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A peculiar mechanism for the photocatalytic reduction of decabromodiphenyl ether over reduced graphene oxide–TiO_2 photocatalyst

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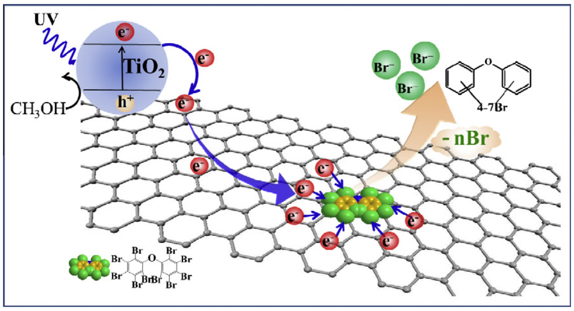
HIGHLIGHTS

- The photocatalytic debromination of BDE209 was efficient on reduced graphene oxide loaded TiO_2.
- Much less toxic products were generated during the BDE209 debromination.
- A total different multi-electron reduction path of BDE209 occurred on RGO/TiO_2.
- RGO as electron shuttle induced an efficient and distinct reduction path of BDE209.

GRAPHICAL ABSTRACT



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ABSTRACT

There remains a significant need for new approaches to photocatalytically destroy refractory halogenated pollutants. Here, efficient photocatalysts (RGO/TiO_2) were prepared by UV treatment of graphene oxide (GO) mixed with Degussa P25 TiO_2, and used to photocatalytically reduce decabromodiphenyl ether (BDE209). The optimized composite yielded a BDE209 degradation of 72.0% and a debromination of 59.4% in anoxic water with methanol as electron donors after 12 h of UV irradiation, being 2 and 4 times that over naked TiO_2, respectively. The BDE209 reduction generated 3Br–9Br PBDEs congeners, which were further debrominated. This led to a debromination of 90% at 24 h of reaction. Unlike the stepwise reduction manner commonly observed in UV–TiO_2, the generation, accumulation and distribution of intermediates in the time course implied that the BDE209 reduction skipped some debromination steps. A novel mechanism for the multi-electron induced debromination pathway of BDE209 was proposed. This originated from the abilities of reduced GO in storing and transporting electrons. RGO not only trapped electrons to improve the charge separation on TiO_2, but also shuttled the accumulated electrons to initiate multi-electron transfer to BDE209. The markedly enhanced debromination demonstrates the multi-electron transfer over RGO/TiO_2 provide a green and efficient method to remove halogenated pollutants.

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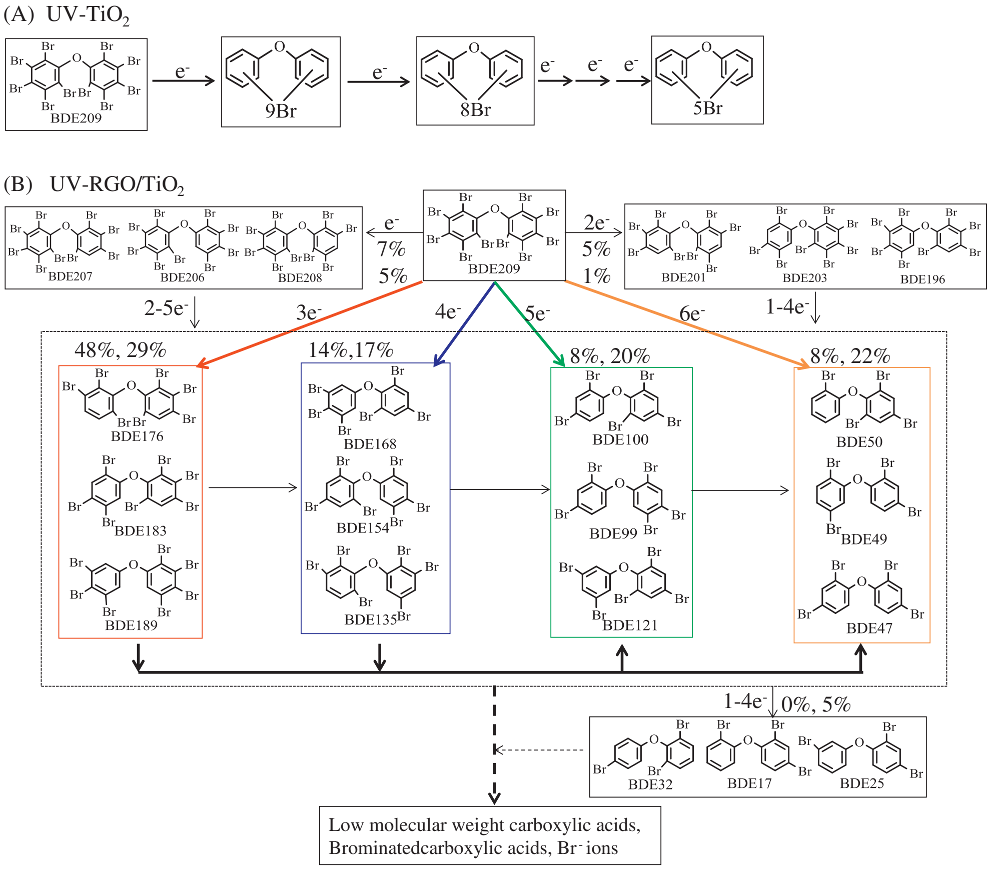
1. Introduction

As a new class of persistent pollutants, polybrominated diphenyl ethers (PBDEs) are becoming "the polychlorinated biphenyls (PCBs) of the future" [1–3]. Decabromodiphenyl ether (BDE209) is still used in industrial products worldwide, but is easily transformed into lower brominated congeners under sunlight. BDE209 is the main source of PBDEs contaminants, and much work has been devoted to the removal of BDE209 [4–7].

Reductive dehalogenation is a common strategy to treat PBDEs. This includes electrocatalytic hydrogenolysis [8], chemical reductions with zero valent irons [9,10] and sodium borohydride [11], and TiO_2 photocatalysis [12,13]. Here, the BDE209 debromination followed a stepwise process [10,12,14]. First, it was transformed to nona-BDEs, then to octa-BDEs, and expected so forth to finally diphenyl ether (DE) (Scheme 1A). However, it was rather difficult to achieve a complete debromination, because the lower brominated PBDEs products are much more resistant to further reduction [12]. For example, it was reported that TiO_2 photocatalysis could rapidly remove BDE209 within 8 min, but provided a debromination efficiency of only 43% within 24 h [12]. Since some less brominated products are potentially more toxic than parent BDE209 [6,7], the intermediates accumulation is a major disadvantage for using these dehalogenation processes.

It is worthy of noting that the photocatalytic debromination is an interfacial electron transfer process, and improving debromination efficiency requires primarily an enhanced charge separation of TiO_2. To enhance the charge separation of TiO_2, surface modifications have been developed by depositing noble metals [15,16] or metallic hydroxide [17], combining carbon nanotubes [18], adsorbing in situ inorganic anions and cations [19–21], and coating molecularly imprinted polymers [22,23]. However, these attempts have failed to completely shield regeneration of electrons and holes. Recently, numerous attempts have been made to combine graphene or graphene oxide (GO) with TiO_2 to enhance its photocatalytic behavior.

Graphene-based semiconductor photocatalysts were first studied by Kamat and co-workers [24,25], who demonstrated the feasibility of graphene in storing and shuttling electrons in the graphene/TiO_2 composites. Zhang et al. [26] used a one-step hydrothermal method to prepare graphene/TiO_2, which exhibited higher photocatalytic ability for oxidizing methylene blue than Degussa P25 TiO_2. Wang et al. also found that hydrothermal graphene/TiO_2 composites enhanced the degradation of acetone in air, which exceeds that of pure TiO_2 by 1.7 times [27]. Our group previously prepared RGO/TiO_2 with a combined liquid phase deposition and subsequent calcination, and found that its photocatalytic activity was 5–7 times that of P25 [28]. Other important milestones in the design and fabrication of graphene-based TiO_2 have been summarized in a recent critical review by Xiang and co-workers [29]. In these composites, the photogenerated electrons in the TiO_2 transfer to graphene sheets, and then scavenged by dissolved oxygen facilitating the hole–electron spatial separation and the subsequent oxidation of organic pollutants. If in an anoxic atmosphere containing hole consumers, the accumulated abundant electrons in graphene may facilitate reduction. Examples include the reduction of CO_2 [30], the synthesis of amines from nitro compounds, and the dehalogenation of toxic halogenated pollutants. However,



Scheme 1. Debromination pathways of BDE209 in the systems of (A) UV–TiO_2 and (B) UV-RGO/TiO_2. In each homologue of scheme B, the former percentage value represents the molar ratio of PBDEs products to the consumed BDE209 at 0.5 h UV irradiation, while the latter one shows the case at 3 h UV irradiation. The results demonstrate that the photocatalytic debromination of BDE209 over RGO/TiO_2 proceeds mainly through $3e^- – 6e^-$ reductions, being markedly different from the commonly stepwise debromination manner.