



Metal oxide semiconductor nanomaterial for reductive debromination: Visible light degradation of polybrominated diphenyl ethers by Cu₂O@Pd nanostructures



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ABSTRACT

Polybrominated diphenyl ethers (PBDEs), which have found extensive use as flame-retarding additives to many polymer materials, are now environmentally ubiquitous and persistent pollutants that present potential health risks to humans and wildlife. Herein, we report for the first time the use of metal oxide semiconductor nanostructures for photocatalytic reductive debromination of PBDEs using visible light. Well-defined cubic Cu₂O crystals, surface-decorated with Pd nanoparticles, were prepared via a hydrothermal approach. The Cu₂O@Pd demonstrated light-activated tandem photocatalysis, in which Cu₂O produces H₂ from H₂O under visible light irradiation; the evolved H₂ is subsequently activated by Pd to achieve the reductive hydrodehalogenation of the PBDE. Cu₂O@Pd demonstrated effective debromination of 2,2',4,4'-tetrabromodiphenyl ether (BDE-47), one of the PBDEs of greatest environmental concern, with initial pseudo-first-order rate constant of 0.21 h⁻¹. It is shown that the reaction proceeds via a reductive mechanism with preferential debromination at the *para* positions. Reaction rates for various monobromo- and dibromo-congeners were evaluated, confirming that the debromination order of preference is *para* > *meta* >> *ortho*, which is opposite to the order reported for direct photolysis. We conclude that Cu₂O@Pd is a promising photocatalyst for reductive dehalogenation of halogenated organic compounds.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of highly stable compounds comprised of 209 congeners, several of which had been employed extensively as chemical flame-retarding agents added to flammable materials such as plastics and textiles used in a wide range of products [1–3]. As additive flame-retardants, PBDEs were mixed with, but not chemically bound to, polymers of a product; the latter is the case with reactive flame-retardants. As such, PBDEs can be readily released into the environment from discarded products and have become a ubiquitous environmental pollutant [4–10]. Widespread distribution of these compounds in the environment is of particular concern, because they are known to act as endocrine disruptors [11–13], impair neurobehavioral development [14], and could cause DNA damage [15]. Because of the potential hazards associated with PBDE exposure, many of these

compounds have recently been banned, whereas the remaining ones have been voluntarily phased-out in the United States [16,17]. Nevertheless, the extensive use of these compounds in the past translates into a large reservoir in the environment [18,19]. On account of their widespread contamination, environmental persistence, and health hazard, it is important to develop new and effective approaches for PBDE mitigation.

A number of natural environmental processes are known to degrade PBDEs. Several bacterial [20–24] and fungal [25] species have been identified that are capable of feeding upon and breaking down PBDEs. While biodegradation occurs naturally, it proceeds very slowly [24]. It should be noted that in the case of oxidative biodegradation processes, many of the products formed, including polybrominated dibenzofurans (PBDFs) and hydroxylated polybrominated diphenyl ethers (HO-PBDEs), could be more hazardous than the parent compounds [26].

Several non-biological degradation methods, principally photolysis [27], dehalogenation by zero-valent iron [28], and photocatalytic degradation by TiO₂ [29], have been proposed for the remediation of PBDEs [30,31]. Photolysis can occur under UV irra-

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diation, which leads to either homolytic or heterolytic cleavage of a C–Br bond or a C–O bond, or in a ring-closure with the elimination of HBr to produce PBDFs. For instance, the prevailing mechanism in the presence of a strongly-nucleophilic solvent such as water, is heterolytic C–Br cleavage [30]. This eventually results in formation of the more hazardous HO–PBDEs through nucleophilic substitution under aqueous conditions. PBDEs also absorb in the UV-A region of the spectrum [27] and, except under special conditions, visible light is insufficient for their photolysis. The exception recently reported by Sun and co-workers utilizes carboxylate anions, which form a visible-light-absorbing halogen bond complex with the PBDE, facilitating its photolysis at a longer wavelength [32]. In this case, however, the photolysis of decabromodiphenyl ether (BDE-209) did not result in the degradation of the material beyond the tetrabromodiphenyl ether congeners.

The photolytic degradation of PBDEs generally takes place in a stepwise fashion, with the loss of one bromine atom at a time. As such reactions proceed, however, the removal of each successive bromine atom becomes more difficult, where the fewer bromine substituents there are on the molecule, the stronger the C–Br bonds become, as evidenced by the shift in absorbance λ_{\max} to shorter wavelengths. Density Functional Theory (DFT) calculations indicate that removal of each successive bromine atom increases the stability of the molecule by about 22 kJ/mol after correction for differences in bromination patterns [33]. This results in a preponderance of congeners with an intermediate number of bromines that are resistant to further debromination, most notably the pentabromo- and tetrabromo- congeners, BDE-99 and BDE-47, respectively [34–36]. Although TiO₂-based materials have demonstrated effective oxidative photocatalytic degradation of PBDEs in organic solvents [30], this reaction still suffers from two major drawbacks: oxidation can produce highly toxic by-products, and UV irradiation is required as TiO₂ is a wide band gap semiconductor. Reductive debromination using TiO₂@Pd [37] or CuO/TiO₂ [38,39] nanocomposite photocatalysts was recently reported. Although these materials resulted in rapid reductive debromination, they still suffer from two major drawbacks: they need UV irradiation and, moreover, the solvent systems consisted of 70–100% methanol, an environmentally unfriendly requirement. An ideal photocatalyst would make use of the abundant visible solar output to drive a non-oxidative degradation mechanism using only environmentally benign solvents.

Reductive debromination by H₂ generated through reaction of nanoscale zero-valent iron (nZVI) or by palladium/iron bimetallic nanomaterials (nZVI@Pd) with water has been investigated as an alternative approach that avoids the formation of toxic oxidative products [30]. Zhuang et al. showed that adding Pd to the surface of nZVI both increases the reaction rate and alters the mechanism to produce different products; the nZVI@Pd particles favor removal of *para* bromines, while pristine nZVI favors *meta*- and *ortho*-debromination [40]. A key drawback to this method, however, is that the production of H₂ from water is a stoichiometric reaction in which the nZVI is oxidized. This results in the formation of iron oxides/hydroxides on the surface of the nZVI, thus adversely impacting the rate of debromination due to the lack of H₂ production from the oxidized surface [41]. As such, a catalytic reaction based upon sustainable materials, consistent with the principles of Green Chemistry [42], has been much sought.

We recently introduced a novel composite material consisting of Cu₂O cubes, surface-decorated with Pd nanoparticles, that has been shown to perform as a tandem photocatalyst in the reductive dechlorination of polychlorinated biphenyls (PCBs) [43]. In this material architecture, Cu₂O nanomaterials are well established p-type semiconductors which are able to generate H₂ via the photocatalytic water splitting reaction [44], while the Pd particles on the Cu₂O cubes provide localized catalytic sites for the hydrode-

halogenation reaction in the vicinity of the photogenerated H₂ [43]. In this approach, the production of H₂ via photocatalytic proton reduction on the surface of Cu₂O crystals is achieved by light activation. Subsequently, this H₂ is activated on the surface of Pd nanoparticles to drive the reductive dehalogenation reaction. Furthermore, the direct band gap of Cu₂O is such that visible light irradiation could be used for exciton generation [44]. Use of this material provides significant advantages over other methods in that it could drive the dehalogenation reaction sustainably using renewable resources, namely sunlight and water.

Herein, we report the visible-light driven reductive debromination of PBDEs using a non-titania-based narrow band gap metal oxide semiconductor nanocomposite photocatalyst. Cubic Cu₂O particles were prepared by a simple hydrothermal process and subsequently surface-decorated with Pd nanoparticles via galvanic replacement. The resulting Cu₂O@Pd multicomponent material was then used as photocatalyst for the reductive debromination of various congeners of PBDEs under visible light. The results show that rapid degradation of BDE-47 is achieved, and the sequence of debromination products is consistent with the reductive mechanism. It was found that the catalyst is most effective in debrominating PBDEs at the *para* positions, whereas direct photolysis is known to debrominate most readily at *ortho* and *meta* positions [31]. Insight into the mechanism of this reaction and a comparison to the direct photolysis of PBDEs were investigated.

2. Experimental details

2.1. Materials and equipment

All reagents were used as received without further purification. BDE-47 (99.5%) was purchased from Chem Service (West Chester, PA). BDE-3 (99%), BDE-15 (99%), glucose (anhyd., 99%), and ethyl acetate (99%) were obtained from Alfa Aesar (Ward Hill, MA). BDE-1, BDE-4, and BDE-8 were purchased from AccuStandard (New Haven, CT), as were reference standard solutions (each 50 µg/mL in isoctane) of BDE-17 and BDE-28. Dibenzofuran (100 µg/mL in methanol) was supplied by Ultra Scientific (Kingstown, RI). Diphenyl ether (>99%) was obtained from TCI (Portland, OR). BDE-2, polyvinylpyrrolidone (avg. MW = 29 kDa), and sodium citrate (ACS) were from Sigma-Aldrich (St. Louis, MO). Sodium carbonate (anhyd., ACS) and hexanes (HR-GC grade) were supplied by EMD (Gibbstown, NJ). Palladium acetate (47.5% Pd) was purchased from Acros Organics (Morris Plains, NJ), copper sulfate pentahydrate (ACS) from BDH (Radnor, PA), and 1,2-dibromobenzene from Oakwood Chemical (West Columbia, SC). Absolute ethanol was obtained from Pharmco Aaper (Shelbyville, KY) and ethanol (95%) from Decon Labs (King of Prussia, PA). Ultra-high-purity N₂ was purchased from Airgas (Miami, FL). Ultra-pure water (18 MΩ) was produced by a Barnstead E-Pure system (Thermo Fisher Scientific, Waltham, MA).

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed in the characterization of the Cu₂O and Cu₂O@Pd materials using a Philips XL30 field-emission environmental SEM equipped with an Oxford energy-dispersive X-ray detector and a JEOL JEM-1400 TEM, respectively. SEM experiments were performed at 20 kV, while TEM experiments were conducted at 80 kV. Debromination reactions were done in a photochemical safety cabinet (Ace Glass, Vineland, NJ, model #7836-20) under irradiation by a 450 W medium-pressure mercury-vapor lamp (Ace Glass #7825-34, light intensity = 60 mW/cm²). Reaction progress was monitored by GC/MS (Agilent 5975C GC/MS with HP-5MS column: 30 m length, 0.250 mm ID, 0.25 µm film thickness, Santa Clara, CA) using 1,2-dibromobenzene as an internal standard [41,43].

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