Photocatalysis

Rapid, Photocatalytic, and Deep Debromination of Polybrominated Diphenyl Ethers on Pd–TiO₂: Intermediates and Pathways

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Abstract: Titanium dioxide with surface-loaded palladium (Pd–TiO₂) was able to easily remove all ten bromine atoms from decabromodiphenyl ether (BDE209) within 1 h under the irradiation of sunlight or an artificial light source. By contrast, fewer than three bromine atoms were eliminated on the pristine TiO₂ even with prolonged irradiation (5 h). During the photocatalytic debromination, moreover, the formed BDE intermediates exhibited a significant difference between the Pd–TiO₂ and pristine TiO₂ systems, and much less position selectivity for the debromination on Pd–TiO₂

was observed than that on the pristine TiO_2 surface. For another polybrominated diphenyl ether (BDE15), pristine TiO_2 was incapable of its photocatalytic reduction, whereas the loading of Pd enabled its debromination to diphenyl ether within 20 min. In addition, an evident induction period appeared in the photocatalytic debromination of BDE15 on Pd–TiO₂. The experiments imply that the Pd-cocatalyzed effect changes significantly the photocatalytic reductive debromination pathways.

Introduction

Polybrominated diphenyl ethers (PBDEs) are widely applied in electronics, petroleum products, and textiles because of their stability and efficient flame-retardant property. These PBDEs can migrate from the products and release to the environment continuously. As a result, congeners of PBDEs have been detected globally in food, humans, wildlife, and environmental media such as sediments, sewage sludge, and air,^[1-6] and the detected concentrations appear to increase rapidly over time.^[7,8] Recent studies on animals showed that some congeners of PBDEs can disrupt the endocrine system, threaten reproductive health, and impair the development of the immune system in animal bodies.^[9,10]

The penta-, octa-, and deca-BDE products are the common commercially available PBDEs, among which deca-BDE (BDE209), the fully brominated congener, is in greatest demand. In environmental media and biological systems, the most frequently detected PBDEs are the congeners with moderate bromination, such as tri-, tetra-, penta-, and hexa-BDEs,

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whereas the most-used deca-BDE has been detected with much less frequency. Although these moderately brominated congeners, as important components of historically used flame retardants with penta-BDE formulations, can be directly released into the environment from the products, the most important reason for the accumulation is their resistance to degradation. In nature, UV-induced hydrodebromination has been identified as the major abiotic transformation pathway of highly brominated PBDEs.[11-16] Previous reports showed that the degradation of PBDEs by UV light was rather ineffective to the low-brominated diphenyl ethers, which led to the accumulation of hexa-, penta-, and tetra-BDEs.^[11,12] The biotic reductive debromination by microbes or fish, which represents another transformation pathway of PBDEs in the environment, still fails to completely transform BDE209 to nonbrominated compounds, even at prolonged incubation periods (typically several months).^[17-19] Accordingly, the accumulation of these moderately brominated congeners in nature may result from the debromination of higher-brominated congeners, but they themselves are more recalcitrant to further debromination. To make matters worse, these moderately brominated PBDEs (e.g., congeners BDE47, 99, and 100) are known to be the most toxic and bioaccumulative congeners.^[20,21] Their existence in the environment would cause a more serious risk to human health.

The general resistance to degradation and the potential toxicity of PBDEs also triggered substantial investigations on the development of efficient methods and techniques to properly treat this type of compound. Because PBDEs are difficult to oxidatively degrade, most of their decontamination methods are based on reductive debromination. Although these reduction

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technologies are effective for the decomposition of highly brominated PBDEs such as BDE209, the debromination reaction becomes rather difficult for the low-brominated intermediates. For example, the reductive debromination of PBDEs by widely studied zerovalent iron (ZVI) particles was ineffective in reducing the low-brominated congeners of PBDEs, which led to the accumulation of a lot of PBDEs with three to six bromides in the systems at the end of reaction (weeks to months).^[22,23] For these reasons, it is urgent to develop effective remediation technologies to achieve the deep debromination of the PBDEs.

In our previous study, we reported that TiO_2 -mediated photocatalysis can be used to achieve rapid reductive debromination of BDE209, in which nearly all the original BDE209 could be degraded within 8 min of UV irradiation. However, this system still suffered from the problem of ineffectiveness for the low-brominated PBDEs. After prolonged irradiation (24 h), the BDE209 was observed to be reduced only to hepta- and hexa-BDEs, with a small amount of penta- and tetra-BDEs.^[14]

Herein, we report that BDE209 (10 μ M) can be debrominated rapidly and completely by surface-palladized TiO₂ (Pd–TiO₂) photocatalyst (0.2 g L⁻¹) within 1 h under UV irradiation. In addition, the low-debrominated PBDE (BDE15), which is resistant to photocatalytic debromination on the pristine TiO₂, also undergoes a rapid reaction in the Pd–TiO₂ system. By a detailed comparison of the photocatalytic degradation kinetics of PBDEs and the reaction intermediates with those in the pristine TiO₂ system, the mechanism of photocatalytic debromination of PBDEs on Pd–TiO₂ is further discussed. The present study provides an efficient method for the rapid full debromination of PBDEs and an insightful understanding of the TiO₂ or Pd–TiO₂ photocatalyzed debromination reaction mechanism, which may extend to other photocatalytic dehalogenation reactions of halogenated pollutants.

Results and Discussion

Catalyst characterization

After loading of palladium, the color of TiO_2 turned from milky white to gray, and Pd– TiO_2 exhibited a strong absorption in the visible-light region (Figure S1 in the Supporting Information) accordingly, which suggested that Pd should be in its metallic state. Figure 1 a and b show the TEM images of Pd– TiO_2 (2 wt% Pd) and the pristine TiO_2 , respectively. It was found that, in comparison with the clean features of the TEM image of pristine TiO_2 (Figure 1 b), the TEM image of the asprepared Pd– TiO_2 catalyst was clearly covered by dispersed spots (Figure 1 a). As indicated by high-resolution TEM (HRTEM, Figure 1 c), these spots had a lattice spacing of 0.19 nm, corresponding to the (200) facet of metallic Pd and confirming that these spots were well-defined palladium particles. The HRTEM image also showed that the palladium particles have a diameter of about 7 nm.

Furthermore, the existence of palladium particles was also confirmed by X-ray photoelectron spectroscopy (XPS; Figure 1 d and Figure S2 in the Supporting Information). The Pd 3d spectrum in XPS shows two peaks at 334.4 and 349.5 eV





Figure 1. TEM images of a) Pd–TiO₂ (2 wt % Pd) and b) TiO₂ particles; c) HRTEM image of Pd–TiO₂ particles; d) X-ray photoelectron spectrum of the prepared Pd–TiO₂ nanoparticles at the Pd 3d region. CPS = counts per second.

from Pd 3d_{5/2} and Pd 3d_{3/2}, respectively, which are consistent with the binding energy of metallic Pd^{0.[24,25]} As shown in Figure S3 in the Supporting Information, besides the diffraction peaks of anatase and rutile phases, the Pd(111) and Pd(200) diffraction peaks with their respective $2\theta = 40.2$ and 46.8° were clearly observed (JCPDS 87-0638).^[26-28] An inductively coupled plasma–atomic emission spectroscopy measurement indicates that the actual loading of palladium on TiO₂ is 1.37 wt%, which is less than the nominal content (2 wt%), probably because of its loss during the loading process.

Reductive debromination of BDE209 on Pd-TiO₂

A mercury lamp was chosen as the light source. To eliminate the direct photolysis of BDE209, the irradiation below the wavelength of 360 nm was filtered off. Figure 2 shows the temporal concentration changes (c/c_0) of BDE209 under different conditions. Although, as reported in our previous study,^[14] BDE209 undergoes efficient degradation in anoxic methanol suspensions of TiO₂ under UV irradiation (Figure 2, curve c), its degradation was much more rapid on the Pd-TiO₂ surface (Figure 2, curve d). BDE209 disappeared completely after only 4 min of irradiation on the Pd–TiO2, whereas only about 40 %of BDE209 was degraded in the pristine TiO₂ system at the same irradiation time, thus indicating a much superior reactivity of the Pd-TiO₂ toward the debromination of PBDE. It is known that the supported Pd particles can catalytically activate donors of hydrogen/electron (such as H₂) to reduce many halogenated organic compounds.^[29,30] To exclude the possibility that the enhancing effect of Pd-TiO₂ is caused by such thermal catalytic reactions, the concentration change of BDE209 was



Figure 2. Temporal curves of the photocatalytic degradation of BDE209 in 25 mL methanol solution under different conditions. TiO₂: in a suspension of pristine TiO₂; Pd–TiO₂: in a suspension of surface-palladized TiO₂; UV: under irradiation at wavelength > 360 nm; Ar: purged with argon; air: air-saturated; BDE209: 10 μ mol L⁻¹; photocatalysts: 0.2 g L⁻¹.

examined by keeping the BDE209/Pd–TiO₂ suspensions in the dark. No degradation of BDE209 in this control experiment (Figure 2, curve a) indicates that the enhancing effect of Pd is not attributable to the Pd-catalyzed thermal reaction between BDE209 and methanol. In another control experiment, the photocatalytic reaction was performed in an air-saturated Pd–TiO₂ suspension under UV irradiation. The degradation of BDE209

was also negligible (Figure 2, curve b). This result implies that, compared to O_2 , BDE209 is less competitive for the photogenerated conduction band electron (e_{cb} ⁻), despite the catalytic properties of Pd for the reduction of BDE209. It should be pointed out that the ineffectiveness of debromination under air-saturated conditions may limit the practical application of Pd–TiO₂ in many environmental systems. Nevertheless, besides its fundamental interest, photocatalytic debromination on Pd–TiO₂ can be used to treat wastewater with a high concentration of PBDEs before its discharge.

The intermediates during the degradation of BDE209 in TiO₂ and Pd–TiO₂ systems were analyzed by gas chromatography with micro electron capture detection (GC- μ ECD). As shown in Figure 3, in the pristine TiO₂ system the nona-BDE congeners were observed as the dominant degradation intermediates of BDE209 (with minor octa-BDEs) after irradiation for 10 min. Further irradiation led to the gradual decrease of the nona-BDEs, and concomitantly the accumulation of octa-BDEs. After 2 h, octa-BDEs became the only dominant products. However, further transformation of octa-BDEs was rather slow. After up to 5 h of irradiation, very few hepta-BDEs were observed (Figure 3 a and c), which is in line with the general trend that the less brominated BDEs are much more resistant to further reductive debromination than BDE209. In contrast, in the BDE209/Pd–TiO₂ suspension, nona-, octa-, and hepta-BDEs



Figure 3. GC- μ ECD chromatograms and relative changes in distribution of photodegradation products of BDE209 in a, c) 0.2 g L⁻¹ TiO₂ and b, d) 0.2 g L⁻¹ Pd-TiO₂ suspensions at different irradiation times. For comparison, the chromatogram of the standard sample of PBDEs (EO5113) under identical conditions is also given in panels (a) and (b) (bottom curves).

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were all detected in considerable amounts within only 2 min of irradiation. From 2Br to 9Br, BDEs with the dominance of 5Br to 8Br congeners were observed after 4 min, and further irradiation shifted the main intermediates to the 2Br–4Br BDEs. After irradiation for 1 h, no brominated intermediates were detected in the gas chromatogram (Figure 3 b and d), which indicated the full debromination of PBDEs. Meanwhile, a measurement of Br⁻ concentration by ion chromatography (Figure S4 in the Supporting Information) showed that the bromine atoms in BDE209 (100 μ M) were released nearly stoichiometrically in the form of inorganic Br⁻ at the end of the reaction in the Pd–TiO₂ system after irradiation for 60 min.

To detect intermediates other than PBDEs, the supernatants at a given irradiation time were concentrated to 1/20 of the original volume by freeze-drying, and analyzed by HPLC. More than a dozen non-PBDE intermediates were observed during the photocatalytic reactions in the Pd-TiO₂ system (Figure S5a in the Supporting Information). The fully debrominated product diphenyl ether (DE) was detected as the main product at the late stage of irradiation (Figure S5a in the Supporting Information). After irradiation for 60 min, only 15.7% of the DE yield relative to BDE209 was monitored. By comparing with the standard samples, another two non-PBDE intermediates were also identified to be 2,4-dibromophenol and pentabromophenol (PBP). These phenolic intermediates originating from BDE-209 are derived from the cleavage of the C-O-C ester bond, probably due to the Pd-catalyzed hydrogenation of the oxygen. In addition, PBP was observed as a main intermediate at an early stage (10 min) but disappeared with further irradiation. These results indicate that the cleavage of the ester bond begins to occur at an early irradiation time and the bromophenols can be further debrominated on the Pd-TiO₂ surface. On the pristine TiO₂ surface, however, few intermediates were detected at the same HPLC region during the whole irradiation time up to 300 min (Figure S5b in the Supporting Information), thus indicating that the cleavage of the ester bond of PBDEs does not occur on the pristine surface.

Practically, natural solar light is much more desirable for irradiation than an artificial light source. Hence, the photocatalytic debromination of BDE209 was also examined under the irradiation of outdoor sunlight. It was observed that, under sunlight, the surface palladization of TiO₂ exhibited similar effects on the degradation rates and intermediate distribution to those under the artificial light source (Figure S6 in the Supporting Information). In the Pd-loaded system, BDE209 was almost degraded after sunlight irradiation for 30 min, and 5Br- to 8Br-BDEs were all detected as primary intermediates. Sunlight exposure for 1 h transformed the BDE209 to its congeners with fewer than 3Br. However, the octa-BDEs were still the dominant intermediates in the pristine TiO₂ systems even with sunlight exposure for 5 h. We also noted that the degradation rate and emergence of intermediates under sunlight irradiation were somewhat slower than that in the artificial mercury lamp cases. At 365 nm wavelength, the mercury lamp has a constant light intensity of about 130 $\mu W\,cm^{-2}$, whereas the intensity of sunlight changes against time, with the maximum about 92 μ W cm⁻² at noon (12:00) (Figure S7 in the Supporting Information). This difference in light intensity can explain the different reduction rate of BDE209 under artificial mercury lamp and sunlight irradiation.

The bioaccumulation and toxicity of PBDEs were known to depend greatly on both the number of bromine atoms and their substituted positions. It is therefore necessary to identify the intermediates and the products of BDE209 in a more detailed manner during its photocatalytic degradation. During the debromination of BDE209, the loss of the first bromine atom may lead to three nona-BDE congeners (BDE206, BDE207, and BDE208, corresponding to removing one bromine atom from the *ortho*, *meta*, and *para* positions of BDE209, respectively). In the present study, all three nona-BDE congeners were detected in considerable amounts at the beginning of irradiation in both the TiO₂ and Pd–TiO₂ systems. The relative distributions (ratios of GC peak areas) of these three nona-BDEs remained quite stable along with the reaction time in each system (Figure 4, Figure S8 in the Supporting Informa-



Figure 4. Comparison of the abundance of the nona- (a) and octa-BDE (b) intermediates during the photocatalytic debromination of BDE209 on the pristine and the palladized TiO₂.

tion), but were quite different between the two systems. In the pristine TiO₂ system, the relative peak areas were in the order of BDE206 > BDE207 > BDE208, indicative of the preference for *ortho* debromination. However, the peak area of BDE207 was larger than those of BDE206 and BDE208 in the Pd–TiO₂ dispersions, which indicated that the *meta*-Br is more sensitive to Pd-cocatalyzed debromination. The sensitivity of the *meta*-Br was also observed in the PBDE reduction by nZVI.^[31]

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In both the pristine and palladized TiO₂ catalytic systems, all three nona-BDE intermediates were found to further undergo reductive debromination, which was concomitant with the dominant accumulation of the octa-BDEs (Figure 3). There are 12 potential congeners for the octa-BDEs. Because not all of these octa-BDE standards are available, some intermediates had to be assigned according to the relative retention times from the literature.^[32] As shown in Figure S9 in the Supporting Information, in the pristine TiO₂ systems, seven peaks of octa-BDEs were observed after 10 min of irradiation. With well-isolated GC peaks, the congeners of BDE195 (2,3,4,4',5,5',6,6'-BDE), BDE194 (3,3',4,4',5,5',6,6'-BDE), BDE196 (2,3',4,4',5,5',6,6'-BDE), BDE197 (2,2',4,4',5,5',6,6'-BDE), BDE204 (2,2',3,4,4',5,6,6'-BDE), and BDE201 (2,2',3,4',5,5',6,6'-BDE) were confidently identified. Two congeners of BDE198 (2,3,3',4,5,5',6,6'-BDE) and BDE199 (2,3,3',4',5,5',6,6'-BDE) with retention time at 24.44 min, which were generated from the debromination of ortho- and meta-Br from one ring and from two rings, respectively, were actually inseparable under GC conditions.[32] Hence, at most eight congeners of octa-BDEs might be detected throughout the photoreaction on pristine TiO2. Further irradiation for 60 min led to the disappearance of BDE195, which indicated that it can be further debrominated, whereas another six peaks remained and their relative intensities did not change much during all the testing time (300 min). A common characteristic for the detected 8Br products, except BDE204, in the pristine TiO₂ system is that the two bromine atoms are removed from the different benzene rings of BDE209. To satisfy this rule, it is plausible that the BDE199, formed by the loss of two Br atoms of BDE209 from different rings, should be dominant in the peak at 24.44 min. On the Pd–TiO₂, however, many more peaks in the octa-BDE region were detected. The most remarkable difference is the appearance of a strong peak with retention time of 24.51 min, which is absent in the pristine systems. This peak was assigned to BDE200 TiO₂ (2,3,4,4',5,5',6,6'-BDE) and/or BDE203 (2,3,3',4,4',5,6,6'-BDE), which are inseparable under the GC conditions. It is notable that these two congeners are formed by debromination of two Br atoms on the same aromatic ring of BDE209. Two minor intermediates with retention times of 23.62 and 25.04 min were also observed on Pd-TiO₂, and assigned to BDE202 (2,2',3,3',5,5',6,6'-BDE) and BDE205 (2,3,3',4,4',5,5',6-BDE). Thus, all the 12 congeners of octa-BDEs during the BDE209 reduction on Pd-TiO₂ can be detected, which indicates that the bromides at all the positions of PBDEs could be removed. However, the formation of only partial 8Br intermediates (seven of 12) on the pristine TiO₂ means that the debromination reaction is difficult for the Br atom in some positions of PBDEs. In this sense, the photocatalytic debromination reaction is less selective on Pd-TiO₂ than on the pristine TiO₂ surface. Evidently, the lack of position selectivity on the Pd–TiO₂ is attributable to the cocatalytic effect of Pd, which makes the cleavage of the C-Br bond at every position of the PBDEs occur at comparable rates, in agreement with the rapid debromination of low PBDEs on Pd-TiO₂ (see below). Moreover, on the Pd–TiO₂, the octa-BDEs formed by loss of one or both the meta-Br atoms (seven in total, i.e., BDE195, 196, 197, 200, 201, 203, and 204) generally appeared as main intermediates, whereas those in which all the *meta*-Br are preserved (five in total, i.e., BDE194, 198, 199, 202, and 205,) were always detected in minor amounts (Figure 4b). This is consistent with the observation in Figure 4a that the *meta*-Br is preferential to leave on Pd–TiO₂.

The further debromination of the octa-BDE intermediates on the pristine TiO_2 surface was rather slow. Only a small amount of 7Br intermediates appeared after irradiation for 5 h. In the Pd–TiO₂ system, in contrast, plenty of intermediates with fewer than 8Br were detected. However, only a few of them were identified by EO5113 standard solution (with 39 known PBDE congeners), including BDE183, 154,138, 116, and 33/28 (Figure 5). Most of the main intermediates were not among the 39 congeners of EO5113. Significantly, BDE47, which is the



Figure 5. Formation of the photodegradation intermediates of BDE209 in Pd-TiO₂ dispersions at different irradiation times. The chromatogram of the standard sample of PBDEs (EO5113) is displayed in the top panel for comparison. The corresponding peaks of the solid lines are assigned to BDE33, BDE28, BDE47, BDE116, BDE154, and BDE183, respectively, but the peaks on the dotted lines are not identified.

most commonly detected PBDE in the environment and in samples collected from organisms,^[33,34] was hardly detected throughout the whole debromination process.

The accumulation of octa-BDEs on pristine TiO₂ during the photocatalytic degradation of BDE209 demonstrates its ineffectiveness on the low-brominated PBDEs. The remarkable characteristic of the photocatalytic reductive debromination on the Pd-TiO₂ system is the emergence of the deep-debrominated congeners even at the very early stage of the reaction, which implies that the Pd-TiO₂ is able to efficiently debrominate the low-bromo DEs. This assertion is in agreement with the observation in the ZVI-Pd system in which the less brominated BDEs exhibited a more significant enhancement in the reduction rates by palladization.[35] To further support this perspective, the photocatalytic reduction of a lower-bromo DE, 4,4'-dibromodiphenyl ether (BDE15), was examined. As shown in Figure 6, the photocatalytic reduction reaction for BDE15 was not detected under UV irradiation on the pristine TiO₂. However, in the Pd-TiO₂ photocatalytic system, BDE15 was degraded quickly within 20 min of irradiation, and concomitantly the 4bromodiphenyl ether intermediate was formed. Further irradiation resulted in the disappearance of 4-bromodiphenyl ether and the accumulation of diphenyl ether. The final yield of di-

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Figure 6. Temporal curves of the photodegradation of BDE15 and the formation of 4-dibromodiphenyl ethers (BDE3) and diphenyl ethers in 25 mL solution under different conditions. BDE15: 10 μ mol L⁻¹; UV: under irradiation of wavelength > 360 nm; Ar: purged with argon; air: air-saturated; Pd–TiO₂, TiO₂: 0.2 g L⁻¹.

phenyl ether was about 60% of the parent BDE15. Intriguingly, unlike the reaction of BDE209 on Pd–TiO₂, in which the debromination of the substrate decreased rapidly at the early stages of the irradiation (Figure 2), the photocatalytic reduction of BDE15 exhibited an evident induction period of 10 min. In this induction period, the degradation of BDE15 was quite slow, and after that the reaction was markedly accelerated (Figure 6).

The presence of an induction period may have much mechanistic implication for the Pd-cocatalyzed debromination of BDE15 to a large extent. In the earlier studies on the noncatalytic debromination of PBDEs, a good correlation between the reduction rates and the heat of formation ($H_{\rm fr}$, which reflects the thermodynamic chemical stability) and the energy level for the lowest unoccupied molecular orbital (E_{LUMO} , which is directly related to the electron affinity) of the PBDEs was usually observed.^[22,35,36] In the present study, the rapid reduction of BDE209 but the ineffective reduction of low-brominated BDEs on the pristine TiO₂ is evidently attributable to their different chemical stabilities and electron affinities, since BDE209 has a much lower stability ($H_f = 414.2 \text{ kJmol}^{-1}$) and much higher electron affinity ($E_{LUMO} = -1.343 \text{ eV}$) than those of BDE15 ($H_f =$ 139.8 kJ mol⁻¹ and $E_{LUMO} = -0.403 \text{ eV}$.^[37] In addition, the observation that most of the 8Br products were formed by debromination from different benzene rings of BDE209 (Figure 4b) on pristine TiO₂ suggests that, once one Br atom is removed from one aromatic ring, the second debromination reaction becomes difficult on this ring. Rather, the second Br atom prefers to leave from the untouched rings with five Br atoms. This can rationalize the dominant accumulation of 8Br congeners, and also implies that the photocatalytic debromination reaction on pristine TiO₂ might proceed by an electron transfer followed by C-Br cleavage, as proposed in our earlier study.^[14]

Under the photocatalytic conditions in the presence of an electron donor (methanol in this study), electrons can accumulate in TiO_2 particles if they cannot be efficiently removed by the electron acceptor (PBDEs). The accumulation of electrons in the conduction band would increase the Fermi level, and consequently enhance the reduction ability of TiO_2 . After loading of the noble metal with a high work function such as Pd

on the TiO₂ surface, the photogenerated conduction-band electron flows from the semiconductor to the Pd particle, which would lead to the formation of a Schottky junction at the metal/semiconductor interface. The electron transfer will continue until the Fermi levels of metal and semiconductor are aligned. The enhancement of BDE209 debromination by surface palladization suggests that the e_{cb}^{-} can be trapped on Pd at the initial irradiation, and the reduction reaction takes place on the Pd particles. However, the reduction of BDE15 does not occur at this stage, evidently due to the low Fermi level of the photocatalyst. With accumulation of e_{cb}^{-} , the reduction reaction of BDE15 gradually becomes possible because of the increased Fermi level. Accordingly, the presence of an induction period for the photocatalytic reduction of BDE15 implies that the electron transfer from TiO₂ to palladium may play an essential role in the Pd-cocatalyzed debromination on the TiO₂ surface. On the other hand, the debromination of BDE15 did not occur on the pristine TiO₂ systems even at the prolonged irradiation time, at which an even higher Fermi level of TiO₂ is expected, thus suggesting that the catalytic function of Pd is also indispensable to the debromination of BDE15. It has been proposed that activated H species on the Pd surface are responsible for the accelerated rates of PBDE debromination through nucleophilic attack at a halogen substituent.^[22, 38] If this is the case in our study, the reduction of both BDE15 and BDE209 would be enhanced at the initial irradiation, since the activated H species, which accelerate the debromination of BDE209, should be equally effective for the reduction of BDE15. The different reaction behaviors of the BDE209 and BDE15 on Pd-TiO₂ imply that this reaction is not in the rate-determining step. C-X bond homolytic cleavage on the Pd catalyst is also reported to be the rate-limiting step in the Pd-catalyzed dehalogenation,^[39] which means that the cleavage of the C-X bond takes place prior to the reduction step. The absence of the dark reaction even for unstable BDE209 in the Pd-TiO₂ systems does not seem to support this possibility. More reasonably, both electron transfer and C-Br cleavage are in the rate-determining step for the debromination on Pd-TiO₂, in which the electron transfer and C-Br cleavage proceed simultaneously, whereas the electron-transfer process should be rate-determining on the pristine TiO₂, as our previous reports mentioned.^[14] According to this mechanism, the cocatalytic effect of Pd is attributable to two factors: Pd can trap the $\mathsf{e_{cb}}$ to enrich electrons on its surface and enhance the photogenerated charge separation, and further transfer the electron to PBDEs by assisting the cleavage of the C-Br bond, probably owing to the high affinity of Pd metal for bromine atoms. Such a concerted electron transfer and C-Br cleavage process avoids the formation of high-energy anionic radical intermediates, and instead a neutral radical intermediate is formed.

Conclusion

By using Pd–TiO₂, a fast debromination of decabromodiphenyl ether (BDE209) has been achieved under the irradiation of sunlight or an artificial light source. Distinguished with the pristine TiO_2 , the low-BDEs, usually the final products in TiO_2 photoca-



tine TiO_2 surface. For another PBDE (BDE15), it was found that only with the Pd-loaded system can the photoreduction of BDE15 be efficiently conducted, and during this photoreduction process an evident induction period is observed. Such a discrepancy between the pristine and Pd-loaded systems can be attributed to the Pd-cocatalyzed effect, in which the electrons can be first stored on the Pd surface and then further transferred to PBDEs for the cleavage of the C–Br bonds.

Experimental Section

Catalyst preparation

The Pd–TiO₂ catalyst with a loading of 2.0 wt % Pd was prepared by a photodeposition method. First, TiO₂–water/isopropanol dispersions were prepared by adding TiO₂ particulates (5 g L⁻¹) to a mixture (100 mL) of water/isopropanol (1:1) in a Pyrex vessel. The vessel was purged with argon for 1 h to remove O₂ and protected under an argon atmosphere during the irradiation. A 300 W xenon lamp (PLS-SXE-300/300UV, Trustech, China) was used as the light source. During the irradiation, a solution of PdCl₂ dissolved in water was introduced dropwise into the TiO₂ suspension under stirring. After irradiation for 2 h, the as-prepared samples were centrifuged and thoroughly washed by water. Finally, they were freeze-dried under vacuum overnight before use.

Debromination experiments and intermediates analysis

BDE209 stock solution (1 mmolL⁻¹) in tetrahydrofuran was diluted with methanol to 10 μmol L⁻¹. The BDE209/Pd–TiO₂ or BDE209/TiO₂ suspensions were prepared by adding Pd-TiO₂ (0.2 gL⁻¹) or TiO₂ (0.2 g L^{-1}) particulates to a solution (25 mL) of BDE209 in a Pyrex vessel. The vessel was sealed with an aluminum cap/rubber plug, and mixed ultrasonically in a water bath for 2 min to disperse the particles. For experiments under anoxic conditions, the vessel was purged with argon for 30 min to remove O2, and the reaction system was protected under an argon atmosphere during the irradiation. The suspensions were stirred in the dark for 1 h before irradiation to reach adsorption/desorption equilibrium. A mercury lamp (100 W, Toyozumi Dengenkiki Co. Ltd.) was used as the light source. To avoid the direct photolysis of BDE209, a cutoff filter (UVCUT 360, Beijing Trusttech Co. Ltd.) was used to cut off the irradiation below 360 nm. During the irradiation, the suspension (1 mL) was collected at given time intervals and centrifuged immediately at 10000 rpm for 10 min to remove the Pd-TiO₂ or TiO₂ particles. The supernatants were used for HPLC and GC-µECD analysis. The debromination of BDE15 was carried out under the same experimental conditions. To test the reproducibility and uncertainty of the degradation experiments, the photochemical reactions were repeated three times. Substrate in samples was quantified by HPLC (Agilent 1260) monitoring at 240 nm, using a DikmaPlatisil ODS C-18 column (250 mm \times 4.6 mm \times 5 μ m). The mobile phase was 100 % acetonitrile at a flow rate of $1 \; mLmin^{-1}$ for BDE209, and $85 \, \%$ CH₃CN/15% H₂O for BDE15.

A gas chromatograph (Agilent 7890A) equipped with an electron capture detector and a DB-5 capillary column (30 m×250 μ m× 0.1 μ m) was used for analyzing the intermediates of BDE209 degra-

dation. The oven temperature was held initially at 100 °C for 2 min, increased at a rate of 15 °C min⁻¹ to 230 °C, 5 °C min⁻¹ to 270 °C, and 10 °C min⁻¹ to 320 °C and kept at this temperature for 12 min. The injection temperature was 300 °C, and the detector temperature was 325 °C. The carrier gas was helium at a constant flow rate of 1 mL min⁻¹. The concentration of Br⁻ was measured by a DX-900 ion chromatograph with an lonPac AS23 column (Dionex). The eluent for ion chromatography was 8 mM KOH solution with flow rate of 1 mL min⁻¹.

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