



Article

Highly Enhanced Photoreductive Degradation of Polybromodiphenyl Ethers with g-C₃N₄/TiO₂ under Visible Light Irradiation

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Academic Editors: Hongqi Sun and Zhaohui Wang

Received: 1 February 2017; Accepted: 30 March 2017; Published: date

Abstract: A series of high activity photocatalysts g-C₃N₄-TiO₂ were synthesized by simple one-pot thermal transformation method and characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy, Brunauer–Emmett–Teller (BET) surface area, and ultraviolet–visible diffuse reflectance spectroscopy (UV-Vis-DRS). The g-C₃N₄-TiO₂ samples show highly improved photoreductive capability for the degradation of polybromodiphenyl ethers compared with g-C₃N₄ under visible light irradiation. Among all the hybrids, 0.02-C₃N₄-TiO₂ with 2 wt % g-C₃N₄ loaded shows the highest reaction rate, which is 15 times as high as that in bare g-C₃N₄. The well-matched band gaps in heterojunction g-C₃N₄-TiO₂ not only strengthen the absorption intensity, but also show more effective charge carrier separation, which results in the highly enhanced photoreductive performance under visible light irradiation. The trapping experiments show that holetrapping agents largely affect the reaction rate. The rate of electron accumulation in the conductive band is the rate-determining step in the degradation reaction. A possible photoreductive mechanism has been proposed.

Keywords: g-C₃N₄; TiO₂; photoreductive; polybromodiphenyl ethers; visible light

1. Introduction

Persistent organic pollutants (POPs) are of significant concern because they are bioaccumulative and harmful to human health [1–4]. Photocatalysis is one of the most effective technologies for the remediation of POPs [5]. TiO₂ has attracted much attention in this field for the degradation of POPs due to its excellent photocatalytic capability, high chemical stability, and environmental friendliness [6]. However, TiO₂ is only excited by UV light, and photoinduced hole–electron pairs can be fast recombined. Therefore, many efforts have been done to overcome these disadvantages [7].

Recently, carbon nitride (C₃N₄) with graphite-like structure—being a wide-band-gap semiconductor—has received wide attention in catalytic applications due to its high chemical stability and appealing electronic structure [8]. The optical band gap of g-C₃N₄ is 2.7 eV ($E_{CB} = -1.3$ V, $E_{VB} = 1.4$ V vs. *NHE*, pH = 7; CB: conduction band, VB: valence band, *NHE*: normal hydrogen electrode), which gives it promising performance in photocatalytic activity [9]. For example, g-C₃N₄ was able to split water into hydrogen or oxygen in the presence of an electron donor or acceptor under irradiation [10]. H₂O₂ could be activated by g-C₃N₄ for the oxidation of benzene to phenol [11]. g-C₃N₄ also showed good photocatalytic activities for the oxidation of various organic dyes

under visible light irradiation [12]. Nevertheless, the separation of charge in the excited g-C₃N₄ needs to be improved to enhance the photocatalytic efficiency.

The synthesis of a heterojunction photocatalyst is a feasible way to overcome the disadvantages of TiO₂ and C₃N₄ [13,14]. A heterojunction with proper band gaps can not only superpose the light response of composed semiconductors, but also help the transformation of photogenerated holes and electrons, and finally improve the photocatalytic capability [15]. Several studies have reported that the photocatalyst g-C₃N₄-TiO₂ performed improved photocatalytic activity. For example, g-C₃N₄-TiO₂ prepared by simple grinded could have better performance in the hydrogen evolution [16]. Hu et al. reported that the hybrid photocatalyst of g-C₃N₄-TiO₂ showed enhanced photogenerated charge separation for dye degradation [17]. Therefore, g-C₃N₄-TiO₂ can perform not only visible light response but also higher effective charge separation [18,19]. However, most of the studies have focused on the photocatalytic oxidation of g-C₃N₄-TiO₂, while the photoreductive capability of g-C₃N₄-TiO₂ for the degradation of pollutants has been largely neglected [16].

In this work, we prepared the heterojunction catalyst g-C₃N₄-TiO₂ with simple one-pot thermal transformation. Decabromodiphenyl ether (BDE209) (Figure S1) is a typical persistent organic pollutant and was selected as the target substrate. The photoreductive activity of g-C₃N₄-TiO₂ was performed by the degradation of BDE209. The g-C₃N₄-TiO₂ showed highly enhanced photoreductive capability compared with g-C₃N₄. Trapping experiments were performed to further understand the rate-determining step of the photoreductive reaction and the reaction mechanism. To the best of our knowledge, it is the first time the highly-improved photoreductive ability of g-C₃N₄-TiO₂ in the degradation of polybromodiphenyl ethers PBDEs under visible light irradiation has been researched.

2. Results

2.1. Catalyst Characterization

2.1.1. TEM and SEM

As shown in Figures S2 and 1, the morphology and microstructure of g-C₃N₄ and g-C₃N₄-TiO₂ were characterized by SEM and TEM. The SEM image of the sample shows small roundish particles, which have slightly irregular edges. The particle sizes are 0.2–0.5 μm (Figure 1a). The TEM image displays the inner structure of the catalyst. The TEM image of g-C₃N₄-TiO₂ shows that TiO₂ particles disperse on the surface of g-C₃N₄ with sizes 5–10 nm (Figure 1b). In the TEM image, roundish TiO₂ particles also show the firm connection with the surface of the lamellar g-C₃N₄ to form the heterojunction interface, which contribute to the better transfer of photoelectrons and separation of charge carriers between g-C₃N₄ and TiO₂.

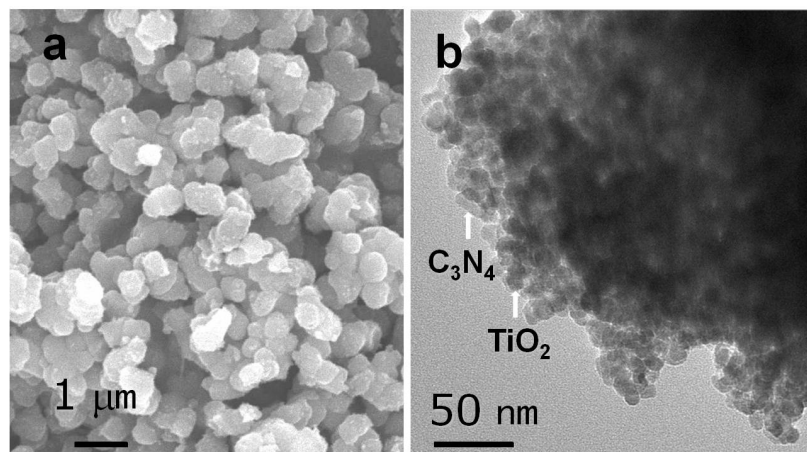


Figure 1. (a) Scanning electron microscopy (SEM) image of 0.02-C₃N₄-TiO₂; (b) transmission electron microscopy (TEM) image of 0.02-C₃N₄-TiO₂.

2.1.2. XRD

Figure 2 shows the X-ray diffraction patterns of X-C₃N₄-TiO₂ and g-C₃N₄. The pattern of the g-C₃N₄ sample has two peaks. The small-angle peak (100) at 12.77 indicates the in-plane structural packing motif. The strongest peak at 27.62 is the characteristic interlayer stacking peak of the aromatic system, indexed as the (002) peak for graphitic materials [20]. The diffraction peaks of TiO₂ exhibit the typical structure of anatase phase. When g-C₃N₄ is combined with TiO₂, all hybrids of g-C₃N₄-TiO₂ show the typical anatase TiO₂ phase [17]. The characteristic peaks of g-C₃N₄ are not observed due to the low content in hybrids and relatively weak diffraction intensity of g-C₃N₄.

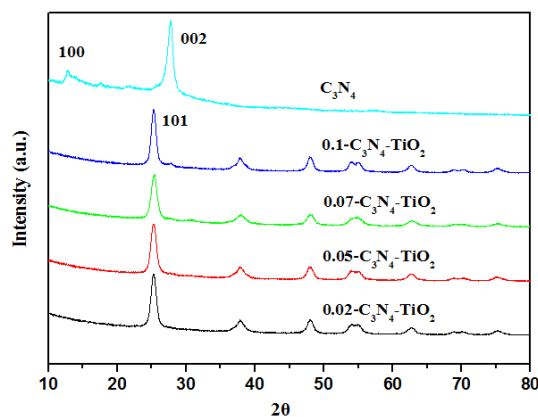


Figure 2. X-ray diffraction (XRD) pattern of g-C₃N₄-TiO₂.

2.1.3. X-ray Photoelectron Spectroscopy (XPS)

XPS measurements demonstrate the oxidation state and surface chemical compositions of 0.02-C₃N₄-TiO₂. As shown in Figure S3, the C1s XPS spectrum shows three main peaks at 284.4 eV, 285.5 eV, and 288.2 eV, corresponding to the adventitious sp² carbon atoms bonded to N inside aromatic units, C-(N)₃ group. The XPS of N1s has three signals at 398.5 eV, 399.5 eV, and 401.2 eV originating from sp² bonded N in the triazine rings, tertiary N in N-(C)₃ and N in the amid group. Ti2p has two peaks corresponding to Ti2p_{3/2} at 458.6 eV and Ti2p_{1/2} at 464.3 eV. O1s shows two peaks at 529.8 eV and 531.4 eV, attributed to the O atom in O-Ti and surface OH, respectively.

2.1.4. UV-Vis Absorption Spectra

The optical properties of g-C₃N₄-TiO₂ samples are investigated by UV-Vis diffuse reflectance spectra. As shown in Figure 3, without modifying the TiO₂ particles, g-C₃N₄ shows broad absorption in the region of 215–600 nm, and the maximum absorbance appears at 370 nm. TiO₂ only shows absorption in the UV region. When g-C₃N₄ is combined with TiO₂, all hybrids of g-C₃N₄-TiO₂ show enhanced absorption in both UV and visible light regions. Obviously, the visible absorption of x-g-C₃N₄-TiO₂ above 400 nm is the contribution of g-C₃N₄, which has a strong and wide absorption band in the visible region. It also implies that x-g-C₃N₄-TiO₂ may have greater photocatalytic activity than g-C₃N₄ and TiO₂. Moreover, slight changes could be observed with increasing TiO₂ content, and among all hybrid samples, 0.02-C₃N₄-TiO₂ showed relatively strong absorption intensity in the visible light region.

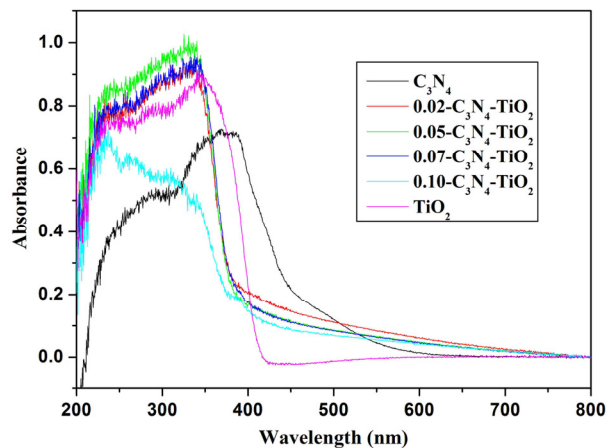


Figure 3. UV-Vis absorption spectra of g-C₃N₄-TiO₂.

2.2. Photocatalytic Reductive Performance Study

2.2.1. Degradation Kinetics

As seen from Figure 4, BDE209 itself shows no degradation under visible light irradiation. This means that BDE209 cannot direct photolysis in this condition. BDE209 also exhibits little degradation in the presence of TiO₂, which has no absorption in visible light. In g-C₃N₄-TiO₂/dark system, BDE209 cannot degrade. This means that the degradation of BDE209 cannot occur without irradiation. In the presence of g-C₃N₄ under visible light irradiation, BDE209 shows slightly degradation. However, rapid degradation of BDE209 is observed with 0.02g-C₃N₄-TiO₂ under visible light irradiation. More than 90% of BDE209 disappeared after 2 h of irradiation. The kinetics are fitted by pseudo-first-order process, giving a rate constant of $0.78 \pm 0.02 \text{ h}^{-1}$ ($t_{1/2} = 0.89 \text{ h}$). Compared with g-C₃N₄ ($0.052 \pm 0.02 \text{ h}^{-1}$), the kinetics rate improves 15-times.

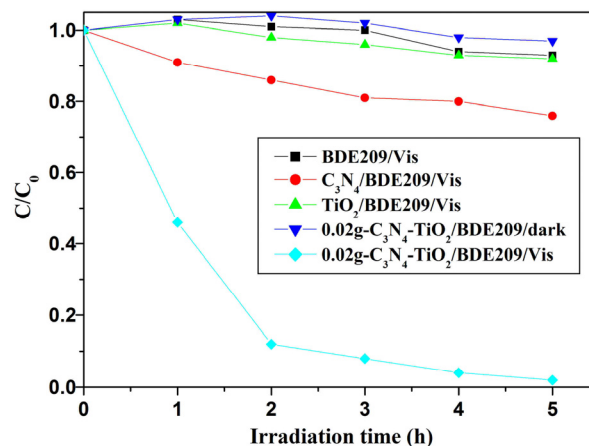


Figure 4. Temporal curves of the degradation of BDE209 under different conditions. BDE209: 1.0×10^{-5} mol/L; 0.02-g-C₃N₄-TiO₂: 1 mg/mL; solvent: CH₃OH; wavelength >420 nm; anoxic condition.

The product analysis by gas chromatography paired with a microcell electron capture detector (GC- μ ECD) shows that the degradation of BDE209 by g-C₃N₄-TiO₂ leads to the formation of its lower brominated congeners in a stepwise way (Figure S4). Before the irradiation, the only dominant GC peak is from BDE209. After 1 h irradiation, nona-BDEs appears as main intermediates. After irradiation of 3 h, the octa-BDEs and hepta-BDEs are measured as the dominant intermediates. Hexa-BDEs and penta-BDEs are observed as main intermediates after 10 h irradiation. Hexa-BDEs and penta-BDEs gradually vanish, and transform to the lower intermediates at further prolonged irradiation to 24 h.

The first debromination step is the formation of nona-BDEs by losing one bromine atom, which provides direct information regarding the debromination pathway of BDE209. There are three nona-BDEs, named BDE206, BDE207, and BDE208, corresponding to *ortho*-, *meta*-, and *para*-debrominated intermediates of BDE209, respectively. As seen from Figure 5, all nona-BDEs are observed, identified to be BDE208, 207, and 206, respectively, according to their well-established GC elution times [3,4,6]. The relatively largest peak areas of nona-BDEs named BDE207 appears, indicating that the *meta* debromination is much easier than those from other positions. This is unlike that in TiO₂ systems [6], in which the predominant degradation product of nona-BDEs is BDE206, but is similar to that in the g-C₃N₄ system [20]. This implies that the debromination patterns of BDE209 by photocatalytic degradation varies in the different systems. In the C₃N₄-TiO₂ system, BDE209 preferentially adsorbs on the surface of g-C₃N₄. Therefore, the debromination pathway is not only affected by the bond dissociation energy of C-Br but also restricted by the space position of BDE209 and photocatalyst, which results in the change of the debromination patterns of BDE209. It also indicates that the reductive debromination of BDE209 occurs on the surface of C₃N₄-TiO₂.

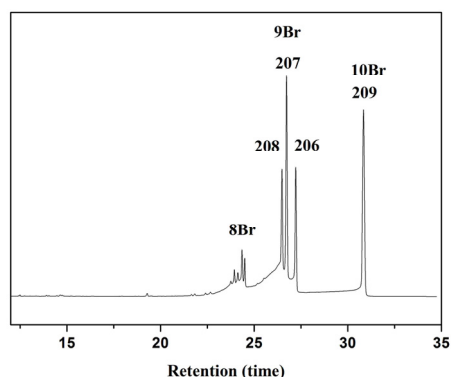


Figure 5. GC- μ ECD (gas chromatography paired with a microcell electron capture detector) chromatograms of degradation products of BDE209 by 0.02-g-C₃N₄-TiO₂ in 2 h irradiation.

2.2.2. The Effects of Loaded Amount, Brunauer–Emmett–Teller (BET) Specific Surface Area, and Absorption Amount

In the solid–liquid two phase catalytic reaction, the active site is on the intersurface of solid and liquid. Therefore, the specific surface area is very important for adsorption of the pollutants, which directly affects photocatalytic efficiency. The specific surface area of g-C₃N₄-TiO₂ hybrids are investigated with N₂ adsorption and desorption isotherms, and estimated by BET method. As shown in Table 1, combined with TiO₂, the specific surface area is largely improved. However, the different loaded amount of g-C₃N₄ shows little effect on the specific surface area of g-C₃N₄-TiO₂, which changed from 112.98 to 120.85 m²/g. In addition, the adsorption experiments matched the value of the specific surface area of the samples well.

Table 1. Brunauer–Emmett–Teller specific surface area (S_{BET} , m²/g), absorption amount, and estimated pseudo-first-order kinetic constant (k) for the degradation of BDE209.

Catalyst	Mass Percentage of C ₃ N ₄ in C ₃ N ₄ -TiO ₂	S_{BET} (m ² /g)	Absorption Amount	Kinetic Constant k (h ^{−1})
g-C ₃ N ₄	0	27.84	0.17	0.05
0.02-g-C ₃ N ₄ -TiO ₂	0.02	120.85	0.27	0.78
0.05-g-C ₃ N ₄ -TiO ₂	0.05	115.16	0.24	0.42
0.07-g-C ₃ N ₄ -TiO ₂	0.07	114.18	0.24	0.63
0.1-g-C ₃ N ₄ -TiO ₂	0.1	112.98	0.22	0.60

Photo-reductive activity of x -C₃N₄-TiO₂ hybrids ($x = 0.02, 0.05, 0.07, 0.1$) was investigated by degradation of BDE209 under visible light irradiation. As shown in Figure 6, all samples of g-C₃N₄-TiO₂ display efficient degradation of BDE209. The photoreductive efficiencies of g-C₃N₄-TiO₂ hybrids can not match with the increase of the loaded amount of g-C₃N₄ from 0.05 to 0.1. 0.02-g-C₃N₄-TiO₂ shows the highest reaction rate among all the g-C₃N₄-TiO₂ hybrids. The degradation rates fit with pseudo-first-order model kinetics. With the loaded mass percentage of g-C₃N₄ changing from 0.05 to 0.1, the reaction rates show a certain degree of decrease compared with 0.02-g-C₃N₄-TiO₂. The optimum loaded amount of C₃N₄ in the hybrids is 2 wt %.

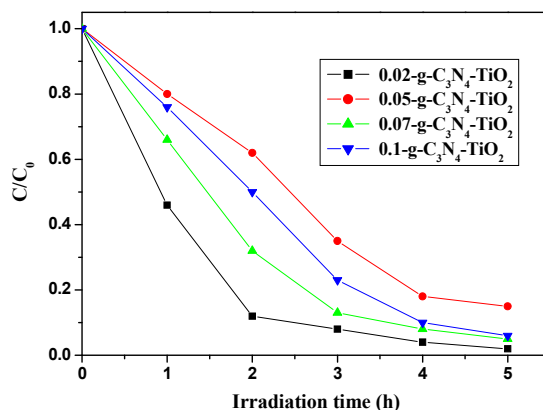


Figure 6. Temporal curves of the photodegradation of BDE209 with $x\text{g-C}_3\text{N}_4\text{-TiO}_2$ ($x = 0.02$ to 0.1) under visible irradiation. BDE209: 1.0×10^{-5} mol/L; $\text{g-C}_3\text{N}_4\text{-TiO}_2$: 1 mg/mL; solvent: CH_3OH ; wavelength >420 nm; anoxic condition.

2.2.3. Photostability of $\text{g-C}_3\text{N}_4\text{-TiO}_2$

Photostability is the key factor for a catalyst in practical application. So, recycling experiments were performed to test the photostability of $\text{g-C}_3\text{N}_4\text{-TiO}_2$. As shown in Figure 7, after four cycles, the photocatalyst still has strong photo-reductive ability for the degradation of BDE209. The reaction rates show no obvious decrease. This implies that $\text{g-C}_3\text{N}_4\text{-TiO}_2$ shows an excellent heterojunction photocatalytic activity. In the heterojunction $\text{g-C}_3\text{N}_4\text{-TiO}_2$, the recombination of electrons and holes are largely inhibited, and the separation of electrons and holes is obviously enhanced. Therefore, $\text{g-C}_3\text{N}_4\text{-TiO}_2$ exhibits not only excellent photoreductive activity, but also good photostability for the degradation of BDE209.

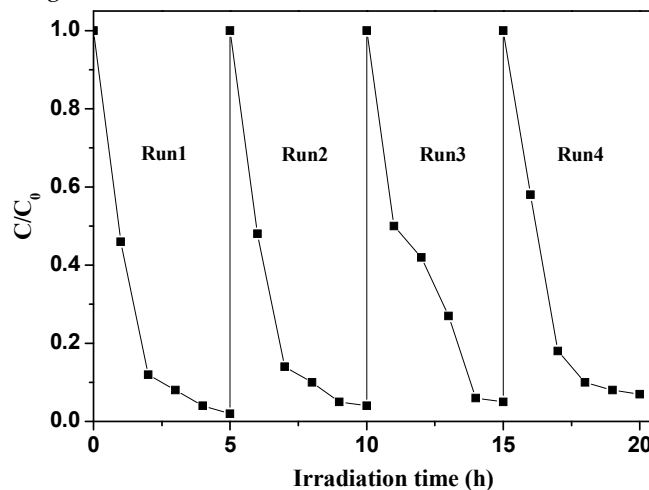


Figure 7. Cycling runs in the degradation of BDE209 with $0.02\text{-g-C}_3\text{N}_4\text{-TiO}_2$ under visible irradiation. BDE209: 1.0×10^{-5} mol/L; $0.02\text{-g-C}_3\text{N}_4\text{-TiO}_2$: 1 mg/mL; solvent: CH_3OH ; wavelength >420 nm; anoxic condition.

2.2.4. The Effect of Trapping Agents

Hole trapping agent experiments are performed to declare the mechanism of the reaction. As seen from Figure 8, the reaction rate is fastest in the presence of isopropyl alcohol, and the slowest rate is using ethanol as a scavenging agent. In the trapping experiment, the degradation rate of BDE209 changes by different trapping agents.

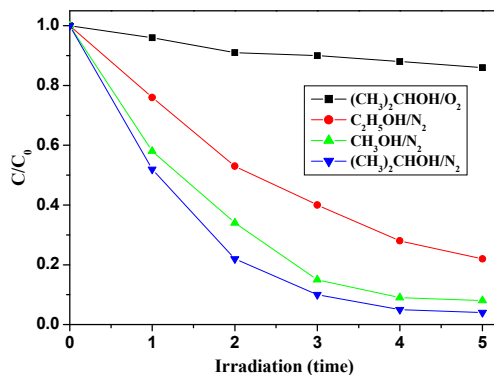


Figure 8. Effect of hole trapping agent on the photoreductive degradation of BDE209 by g-C₃N₄-TiO₂ under visible light irradiation. BDE209: 1.0×10^{-5} mol/L; 0.02-g-C₃N₄-TiO₂: 1 mg/1 mL; wavelength >420 nm; solvent: CH₃CN; trapping agents: isopropanol, methanol, ethanol 0.1 mL.

3. Discussion

The samples of g-C₃N₄-TiO₂ show highly improved photoreductive capability for the degradation of polybromodiphenyl ethers compared with g-C₃N₄ under visible light irradiation. This implies that the well-matched band gap in the heterojunction g-C₃N₄-TiO₂ greatly improves the photoreductive efficiency. 0.02-g-C₃N₄-TiO₂ shows the highest reaction rate among all the g-C₃N₄-TiO₂ hybrids. This indicates that a small amount of C₃N₄ (mass percentage is wt %) in C₃N₄-TiO₂ hybrids may highly improve the photocatalytic activity; on the contrary, a greater loaded amount of C₃N₄ will inhibit the degradation of BDE209.

The hole trapping agent experiments have been performed to declare the rate-determining step and the mechanism of the reaction. During the photocatalytic reaction, an electron is excited from VB into CB of C₃N₄ under visible light irradiation, which results in the generation of VB hole and CB electron. The VB hole is scavenged by hole trapping agent, and the electron is accumulated in CB of C₃N₄. Under the anaerobic photocatalytic conditions, the possible reductive species that are responsible for the reduction of BDE209 are CB electrons. In the hole trapping agent experiment, the reaction rates are in the order of *i*-PrOH > MeOH > EtOH, which is in accordance with the order of the oxidation ability of alcohols with the VB hole via dehydrogenation. The oxidation of alcohols by the VB hole directly results in the accumulation of the electron in CB. This indicates that the key factor of the degradation reaction is the rate of electron accumulation in CB, which is the rate-determining step in the photoreductive degradation of BDE209 by g-C₃N₄-TiO₂. In order to prove the key role of CB electrons in the photocatalytic degradation of BDE209, another control experiment has been performed. This control experiment is conducted under the same conditions with isopropyl alcohol as trapping agent, but O₂ is purged into the reaction solution. Under visible light irradiation, the degradation of BDE209 is largely depressed in the O₂-purged condition. O₂ can react quickly with the CB electron, which results in the inhibition of the degradation of BDE209. This result again proves that it is the CB electron that makes BDE209 reductively degrade and that the rate of accumulation of CB electrons is the rate-determining step. Based on the above experiments, a possible reaction mechanism has been proposed with the degradation of BDE209 in CH₃OH solution by C₃N₄-TiO₂ (Figure 9). Under visible light irradiation, C₃N₄ is excited and forms VB hole and CB electron. When the VB holes are scavenged by trapping agents, the electrons will accumulate in CB. In the heterojunction g-C₃N₄-TiO₂, the CB of C₃N₄ (−1.30 eV) is more negative than that of TiO₂ (−0.25 eV). So, the electron in CB of C₃N₄ prefers to transfer to the CB of TiO₂ via the interface of heterojunction g-C₃N₄-TiO₂. BDE209 receives the electrons in CB of TiO₂ and forms C₁₀Br₉O• and Br[−]. The C₁₀Br₉O• radical abstracts a hydrogen atom from methanol (hole trapping agent) and yields lower bromo congeners C₁₀Br₉OH, and CH₃OH transforms into HCHO by losing a hydrogen atom.

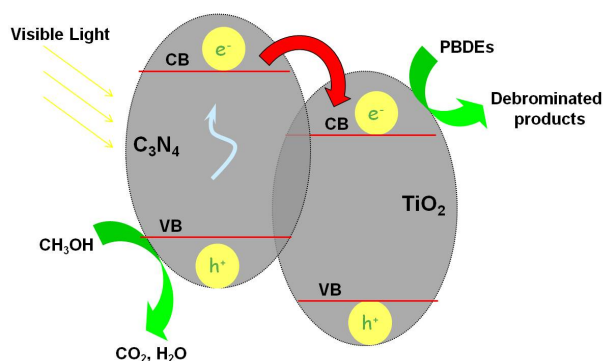


Figure 9. Proposed mechanism of the degradation of PBDEs with g-C₃N₄-TiO₂ in CH₃OH solution under visible irradiation. CB: conduction band; VB: valence band.

4. Materials and Methods

4.1. Materials

BDE209 was purchased from Sigma-Aldrich (St. Louis, MO, USA). BDE203, BDE204, and a standard solution of PBDEs (EO5103) were purchased from Cambridge Isotope Laboratories (CIL, Andover, MA, USA). Tetra-n-butyl titanate, melamine, isopropanol, methanol, ethanol, and acetonitrile were analytical reagents (Chemical Co., Shanghai, China). They were used without further purification. Deionized and doubly distilled water was used throughout the study.

4.2. Methods

4.2.1. Synthesis of g-C₃N₄-TiO₂

A certain amount of melamine was added into 100 mL isopropanol solution and stirred at ambient temperature for 2 h prior to addition of 4 mL Ti(OBu)₄. After stirred 3 h, 40 mL deionized water was added dropwise into the suspension. The mixture was put into a drying oven for 24 h at 60 °C and powder was obtained, which was collected and annealed at 500 °C for 4 h to get the g-C₃N₄-TiO₂. By adjusting the mass percentage ratio of g-C₃N₄ to TiO₂, different amounts of g-C₃N₄ were combined with TiO₂, obtained x-g-C₃N₄-TiO₂. ($x = 0, 0.02, 0.05, 0.07, 0.1$; x refers to the mass percentage of g-C₃N₄ in g-C₃N₄-TiO₂).

4.2.2. Characterization

The morphology of the catalyst samples were determined by scanning electron microscope (SEM) on a Hitachi S4300 and transmission electron microscope (TEM) (Philips CM200 FEG TEM at 200 kV, Tokyo, Japan). The X-ray diffraction patterns of the catalyst powders were performed on a Rigaku D/Max-2500 diffractometer with the Cu K α radiation (1.5406 Å). The X-ray photoelectron spectroscopy (XPS) measurements were carried using a ESCA lab 220i-XL spectrometer with Al K α (1486.6 eV) X-ray source and a charge neutralizer. The specific surface areas of different C₃N₄-TiO₂ samples were determined by Brunauer–Emmett–Teller (BET) method. BDE209 was quantified with a SHIMADZU HPLC system (LC-20AT pump and UV/VIS SPD-20A detector, Kyoto, Japan) with a DIKMA Platisil ODS C-18 column (250 × 4.6 mm, 5 µm film thickness). The mobile phase was 98% acetonitrile and 2% water at 1 mL/min, and the detector wavelength was set at 240 nm. The quantification of BDE209 was performed by a calibration curve with a BDE-209 standard. Products were detected by GC-µECD analysis with GC (Agilent 7890A, Santa Clara, CA, USA) equipped with an electron capture detector (ECD) (Agilent Technologies Co., Santa Clara, CA, USA), a programmable pressure on-column injection port, and a DB-5 capillary column (30 m × 50 µm, i.d. × 0.1 µm film thickness). Splitless 10 µL injection was performed manually at 300 °C. The carrier gas was helium at a constant flow rate of 1.0 mL/min. The oven temperature was kept at 100 °C for 2 min, increased at 15 °C/min to 230 °C, then increased at 5 °C/min to 270 °C, and finally increased at

10 °C/min to 320 °C for 10 min. The standard samples of BDE203, BDE204, and PBDEs (EO5113) were used to identify the degradation products. At given times, 1 mL aliquots were collected and centrifuged, and filtered to remove the solid catalyst particles before analysis with HPLC and GC- μ ECD.

4.2.3. Experimental Setup

BDE209 stock solution (1×10^{-3} mol/L) in tetrahydrofuran was diluted with methanol (1×10^{-5} mol/L). Ten milligrams of g-C₃N₄-TiO₂ was added to 10 mL BDE209 solution in a Pyrex vessel. Reaction solution was magnetically stirred during the irradiation. The Pyrex vessel was purged with argon for 15 min to remove O₂ and protected under argon atmosphere during the irradiation. A PLS-SXE300 Xe lamp (Beijing Trusttech Co. Ltd., Beijing, China) was used as the light source. A cutoff filter ($\lambda > 420$ nm) was placed to ensure visible light irradiation. To investigate the effect of trapping agent on the reaction kinetics, a given amount of isopropanol, ethanol, and methanol were added into BDE209 acetonitrile solution under identical conditions.

5. Conclusions

The photocatalysts of g-C₃N₄-TiO₂ synthesized by simple one-pot thermal transformation method show highly improved photoreductive activity for the degradation of BDE209 under visible light irradiation. Among all the hybrids, 0.02-C₃N₄-TiO₂ with 2 wt % TiO₂ loaded showed the highest reaction rate—15 times higher than bare g-C₃N₄. The heterojunction of g-C₃N₄-TiO₂ with well-matched band gaps strengthened the absorption intensity of TiO₂ and g-C₃N₄, and contributed more effective charge carrier separation. Therefore, the heterojunction of g-C₃N₄-TiO₂ showed highly enhanced photoreductive performance. The trapping experiment indicated that the rate of electron accumulation in the conductive band is the rate-determining step in the degradation reaction.

Supplementary Materials: The following are available online at www.mdpi.com/2079-4991/7/3/76/s1.

Acknowledgments: The generous financial was supported by the National Science Foundation of China (Nos. 21107073 and 21477080).

Author Contributions: Weidong Ye and Yingying Shao did the experiments and data analysis. Xuefeng Hu and Chunlin Liu did data analysis. Chunyan Sun provided the original ideas, wrote this paper and revision of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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