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Photocatalytic Degradation of Polybrominated Diphenyl Ethers on TiO_2-based composites

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Abstract

Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants, and become a new class of global contaminants. Because PBDEs possess typical characteristics of persistent organic pollutants (POPs) like persistent, bioaccumulation, and biotoxicity, their elimination therefore attracts much attention of researchers.

The reductive debromination is a common strategy to treat PBDEs. Among various reductive methods, the photogenerated electron of TiO_2 is considered to be highly efficient to reduce decabromodiphenyl ether (BDE209) [1]. However, this leads to accumulation of brominated intermediates, but the debromination products with less bromine atoms are much more difficult to get further reductive debromination.

To promote the photocatalytic reductive debromination, we developed several TiO_2-based composites including reduced grapheme oxide (RGO) loaded TiO_2 (RGO/TiO_2), Ag/TiO_2, and CuO/TiO_2 to reduce BDE209 and/or 2,2',4,4'-tetrabromodiphenyl ether (BDE47) [2-4]. These heterosturctured photocatalysts have two beneficial roles: charge separation in space, and enhanced adsorption of PBDEs. Thus, the photocatalytic reduction of PBDEs was greatly improved. However, the complete debromination of PBDEs to diphenyl ether through the photocatalytic reduction process is rather difficult. For example, although all the added BDE47 was rapidly reduced, the debromination efficiency was still less than 50% over Ag/TiO_2 and CuO/TiO_2 [3,4]. This is because that the reduction of low-brominated PBDEs is rather difficult, due to their weak electron affinity.

Although most studies indicate that BDE209 is strongly resistant to oxidation, we firstly demonstrated that the h^+/•OH-involved oxidative degradation of BDE209 took place slowly in the UV-irradiated TiO_2 aqueous dispersions [5]. We also noted that the oxidation of BDE209 is much slower than the following oxidation of the less-brominated organic intermediates. Since the highly brominated PBDEs are more easily reduced, and the lower brominated PBDEs become more susceptible to the oxidation, we then developed an effective "one-pot" photocatalytic system for driving concurrently the pre-reduction and consecutive oxidation of BDE47.

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