge separation efficiency were
enhanced [9,10]. Furthermore, heterostructure engineering, which incorporates metallic nanoparticles or alien semiconductors, has been proven to enhance photocatalytic activity by improving interface charge separation efficiency [11,12]. Hence, fabrication of PCN-based heterostructures is highly demanded and still challenging in constructing robust photocatalysts with superior photocatalytic activity.

To effectively decompose organic pollutants, the high redox ability of the photocatalyst is required. To meet this requirement, Z-scheme heterostructures exhibit unique advantages compared with type II [13] and p-n heterojunctions [14] since they possess improved charge separation efficiency and meanwhile maintain high conduction band (CB) and valence band (VB) positions [15], which is thermodynamically favorable for redox reactions. For example, direct Z-scheme Bi$_2$O$_3$/g-C$_3$N$_4$ nanocomposites express superior photocatalytic activity towards MB degradation [16]. In a Z-scheme photocatalytic system, the introduction of an electronic mediator will further improve the separation efficiency of the photogenerated carriers and, thus, further improve the photocatalytic performance of the Z-scheme photocatalyst. Among the common electron mediators, carbon nanotubes (CNTs) have been frequently employed as electron mediators due to their unique one-dimensional structure, light-harvesting capacity, and excellent electron-transport property [17,18]. For instance, all-solid Z-scheme g-C$_3$N$_4$/CNTs/TiO$_2$ self-assembly exhibited improved photocatalytic ability towards phenol removal [19]. It has been found that CNTs can transfer photogenerated electrons from TiO$_2$ to C$_3$N$_4$, thus significantly enhancing photocatalytic activity. However, the overall performance of Z-scheme heterostructures is still limited by the intrinsic drawbacks of pristine graphitic carbon nitride. Our recent work revealed that, by tailoring the electronic structure of PCN, a PCN-based Z-scheme exhibited more abundant activity than conventional g-C$_3$N$_4$-based heterojunctions [20]. It is reasonable that a PCN-based all-solid Z-scheme heterostructure would show great potential for superior photocatalytic activity, which has rarely been studied.

Ferric oxide (Fe$_2$O$_3$) is an n-type semiconductor with a narrow band gap (ca. 2.1 eV) that is popularly used as a visible-light-driven photocatalyst for decomposition of various organic compounds [21]. Most importantly, the CB and VB levels of Fe$_2$O$_3$ are lower than carbon nitride, which is expected to maintain strong redox activity and enhance charge separation in Z-scheme heterojunctions. Therefore, in this study, PCN was synthesized by copolymerization of cyanimide and terephthalonitrile, and then a PCN-based all-solid Z-scheme heterojunction was fabricated by combing CNTs and Fe$_2$O$_3$ through precipitation and the in situ deposit method. Upon optimizing the ratio between PCN, CNTs, and Fe$_2$O$_3$, the composites expressed superior activity towards methylene blue (MB) and crystal violet (CV) compared with pristine PCN and Fe$_2$O$_3$. The Z-scheme mechanism was verified by band alignment and metal selective deposition. The CNTs in the heterojunction played the role of an electron shuttling mediator and hence improved charge separation efficiency. This work provides ideas for the construction of polymer-inorganic all-solid Z-scheme photocatalysts for practical applications.

2. Results and Discussion

2.1. Morphology and Structure

The morphology and composition of the synthesized CCF-10 (CF-3) samples are shown in Figure 1. The SEM and TEM images (Figure 1a,b) clearly show the presence of PCN and Fe$_2$O$_3$, which were connected with CNTs and formed an interlinked ternary composite. The energy dispersive X-ray spectroscopy (EDS) mapping results (Figure 1c–g) confirmed the presence of the elements C, N, O, and Fe in the CCF-10 (CF-3) sample. No other elements were detected, indicating the high purity of the composite. Moreover, from the distribution of C and N, the morphology of CNTs can be differentiated and inconsistent with the TEM image. Likewise, the distribution of O and Fe confirmed the presence and morphology of Fe$_2$O$_3$. This result suggested the successful fabrication of the CCF-10 (CF-3) composite.
The crystalline structure of the composite was analyzed by XRD, as well as the control samples of PCN, α-Fe₂O₃, CCF-5 (CF-3), CCF-10 (CF-3), CCF-5 (CF-5), and CCF-10 (CF-5). As shown in Figure 2a, the diffraction peak of PCN at 27.3° corresponds to the (002) crystal planes induced by interplanar stacking of the conjugated heptazine units [22,23]. For pristine α-Fe₂O₃, the peaks at 24.2°, 33.1°, 35.6°, 40.7°, 49.3°, 54.1°, 62.4°, and 64.1° are indexed to the (012), (104), (110), (113), (024), (116), (214), and (300) crystalline facets (JCPDS#33-0644) [24]. The composites exhibited diffraction peaks of PCN and α-Fe₂O₃, but no peaks from CNTs were detected. This may be caused by the small amount of CNT content. The FTIR spectrum showed the characteristic bands of tri-s-triazine (813 cm⁻¹ corresponding to the stretching vibrational mode of the CN heterocycle [25]), indicating the successful copolymerization. In the composites, the bands are similar to that of PCN, suggesting the presence of PCN in the composite, which is in agreement with the XRD and TEM results, confirming the successful synthesis of the composites.

![Figure 1. (a) SEM and (b) TEM images of the CCF-10 (CF-3) sample, EDS mapping of the SEM region (c) showing the elemental distribution of (d) C, (e) N, (f) O, and (g) Fe.](image1)

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**2.2. Optical Absorption and Photoluminescence (PL) Spectra**

The light absorption properties of the PCN/CNTs/α-Fe₂O₃ samples were investigated by UV-Vis absorbance spectroscopy, and the results are shown in Figure 3a. The PCN shows an absorption edge at about 450 nm, and α-Fe₂O₃ exhibits a significant absorption at 550 nm in the visible region. The light absorption edge of the PCN/CNTs/α-Fe₂O₃ samples

![Figure 2. (a) XRD patterns and (b) FTIR spectrum of PCN, α-Fe₂O₃, and PCN/CNTs/α-Fe₂O₃ samples.](image2)

**Figure 2.** (a) XRD patterns and (b) FTIR spectrum of PCN, α-Fe₂O₃, and PCN/CNTs/α-Fe₂O₃ samples.
was extended to the visible region due to the presence of Fe$_2$O$_3$, and the absorption in the range from 600 to 800 nm can be ascribed to the CNTs [26,27]. In other words, the visible light absorption of the PCN/CNTs/α-Fe$_2$O$_3$ samples was enhanced compared with pristine PCN and Fe$_2$O$_3$, which is beneficial for visible light-induced catalytic activity.

As for semiconductor materials, PL emission originated from the radiative recombination of photoexcited electrons and holes. The peak intensity reflected the charge separation efficiency when the charge carriers recombined in a non-radiative way [28]. As shown in Figure 3b, the emission peak of PCN is 475 nm [8], with the highest intensity among all the samples. In contrast, the peak intensity of the PCN/CNTs/α-Fe$_2$O$_3$ samples decreased, which indicated that the charge separation efficiency was improved in the heterostructure [29]. In particular, the CCF-10 (CF-3) sample showed the lowest intensity among them, suggesting that the charge separation efficiency was the highest among all the samples. The optical absorption and PL spectra pointed to the CCF-10 (CF-3) exhibiting the best photocatalytic activity among the samples.

2.3. Photoelectrochemical (PEC) Properties

The PEC measurements were carried out to evaluate the charge transfer behavior of the composite heterostructure. From the transient current response (Figure 4a), it can be observed that the photocurrent density of the CCF-10 (CF-3) sample (0.67 uA/cm$^2$) is approximately five times and seven times higher than that of pristine PCN (0.14 uA/cm$^2$) and α-Fe$_2$O$_3$ (0.09 uA/cm$^2$), respectively. In the EIS spectrum (Figure 4b), the fitted arc radius of the CCF-X (CF-X) sample is the smallest among all the samples, indicating the lowest electrical resistance [30], which is in agreement with the photocurrent response. These results suggested that the heterostructure possessed higher charge carrier density and better electrical conductivity than pristine PCN and ferric oxide, which can be ascribed to the CNTs with excellent electrical conductivity for smooth electron transfer.

2.4. Assessment of Photocatalytic Performance

Based on the above results, the photocatalytic performance of the samples was evaluated by using MB and CV as the typical organic dye substrates, as shown in Figure 5a,b. Before irradiation, 30 min dark adsorption was adopted to achieve adsorption–desorption equilibrium. It is obvious that the PCN/CNTs/α-Fe$_2$O$_3$ samples expressed significant adsorption towards MB and CV. This could be ascribed to the high specific surface area and will be discussed later. In the absence of a photocatalyst, there was no obvious degradation of the dyes under light irradiation. This indicates that the MB and CV molecules are stable under irradiation without self-photodegradation. The degradation efficiency of pristine PCN and α-Fe$_2$O$_3$ were 63.9% and 26.2% for MB and 45.9% and 17.2% for CV, respectively. In contrast, the PCN/CNTs/α-Fe$_2$O$_3$ samples exhibited significant degradation efficiency.
that all reached over 90%. The photocatalytic degradation kinetics was investigated by fitting \( \ln(C/C_0) = -kt \), where \( k \) is the apparent kinetic rate constant; the logarithmic plots shown in Figure 5c,d describe straight lines, corresponding to pseudo-first-order kinetics. The calculated rate constants are also listed in Table S1. The \( k \) value of CCF-10 (CF-3) over MB degradation reached 0.022 min\(^{-1}\), which is two times and seven times that of PCN (0.011 min\(^{-1}\)) and Fe\(_2\)O\(_3\) (0.003 min\(^{-1}\)), respectively. The \( k \) value of CV degradation over CCF-10 (CF-3) (0.033 min\(^{-1}\)) is 2 times and 30 times that of PCN (0.017 min\(^{-1}\)) and Fe\(_2\)O\(_3\) (0.001 min\(^{-1}\)), respectively. The excellent photocatalytic activity of the PCN/CNTs/\(\alpha\)-Fe\(_2\)O\(_3\) samples can be attributed to the formation of the Z-scheme heterostructure among the three components.

![Figure 4](image)

**Figure 4.** (a) Transient photocurrent response curves and (b) electrical impedance spectra of PCN, \(\alpha\)-Fe\(_2\)O\(_3\), and CCF-X (CF-X) samples.

![Figure 5](image)

**Figure 5.** Pseudo-first-order kinetic curves for visible light degradation of MB (a), CV (b), and photocatalytic degradation of MB (c) and CV (d) for g-C\(_3\)N\(_4\), \(\alpha\)-Fe\(_2\)O\(_3\), and PCN/CNTs/\(\alpha\)-Fe\(_2\)O\(_3\) samples.

To emphasize the role of the ternary components and the effect of CNTs, binary composites of PCN/CNTs, PCN/\(\alpha\)-Fe\(_2\)O\(_3\), and \(\alpha\)-Fe\(_2\)O\(_3\)/CNTs were prepared (SI) and used as the control for photocatalytic degradation of MB and CV. As shown in Figure 6a,b, the CCF-10 (CF-3) samples exhibited higher photocatalytic degradation efficiency than the binary composites (PCN/CNTs, PCN/\(\alpha\)-Fe\(_2\)O\(_3\), and \(\alpha\)-Fe\(_2\)O\(_3\)/CNTs) towards MB and CV. From the pseudo-first-order kinetic curves (Figure 6c,d), it can be seen that the rate constant follows the order of CCF-10 (CF-3) > PCN/CNTs > PCN/ PCN/\(\alpha\)-Fe\(_2\)O\(_3\) > \(\alpha\)-Fe\(_2\)O\(_3\)/CNTs for MB and CV. This result confirmed that the improved photocatalytic activity comes from the special surface and electronic structure caused by the indispensable ternary components.
To emphasize the role of the ternary components and the effect of CNTs, binary composite pseudo-first-order kinetic profiles of (c) MB and (d) CV.

2.5. BET Tests and Dye Adsorption Capacity

To investigate the origin of improved photocatalytic activity, the specific surface area and pore structure were evaluated by N₂ adsorption–desorption isotherms and BJH pore size distribution. As shown in Figure 7a, all the samples followed type IV isotherms [31,32]. The BET surface area for PCN, α-Fe₂O₃, and CCF-10 (CF-3) are 11.33, 14.54, and 23.34 m² g⁻¹, respectively (Table S2). The surface area was significantly increased in the heterostructure ternary composite. It should be noted that the CCF-10 (CF-3) sample presented a larger H₃-type hysteresis loop than that of PCN, which indicates the presence of a macropore structure [33]. It can be observed from the BJH pore size distribution (Figure 7b) that the pore size of PCN and α-Fe₂O₃ is in the range of 2–70 nm, which is ascribed to the nanostructured morphology. The size pore distribution of CCF-10 (CF-3) indicated the presence of mesopores and macropores, which may be caused by the interlayer stacking between PCN and CNTs. The pore volume of CCF-10 (CF-3) increased to 0.064 with respect to PCN and α-Fe₂O₃. The high specific surface area and pore volume afford the composite excellent adsorption capability toward organic dyes. The adsorption capacity of the PCN, α-Fe₂O₃, and PCN/CNTs/α-Fe₂O₃ samples on MB and CV were investigated (Figure S1). The adsorption capacities of the CCF-X (CF-X) samples were all higher than that of g-C₃N₄ and α-Fe₂O₃, which could be attributed to the increase in the specific surface area of the composite samples.

2.6. Energy Band Alignment Analysis

The VBs of PCN and α-Fe₂O₃ were calculated by XPS valence band spectroscopy, and the results are shown in Figure 8a,b. The valence bands of PCN and α-Fe₂O₃ are 1.73 eV and 2.31 eV, respectively. The band gap energies were estimated from UV-Vis DRS and Tauc plots [34,35] (Figure 8c). The band gaps of PCN and α-Fe₂O₃ are 3.22 eV and 2.03 eV, respectively. Based on the relationship of Eg = E_Cb − E_VB, the CBs of PCN and α-Fe₂O₃ are calculated as −1.49 eV and 0.28 eV, respectively. So, the Eg, VB, and CB are listed in Table S3. Based on the band gap energy and the positions of the conduction band valence bands, the energy band structure is drawn schematically, as shown in Figure 8d.
2.6. Energy Band Alignment Analysis

The VBs of PCN and \(\alpha\)-Fe\(_2\)O\(_3\) were calculated by XPS valence band spectroscopy, and the results are shown in Figure 8a,b. The valence bands of PCN and \(\alpha\)-Fe\(_2\)O\(_3\) are 1.73 eV and 2.31 eV, respectively. The band gap energies were estimated from UV-Vis DRS and Tauc plots \[34,35\] (Figure 8c). The band gaps of PCN and \(\alpha\)-Fe\(_2\)O\(_3\) are 3.22 eV and 2.03 eV, respectively. Based on the relationship of \(E_g = E_{CB} - E_{VB}\), the CBs of PCN and \(\alpha\)-Fe\(_2\)O\(_3\) are calculated as -1.49 eV and 0.28 eV, respectively. So, the \(E_g\), VB, and CB are listed in Table S3. Based on the band gap energy and the positions of the conduction band valence bands, the energy band structure is drawn schematically, as shown in Figure 8d.

2.7. Identification of Z-Scheme Mechanism

The Z-scheme can be identified by the photocharge transport direction, which is distinct from a type II heterojunction. The EPR spin trapping result showed a clear DMPO\(-\bullet\text{O}_2^-\) signal upon irradiation of the CCF-10 (CF-3) sample (Figure 9a). It represented the formation of superoxide radicals, which originate from the reduction of oxygen molecules by photoelectrons \[36\]. It should be noted that the reduction potential of the \(\alpha\)-Fe\(_2\)O\(_3\) CB is insufficient to reduce \(\text{O}_2\) (\(\bullet\text{O}_2^- / \text{O}_2 = -0.33\) V vs. NHE) \[37\]. So, the superoxide radicals were generated on PCN, and the CB potential is negative enough to fulfill the \(\text{O}_2\) reduction to \(\bullet\text{O}_2^-\). This confirmed that, upon excitation, photoelectrons in PCN did not...
transfer to the CB of \( \alpha-\text{Fe}_2\text{O}_3 \). Otherwise, superoxide radicals would not be generated. The photoelectron flow was also confirmed by spatial photodeposition [38]. The Pt nanoparticles prefer depositing on the PCN region in the CCF-10 (CF-3) upon photoreduction, as shown in Figure 9b. It further confirmed that the photoelectrons in PCN remain in the CB rather than flowing to the CB of \( \alpha-\text{Fe}_2\text{O}_3 \), excluding the type II heterojunction.

2.7. Identification of Z-Scheme Mechanism

The Z-scheme can be identified from a type II heterojunction. The EPR spin trapping result showed a clear signal upon irradiation of the CCF-10 (CF-3) sample (Figure 9a). It represented the formation of superoxide radicals, which originate from the reduction of oxygen \( \text{O}_2 \) by photoelectrons in the CB of \( \alpha-\text{Fe}_2\text{O}_3 \). Otherwise, superoxide radicals would not be generated. The \( \text{Fe}_2\text{O}_3 \) CB is insufficient to reduce \( \text{O}_2 \) (•\( \text{O}_2^- \)) to \( \text{H}_2\text{O}_2 \) (•\( \text{H}_2\text{O}_2 \)). This confirmed that, upon excitation, photoelectrons in PCN did not flow to the CB of \( \alpha-\text{Fe}_2\text{O}_3 \), which is preferred to deposit on the PCN region in the CCF-10 (CF-3) upon photoreduction, as shown in Figure 9c. The Pt nanoparticles prefer depositing on the PCN region in the CCF-10 (CF-3) upon photoreduction, as shown in Figure 9b. It further confirmed that the photoelectrons in PCN remain in the CB rather than flowing to the CB of \( \alpha-\text{Fe}_2\text{O}_3 \), excluding the type II heterojunction.

The reactive species were identified by radical trapping experiments using isopropanol (IPA), ethylenediaminetetraacetic acid (EDTA), and benzoquinone (BQ) as hydroxyl radicals, photoholes, and superoxide radical scavengers. Figure 9c,d show that, in the presence of scavengers, the degradation efficiency of MB CV removal decreased. This indicated that •OH, \( h^+ \), and \( \bullet \text{O}_2^- \) are all the reactive species for dye degradation. And the effect of the reactive species follows the order of \( \bullet \text{OH} > \text{h}^+ > \bullet \text{O}_2^- \).

2.8. Proposed Z-Scheme Photocatalytic Mechanism

Based on the energy band alignment and EPR trapping, a possible Z-scheme mechanism was proposed for the CCF-10 (CF-3) photocatalytic degradation of organic dyes, as shown in Figure 10. Under light irradiation, both PCN and \( \alpha-\text{Fe}_2\text{O}_3 \) are excited, and photogenerated electrons were excited to the CB ((1), (2)). Thanks to the Z-scheme, the photoelectrons in the CB of \( \text{Fe}_2\text{O}_3 \) were transported by the CNTs to the VB of PCN, where the charge carrier recombined (3). Thus, the net photoelectrons in the CB of PCN and the photoholes in the VB of \( \text{Fe}_2\text{O}_3 \) were retained. In this case, the charge separation efficiency was significantly improved, while the redox ability was kept at a high level. The photoelectrons in the CB of PCN were consumed by \( \text{O}_2 \) to form superoxide radicals (4), and the photoholes in the VB of \( \alpha-\text{Fe}_2\text{O}_3 \) oxidized water to hydroxyl radicals (5). Both the superoxide radicals and hydroxyl radicals are active species that decompose organic dyes (6). The photocatalytic degradation of dye reactions is as follows:

\[
\text{PCN} + h\nu \rightarrow \text{PCN} (h^+ + e^-) \quad (1)
\]
1.524 g of terephthalonitrile (Sigma-Aldrich, 98%) were thoroughly ground in a bowl and was collected by centrifugation and washed with water several times. The final solid was obtained and suspended in water with an adjusted concentration of 10 mg/mL for further use.

3.1. Synthesis of Polymeric Carbon Nitride (PCN)

The PCN was synthesized by copolymerization followed by a dissolution-precipitation process [39]. Typically, 1 g of cyanamide (Sigma-Aldrich, St. Louis, MO, USA, 99%) and 1.524 g of terephthalonitrile (Sigma-Aldrich, 98%) were thoroughly ground in a bowl and transferred to a muffle furnace for thermal polycondensation at 400 °C for 4 h. After being cooled to room temperature, the solid was ground into powder and was dissolved in conc. H\textsubscript{2}SO\textsubscript{4} (Sigma-Aldrich, St. Louis, MO, USA, 94%) was dissolved in conc. H\textsubscript{2}SO\textsubscript{4} was used to form a PCN/H\textsubscript{2}SO\textsubscript{4} solution (0.5 g/mL) at 100 °C. The dark brown solution was then subjected to dropwise adding to deionized water under vigorous stirring. The precipitate was collected by centrifuge and washed 3 times with water. The final PCN was synthesized by copolymerization followed by a dissolution-precipitation process [39].

3.2. Synthesis of α-Fe\textsubscript{2}O\textsubscript{3}

In a typical procedure [24], 0.546 g of FeCl\textsubscript{3} 6H\textsubscript{2}O (Sigma-Aldrich, 94%) was dissolved in a mixture of 20 mL of ethanol and 1.4 mL of H\textsubscript{2}O. Then, 1.6 g of CH\textsubscript{3}COONa was added, and the mixture was transferred to a PTFE-lined stainless steel autoclave, which was placed in an oven at 180 °C for 12 h. After cooling to room temperature, the dark-red precipitate was collected by centrifugation and washed with water several times. The final solid was dried at 80 °C in an oven.

\begin{equation}
\alpha-\text{Fe}_2\text{O}_3 + h\nu \rightarrow \alpha-\text{Fe}_2\text{O}_3 (h^+ + e^-) \tag{2}
\end{equation}

\begin{equation}
\alpha-\text{Fe}_2\text{O}_3\text{CB} (e^-) + \text{PCN}_{\text{VB}} (h^+) \rightarrow \text{heat energy} \tag{3}
\end{equation}

\begin{equation}
\text{PCN}_{\text{CB}} (e^-) + \text{O}_2 \rightarrow \cdot \text{O}_2^- \tag{4}
\end{equation}

\begin{equation}
\alpha-\text{Fe}_2\text{O}_3 (h^+) + \text{H}_2\text{O} \rightarrow \cdot \text{OH} + \text{H}^+ \tag{5}
\end{equation}

\begin{equation}
(\cdot \text{O}_2^-, \cdot \text{OH}) + \text{Dyes} \rightarrow \text{Intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \tag{6}
\end{equation}

Figure 10. Proposed photocatalytic degradation mechanism of organic dyes by PCN/CNTs/α-Fe\textsubscript{2}O\textsubscript{3} all-solid Z heterojunction under light irradiation.

So, the enhancement of photocatalytic activity of the PCN/CNTs/α-Fe\textsubscript{2}O\textsubscript{3} all-solid Z heterojunction composites can be ascribed to the high specific surface area and pore volume, as well as the improved charge separation efficiency. The CNTs play the key role of a “bridge”; that is, CNTs are a “structural bridge” that connects PCN and Fe\textsubscript{2}O\textsubscript{3}, fabricating a hierarchical structure with a large pore volume. Meanwhile, it acts as an “electronic bridge” that speeds up the electron transport, creating a Z-scheme heterojunction with improved charge separation efficiency.

3. Experimental Section

3.1. Synthesis of Polymeric Carbon Nitride (PCN)

The PCN was synthesized by copolymerization followed by a dissolution-precipitation process [39]. Typically, 1 g of cyanamide (Sigma-Aldrich, St. Louis, MO, USA, 99%) and 1.524 g of terephthalonitrile (Sigma-Aldrich, 98%) were thoroughly ground in a bowl and transferred to a muffle furnace for thermal polycondensation at 400 °C for 4 h. After being cooled to room temperature, the solid was ground into powder and was dissolved in conc. H\textsubscript{2}SO\textsubscript{4} was used to form a PCN/H\textsubscript{2}SO\textsubscript{4} solution (0.5 g/mL) at 100 °C. The dark brown solution was then subjected to dropwise adding to deionized water under vigorous stirring. The precipitate was collected by centrifuge and washed 3 times with water. The final PCN was synthesized by copolymerization followed by a dissolution-precipitation process [39].

3.2. Synthesis of α-Fe\textsubscript{2}O\textsubscript{3}

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3.3. Synthesis of PCN/CNTs/$\alpha$-Fe$_2$O$_3$

A desired amount of PCN/H$_2$SO$_4$ solution (0.5 g/mL) in a 2.1 ratio was mixed with an appropriate amount of CNTs (Sigma-Aldrich). Then, deionized water was added dropwise under stirring and left for 2 h. The precipitate was filtered and washed with copious amounts of water until it was neutral. The solid was re-dispersed into the water, and a calculated amount of FeCl$_3$ 6H$_2$O (Sigma-Aldrich, 94%) was added, followed by adding ethanol and CH$_3$COONa. The rest of the steps were the same as for the synthesis of Fe$_2$O$_3$ (Scheme 1). The amount of $\alpha$-Fe$_2$O$_3$ in the composite was controlled to 1/3 and 1/5 of the weight of PCN, respectively, and the content of CNTs was controlled as 1/5 and 1/10 of the weight of the $\alpha$-Fe$_2$O$_3$ and PCN. The obtained samples were named according to the different ratios. For example, the sample CCF-5 (CF-3) means that in the composite, CNTs are 1/5 the weight of the composite, and Fe$_2$O$_3$ is 1/3 the weight of PCN. The other samples, CCF-10 (CF-3), CCF-5 (CF-5), and CCF-10 (CF-5), were named according to the same rules and were used as control samples.

![Scheme 1](image)

Scheme 1. Schematic diagram of synthetic procedure for PCN/CNTs/$\alpha$-Fe$_2$O$_3$.

3.4. Characterization

Fourier transform infrared spectra (FTIR) were obtained by a Perkin Elmer FTIR spectrometer. The morphology and microstructure of the samples were characterized by SEM (FESEM 7600F, JEOL, Tokyo, Japan) and TEM (2100F, JEOL, Tokyo, Japan). The UV-Vis diffuse reflectance spectra (DRS) were measured with a Lambda 750 UV-Vis spectrophotometer (Perkins-Elmer, Waltham, MA, USA). Solid-state photoluminescence (PL) spectra were obtained using a Shimadzu RF5301 fluorescence spectrophotometer with an excitation wavelength of 350 nm. Brunauer–Emmet–Teller specific surface area and Barrett–Joyner–Halenda pore size distribution data were collected using a JW-BK122W (Beijing, China) surface area analyzer. The crystal structures of the synthesized samples were examined by X-ray powder diffractometer (D8 ADVANCE A25, Bruker, KIT, Karlsruhe, Germany). The XPS-VBs of the samples were obtained by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI, Waltham, MA, USA).

3.5. Photoelectrochemical Measurements

Photoelectrochemical measurements were carried out using an electrochemical potentiostat (CHI 660D, CHI Shanghai, Inc., Shanghai, China) equipped with a three-electrode system. Working electrodes were prepared by depositing sample suspensions (15 mg/mL) on the FTO slides (1 x 4 cm). Ag/AgCl was used as the reference electrode, and Pt wire was used as the counter electrode. A Xenon lamp (300 W, Newport, CA, USA) was used to simulate sunlight irradiation, and Na$_2$SO$_4$ aqueous solution (0.5 M) was used as the electrolyte for the i-t and EIS tests.
3.6. Photocatalytic Degradation of Organic Dyes

Organic dyes of methylene blue (MB) and crystal violet (CV) were selected as the substrate to evaluate the photocatalytic activity of the prepared samples. In a typical procedure, 5 mg of prepared catalyst was dispersed in 25 mL of MB or CV (20 mg/L) dye solutions in a glass tube, which was placed in a water bath to maintain the temperature at 27–30 °C. The dye and catalyst suspensions were stirred continuously in dark conditions for 30 min to reach adsorption–desorption equilibrium before illumination. The reaction was then carried out under a 300 W Xe lamp used as light source, and the suspension was taken out by syringe at equal time intervals. The clear solution separated by centrifuge was used to analyze absorbance under UV-Vis spectroscopy. The concentration of dyes was monitored by the change in absorbance at 664 nm for MB and 590 nm for CV.

3.7. Adsorption Measurements

Amounts of 5 mg of the samples were added to 25 mL of dye solution (20 mg/L) and stirred in a dark, closed reactor for 12 h. Then, the catalysts were removed by centrifugation. The concentration of the dyes was determined by UV-Vis spectra.

4. Conclusions

To summarize, copolymerized PCN was constructed with CNTs and ferric oxide to fabricate PCN/CNTs/α-Fe2O3 all-solid Z-scheme heterojunction composites. Upon optimization of the content ratio between PCN, CNTs, and α-Fe2O3 (10:1:3 by weight), the PCN/CNTs/α-Fe2O3 exhibited superior photocatalytic degradation activity towards both MB and CV, compared with pristine PCN and ferric oxide, which is consistent with the higher photocurrent response and lower electrical resistance. The activity enhancement can be attributed to the extended light absorption, high specific surface area, and enhanced charge separation efficiency within the PCN/CNTs/α-Fe2O3. The Z-scheme mechanism was confirmed by selective spatial deposition. The role of the CNTs was revealed as a “structural and electronic bridge” that created a diversified spatial structure and photoelectron transport channels, thus promoting the adsorption capacity and charge separation efficiency. This work has taken another step forward in the preparation of all-solid Z-scheme heterojunctions and provides valuable experience and fundamentals for fabricating robust PCN-based composite photocatalysts.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/catal14080516/s1, Table S1: The calculated reaction rate constants for all the samples; Table S2: Physical properties of samples; Table S3: Valence band, conduction band, and band gap energies of PCN and α-Fe2O3 samples; Figure S1: UV-Vis absorbance spectra of MB and CV after 30 min dark adsorption and calculated adsorption capacities over the different samples; Figure S2: Time-dependence of the UV-Vis absorption spectra of MB in the presence of different samples under light irradiation; Figure S3: Recycling test and reusability of CCF-10 (CF3) sample using the MB as target substrate.

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