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Peculiar and rapid photocatalytic degradation of tetrabromodiphenyl ethers over Ag/TiO_2 induced by interaction between silver nanoparticles and bromine atoms in the target

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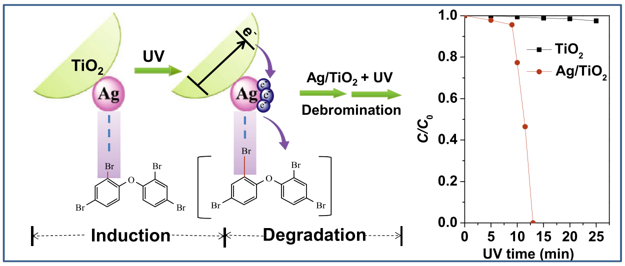
HIGHLIGHTS

- A rapid photocatalytic debromination of BDE47 achieved on silver-loaded TiO_2.
- Ag^0 exerted affinity interaction with Br of BDE47 for promoting its C-Br cleavage.
- Ag^0 particles need induction period to enrich a critical amount of electrons.
- The electron storing on Ag^0 enhanced the driving force for the C-Br cleavage.

GRAPHICAL ABSTRACT



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ABSTRACT

As a typical moderately-brominated diphenylethers, 2,2′,4,4′-tetrabromodiphenyl ether (BDE47) is hardly debrominated by a conventional TiO_2-mediated photocatalysis. However, its reductive debromination was rapid achieved over silver nanoparticle-loaded TiO_2 (Ag/TiO_2) in UV-irradiated anoxic acetonitrile–water within 13 min. An “Ag-promoted electron transfer and C-Br cleavage” concept was proposed based on experimental results and density functional theory calculations. Ag^0 exerted affinity interaction with bromine atoms, and the storing of electrons on Ag^0 increased the binding interaction, which elongated the C-Br bond of BDE47 and facilitated its cleavage. The initiating of the BDE47 debromination on Ag^0 required an induction period to enrich a critical amount of electrons, leading to a stronger driving force for both injecting electron to BDE47 and stretching the C-Br bond. Stronger photoexcitation, higher polar solvent, and a moderate Ag^0 load strengthened the interfacial electron transfer over Ag/TiO_2, and thereby shortening the induction time and accelerating the BDE47 degradation.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used as additive flame retardants in resins and plastics (La Guardia et al., 2006). The most frequently detected PBDEs in environment were three moderately-brominated congeners: 2,2′,4,4′-tetrabromodiphenyl ether (BDE47), 2,2′,4,4′,5-pentabromodiphenyl ether (BDE99), and 2,2′,4,4′,6-pentabromodiphenyl ether (BDE100) (Sánchez-Prado et al., 2005). This is because highly-brominated PBDEs are easily transformed to less brominated

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congeners, and the less brominated products are much more resistant to further natural degradation (Niu et al., 2006). However, the moderately-brominated congeners are more toxic, bioaccumulative and bioactive (Eriksson et al., 2004). Therefore, an effective way to eliminate the contamination of these PBDEs becomes an urgent need.

Oxidative debromination of PBDEs is only possible under very special conditions (Huang et al., 2013), and most studies on the PBDEs removal are primarily focused on the reductive debromination. Liang et al. utilized nonionic surfactant to enhance the reduction of PBDEs with nanoscale zero-valent iron (nZVI), and found that this system is more effective for reductive degradation of BDE209 than for BDE47 (Liang et al., 2014), being consistent with the results of Keum et al. (Keum and Li, 2005) and Xie et al. (Xie et al., 2014). The electron density of benzene ring in PBDEs increases as decreasing the number of bromines, which makes them more resistant to reduction. To improve the reduction of BDE47, Luo et al. coupled microwave radiation with Fe–Ag bimetallic nanoparticles (Luo et al., 2012). Su et al. reported that macroporous silicon/graphene heterostructure (MPG/Gr) could photocatalytically reduce BDE47 under a bias potential of -1.0 V (Su et al., 2012a). Several cathode materials such as vertically aligned nitrogen-doped nanodiamond (VA-NDD)/Si rod array) (Su et al., 2012b) and nano-cubic structured titanium nitride particle films (Liu et al., 2014) were developed to electrochemically reduce BDE47 under negative bias potentials. In these treatments under special conditions such as microwave radiation, or a lager bias potential, hydrogenation is a still key step of the catalytic debromination of BDE47.

Besides the hydrogenation pathway, the debromination of PBDEs may be also initiated by electron injection. TiO_2-mediated photocatalysis is a promising method for producing electrons with strong reductive ability. Sun et al. reported that the photogenerated electrons of TiO_2 could rapidly reduce BDE209 (Sun et al., 2009), being much faster than that in the zero-valent iron systems (Keum and Li, 2005). However, this system led to significant accumulations of 4Br–7Br brominated PBDEs, signing that TiO_2 was ineffective in reducing low brominated congeners. Li et al. observed a complete debromination of BDE209 on surface-palladized TiO_2 (Pd/TiO_2) under UV irradiation, and they suggested that Pd can enrich and further transfer electrons to PBDEs, favoring the cleavage of the C-Br bond (Li et al., 2014). Recently, we also observed that the photocatalytic reduction of BDE209 was greatly enhanced over the composite of TiO_2 and reduced graphene oxide (RGO) due to RGO as both the electron trapper and transport medium improved the electron generation and transfer (Lei et al., 2014). But this composite was still less effective in the photocatalytic reduction of BDE47. Therefore, the BDE47 degradation requires more special measures instead of simply enhancing the electron generation.

It is worth noting that after PBDEs gain electrons, the subsequent elimination of Br strongly depends on the strength of the C-Br bond. For this reason, some approaches that can weaken the C-Br bond may be developed to enhance the photocatalytic reduction of BDE47. Among mercury (Hg), silver (Ag) and platinum (Pt), Koper et al. found that Ag has the highest affinity to the halogens (Koper and Van Santen, 1999). Antonio Laguna et al. also found a notably strong and directional interaction between halogen atom and silver atom (Laguna et al., 2010). In addition, Takai et al. reported that Ag is much more effective in storing electrons than Au, Pt and Pd (Takai and Kamat, 2011). This in turn facilitates the improvement of charge separation in semiconductor-metal composite systems for injecting electrons to PBDEs. Several work has employed Ag/TiO_2 to improve the photocatalytic oxidation of organic pollutants on TiO_2. For example, Tunc reported that the degradation rate of the oxalic acid over Ag/TiO_2 composites is three times higher than that of pure P25 TiO_2 (Tunc, 2014). Yu et al. found that TiO_2/Ag sponge-like nanocomposites exhibited higher photocatalytic activities than pure TiO_2 powders towards the degradation of RhB and salicylic acid (Yu et al., 2012). Therefore, Ag-loaded TiO_2 (Ag/TiO_2) photocatalysts received our considerable attention, and we expected that the interaction between the loaded Ag nanoparticles and PBDEs would favor the C-Br bond cleavage, as well as the enhanced charge separation would provide abundant photogenerated electrons to reduce BDE47.

In this study, we utilized Ag/TiO_2 to photocatalytically reduce a typical moderate brominated PBDE, i.e., BDE47, and found that the optimized Ag/TiO_2 composites yielded a rapid removal of BDE47 within 13 min of UV irradiation. A different debromination process including an induction period and a degradation phase was observed in the present Ag/TiO_2 photocatalytic system. A detailed theoretical analysis clearly revealed the high affinity of Ag to bromines drove the C-Br cleavage of BDE47.

2. Experimental section

2.1. Materials

BDE47 (purity > 98.5%) was purchased from J&K chemical. A standard solution of 39 kinds of PBDEs (i.e., product BDE-AAP-A) was obtained from AccuStandard, Inc. P25 TiO_2 powders were supplied by the Degussa Company (Germany). $AgNO_3$ (analytical grade) was provided by Shanghai Chemical Company. All other reagents were analytical grade and used without further purification.

Ag/TiO_2 nanocomposites were prepared by a UV-assisted photocatalytic reduction method. The detailed information was shown in Section S1.

2.2. Photocatalytic degradation

In a typical photocatalytic experiment, BDE47 stock solution (1000 mg L^{-1} in tetrahydrofuran) (0.5 mL) was added to Ag/TiO_2 suspension (0.1 g L^{-1}) in acetonitrile–water (1:1) solvent (100 mL) in a quartz vessel, followed by adding methanol (1 mL) as electron donors. The resultant mixture was purged with nitrogen for 30 min and protected under nitrogen atmosphere during the UV irradiation all under magnetic stirring at a temperature of 30 °C. A PLS-SXE300 Xe lamp (Beijing Perfect Light Co., Ltd) was used as the light source. After turning on the light, 1 mL suspension was sampled at given time intervals, and immediately centrifuged at 16,000 rpm for 3 min. The supernatants were filtered through a 0.22 μm membrane and immediately analyzed by HPLC. All degradation experiments were conducted in duplicate.

2.3. Analysis

The concentration of BDE47 and its products were analyzed by HPLC (Agilent 1260 series, USA) equipped with a diode array detector and an SB-C18 column (4.6 × 150 mm). The mobile phase was 90% acetonitrile and 10% water at 1.0 mL min^{-1}, and the detector wavelength was set at 240 nm. To identify degradation intermediates, the samples after removing photocatalysts were concentrated with the aid of steaming N_2, and then analyzed by GC–MS under the same instrumental conditions as described in our previous study (Lei et al., 2014). The concentration of produced Br^- was monitored by ion chromagraphy (IC) on an IC-2010 (TOSOH) equipped with a conductivity detector and TSKgel SuperIC-AZ. The eluent was a mixture solution composed of 1.7 mmol L^{-1} Na_2CO_3 and 6.3 mmol L^{-1} $NaHCO_3$ at 0.8 mL min^{-1}.

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