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PAPER

Selective photocatalytic reductions of nitrobenzene derivatives using $PbBiO_2X$ and blue light†

Stefan Füldner,[a] Patrick Pohla,[b] Hanna Bartling,[a] Stephan Dankesreiter,[b] Roland Stadler,[b] Michael Gruber,[c] Arno Pfitzner*[b] and Burkhard König*[a]

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Blue light irradiation of heterogeneous photocatalysts $PbBiO_2X$ (X = Cl, Br) in the presence of triethanolamine as an electron donor leads to hydrogen evolution, and the selective, clean and complete reduction of nitrobenzene derivatives to their corresponding anilines.

Sunlight is the only sustainable energy resource on earth, and photovoltaic systems for the conversion of solar energy into electrical power have evolved into a wide range of applications.[1] Photocatalysts, converting visible light energy into chemical energy, are known but they are less well-developed. Recent examples of homogeneous photocatalysts include the hydrogenation of alkynes,[2] the asymmetric alkylation of aldehydes[3] and the dehalogenation of α-alkylated esters.[4] Heterogeneous photocatalysts are typically semiconductors based on modified or unmodified TiO_2 or CdS. Unmodified TiO_2 has been investigated for the reduction of nitrobenzenes to their corresponding anilines under UV light[5] irradiation, whereas modified and dye-sensitized TiO_2 reduces these molecules or oxidizes alcohols with blue or green light.[6] CdS quantum dots have been found to be suitable photocatalysts for the reduction of azides to anilines,[7] but these systems have disadvantages: UV light is only a small part of the solar spectrum, which diminishes the efficiency of unmodified TiO_2 in sunlight. Modified CdS and TiO_2 absorbing in the visible range require special preparation. Oxide halides, such as $PbPnO_2X$ (Pn = Bi, Sb; X = Br, Cl), have been structurally characterized and applied to the oxidative photodegradation of organic dyes, *e.g.* methylene blue and methyl orange.[8] These materials are potential heterogeneous photocatalysts for organic chemical synthesis using visible light and may nicely complement the green light-induced reductions of nitrobenzene derivatives with dye-sensitized TiO_2.[6]

Here, we report a method for the selective reduction of nitroarenes with blue light using $PbBiO_2X$ particles. These effective heterogeneous photocatalysts are prepared from stoichiometric amounts of PbO, Pn_2O_3 and PnX_3 (Pn = Sb, Bi, X = Cl, Br, I; ratio 3 : 1 : 1) in evacuated silica ampoules by annealing at 500–650 °C for several days.[8] They show the quantitative photoreduction of nitrobenzenes to anilines when irradiated with a blue high powered LED light or sunlight. The observed photoconversions of organic substrates are very clean, as verified by gas chromatographic monitoring, and in many cases are quantitative.

All $PbPnO_2X$ photocatalysts absorb in the blue range of the visible spectrum (Fig. 1).

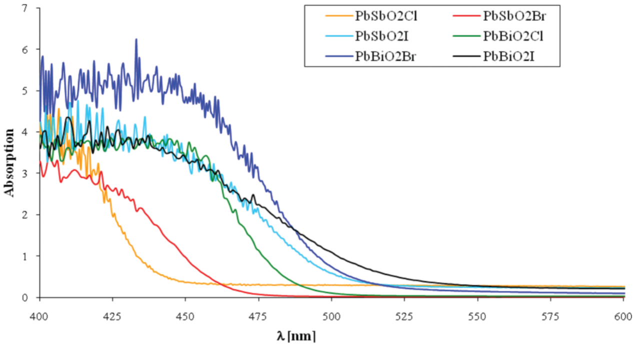

Fig. 1 Absorption spectra of $PbPnO_2X$ (Pn = Bi, Sb; X = Br, Cl, I).

The reduction of nitrobenzene derivatives was chosen to monitor the photocatalysts' efficiency, because of the transfer of six equivalents of hydrogen.[9] The selective photoreduction of nitrobenzenes has been described using TiO_2 and UV irradiation[10] or dye-sensitized TiO_2 and green light irradiation.[6]

All oxide halides have been investigated for their ability to photoreduce nitrobenzenes, but the irradiation of samples containing $PbSbO_2X$ (X = Br, Cl, I) as the catalyst did not

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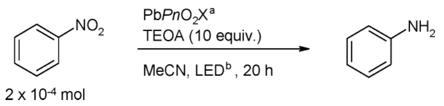
[a] *Institute of Organic Chemistry, University of Regensburg, Universitätsstrasse 31, 93040, Regensburg, Germany. E-mail: Burkhard.koenig@chemie.uni-regensburg.de; Fax: +49 941 9434566; Tel: +49 941 9434575*

[b] *Institute of Inorganic Chemistry, University of Regensburg, Universitätsstrasse 31, 93040, Germany. E-mail: arno.pfitzner@chemie.uni-regensburg.de; Fax: +49 941 943 4983; Tel: +49 941 943 4552*

[c] *Department of Anaesthesia, University Hospital Regensburg, 93051, Regensburg, Germany. E-mail: michael.gruber@klinik.uni-regensburg.de; Fax: +49 941 944 7801; Tel: +49 941 944 7870*

† Electronic supplementary information (ESI) available: See DOI: 10.1039/c0gc00857e

Table 1 Photocatalytic reduction of nitrobenzene to aniline *via* PbPnO$_2X$



Entry	PbPnO$_2X$	LED wavelength/nm^b	Nitrobenzene conversion (%)^c
1	$PbSbO_2Br$	440	≤4
2	$PbSbO_2Cl$	440	≤4
3	$PbSbO_2I$	440	≤4
4	$PbBiO_2Br$	440	>99
5	$PbBiO_2Cl$	440	>99
6	$PbBiO_2I$	440	≤1
7	$PbBiO_2I$	530	≤1

[a] 50 mg oxide halide. [b] LED with 3 W electrical power, 80 Lumen. [c] From the integration of signals in the GC chromatogram.

lead to any conversion (Table 1, entries 1–3). The exchange of Sb^{3+} for Bi^{3+} in the composition of the photocatalyst lead to an almost quantitative conversion of nitrobenzene to aniline within 20 h of blue light irradiation for X = Cl or Br. In case of X = I, no conversion was observed (Table 1). Previous reports have discussed mainly electronic reasons for the different catalytic activities of layered PbPnO$_2X$-type materials (Pn = Sb, Bi; X = Cl, Br, I).[8,11] However, crystal-chemical arguments should also be taken into consideration to explain the photocatalytic properties of the compounds. A possible reason for the different catalytic activity of the oxides may be derived collectively from their crystal structures, their optical and their redox properties. All the solid materials under discussion crystallize in a layered structure. They exhibit covalent metal oxygen layers $^{2}_{\infty}[\mathrm{PbBiO_2}^+]$ separated by halide layers, which are stacked along [001].[8] One can assume that the crystal surface consists of metal oxygen layers, *i.e.*, the metal atoms are expected to form the (001) surfaces. In case of the bismuth compounds, the metal position is statistically occupied by lead and bismuth in the ratio 1 : 1, whereas in the synthetic antimony compounds $PbSbO_2Br$ and $PbSbO_2I$, the antimony atoms are slightly displaced parallel [001] towards the oxygen atoms. By way of contrast, $PbSbO_2Cl$ has an ordered structure. However, therein, the antimony atoms are also displaced towards the oxygen atoms. Therefore, the antimony atoms do not reach the outer crystal surface and thus are not accessible for catalytic processes (Fig. 2).

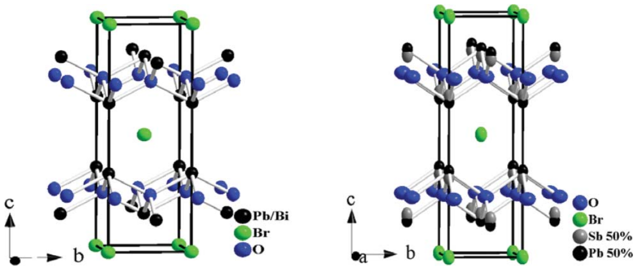


Fig. 2 Crystal structures of $PbSbO_2Br$ (right) and $PbBiO_2Br$ (left). Ellipsoids correspond to a probability of 70%. The position of the metal is occupied statistically by 50% Bi and 50% Pb in the case of $PbBiO_2X$. In the case of $PbSbO_2X$, the positions of Pb and Sb can be resolved.

Photocatalytic measurements with PbO, which has a layered structure similar to the polycationic sheets $^{2}_{\infty}[\mathrm{PbBiO_2}^+]$ in the title compound, did not show any catalytic activity at all, although the absorption spectra were quite similar. Therefore, activity due to Pb^{2+} can be ruled out.

As the surface is only built up of Pb^{2+} (in the antimony-containing materials) or by both Pb^{2+} and Bi^{3+} (in the bismuth-containing materials), it is likely that Bi^{3+} is responsible for the photocatalytic properties in this system. Surprisingly, only $PbBiO_2X$ where X = Cl and Br catalyzed the photoreduction of nitrobenzene to aniline, while no conversion occurred for $PbBiO_2I$ when irradiated under comparable conditions. Furthermore, the latter materials absorb a significant part of the visible spectrum (see Fig. 1). The experimentally determined optical band gaps were 2.55 eV ($PbBiO_2Cl$), 2.47 eV ($PbBiO_2Br$) and 2.39 eV ($PbBiO_2I$).[11] It seems that the gaps of all these semiconductors are in the right range to catalyze the observed reaction. Therefore, changes in the structural nature of the materials may be decisive; increasing the iodine content in $PbBiO_2X$ leads to a change of the preferred crystal growth directions. Thus, $PbBiO_2Cl$ and $PbBiO_2Br$ form layered crystals along (001), whereas $PbBiO_2I$ crystallizes as rods with [001] as the rod axis (see the ESI for pictures of the crystals†). Changes in the bonding interactions between the halide and metal atoms indicate this clearly. In the case of rod-like crystals, the surface of the material is significantly different; the surface changes from mainly (001) for chloride and bromide to mainly (100) and (010) for iodide, which may alter the catalytic activity. The stronger bonds of iodine to Pb or Bi, well known for the binary metal halides, change the crystal growth and may deactivate the surface.

Moreover, redox quenching by iodine may intercept the catalysis as well. Therefore, the redox potentials of the oxide halides were measured, revealing multiple redox processes that did not allow the derivation of exact values.[16] However, iodide inactivation has been investigated with the semiconductors $PbBiO_2Br_nI_m$ and $PbBiO_2Cl_nI_m$ with varying ratios of their halogen content and analyses of their photocatalytic activities in nitrobenzene reduction. With an increasing amount of iodine in $PbBiO_2Br_nI_m$ and $PbBiO_2Cl_nI_m$, the photocatalytic activity decreased dramatically (Fig. 3). Similar effects have been reported for the photodegradation of Rhodamine B with BiOX (X = Cl, Br and I).[12] These materials are isostructural,

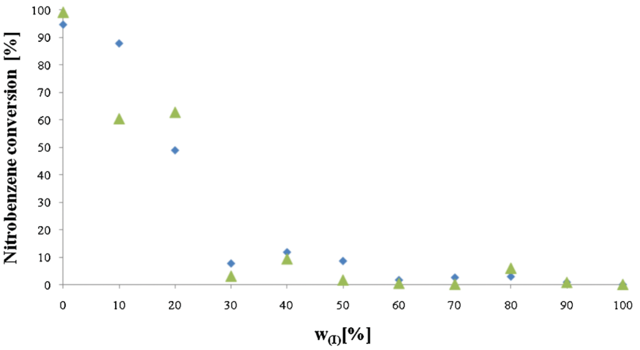


Fig. 3 Photoconversion of nitrobenzene after 20 h, depending on the iodine content, for $PbBiO_2Br_nI_m$ (green) and $PbBiO_2Cl_nI_m$ (blue).

their optical band gaps are in the right region for visible light photocatalysis, but only BiOBr and BiOCl showed activities towards the oxidative photodegradation of Rhodamine B.

These semiconductors were investigated in the photoreduction of nitrobenzene to aniline as well, but only in the case of BiOBr and BiOCl were full conversions observed under identical experimental conditions. Irradiation of BiOI did not induce any photocatalytic activity for nitrobenzene reduction. Such electronic quenching in semiconductor photocatalysis has already been reported for the UV photodegradation of acid orange[13] and curcumin[14] with TiO_2 in the presence of iodide. Furthermore, the UV light-induced reduction of nitrobenzene to aniline has been inhibited by adding small amounts of iodide to TiO_2 and TEOA. Hence, the same argument should be valid for the investigated $PbBiO_2X$ semiconductors, as they show similar redox potentials, band gaps and crystal structures. We therefore relate the observed dependence of the $PbBiO_2X$ photoactivity on the iodine content to electronic quenching and changes in their surface properties.

A kinetic analysis of the photoreduction of nitrobenzene to aniline with $PbBiO_2Br$ and $PbBiO_2Cl$ showed an increase in the rate of nitrobenzene to aniline conversion after approximately 6 h of irradiation with blue light (Fig. 4). This induction period indicates catalyst activation or gas evolution, as reported in the photoreductions of nitrobenzenes to anilines *via* dye-sensitized TiO_2 and metal salts.[6] Head space gas chromatographic analysis revealed the presence of dihydrogen gas after 14 h of irradiation, which explains the selectivity for the exclusive reduction of nitrobenzenes to their corresponding anilines (Table 2).

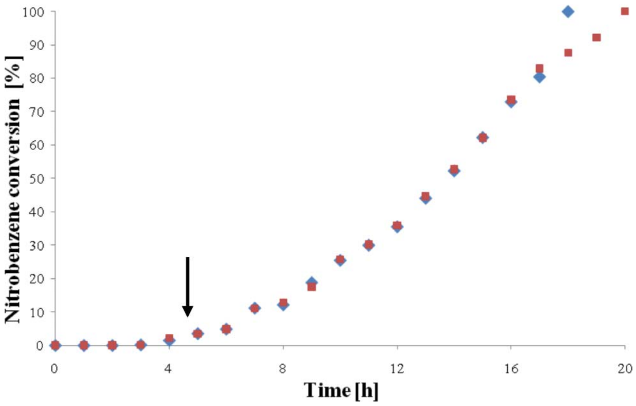
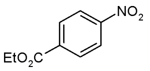
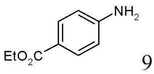
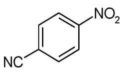
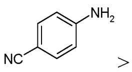
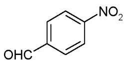
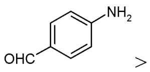
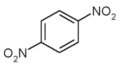
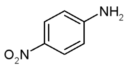
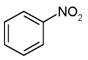
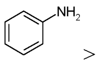
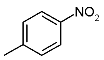
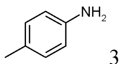
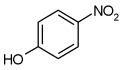
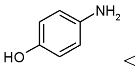
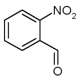
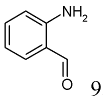
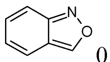
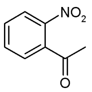
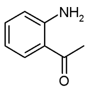
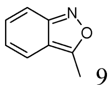
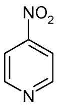
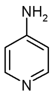
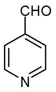
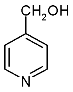
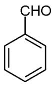
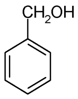


Fig. 4 Kinetics of the reduction of nitrobenzene to aniline *via* $PbBiO_2X$ (X = Br, Cl).

The stability of $PbBiO_2Br$ has been investigated by XRD analysis of the semiconductor before and after the photoreaction. After irradiation for 20 h, the semiconductor became grey, but only in the presence of TEOA. The grey color slightly disappeared when the sample was treated in an ultrasonic bath. X-Ray powder diffraction patterns clearly show no changes in the crystal structure under the experimental conditions (Fig. 5).

Similar observations have been described in the photocatalytic oxidation of isopropyl alcohol to CO_2 with BiOCl.[12] Therefore, we suggest surface passivation processes on $PbBiO_2Br$ during the photocatalysis.[15]

Table 2 Photoreduction of nitrobenzene derivatives *via* $PbBiO_2Br^a$

Entry	Starting material[b]	Product (%)[c]	
1		 95	
2		 > 99	
3		 > 99	
4		 35	
5		 > 99	
6		 30	
7		 < 1	
8		 95	 0
9		 81	 9
10		 90	
11		 54	
12		 0	

[a] 50 mg and irradiation with a 440 nm LED with 3 W electrical power, 80 lumen. [b] 2×10^{-4} mmol. [c] From the integration of signals in the GC-/GC-MS chromatogram.

The maximum number of catalyst reuses was determined; after every catalytic cycle, the grey catalyst was filtered, sonicated in an ultrasonic bath and used again for the photoreduction of nitrobenzene to aniline. After five catalytic cycles, the photocatalytic activity had not decreased; after eight reuses, the conversion under identical experimental conditions had decreased to give 50% conversion. Treatment of the catalyst in an ultrasonic bath is essential to retain its photocatalytic activity, which otherwise decreases dramatically within five cycles (Fig. 6).

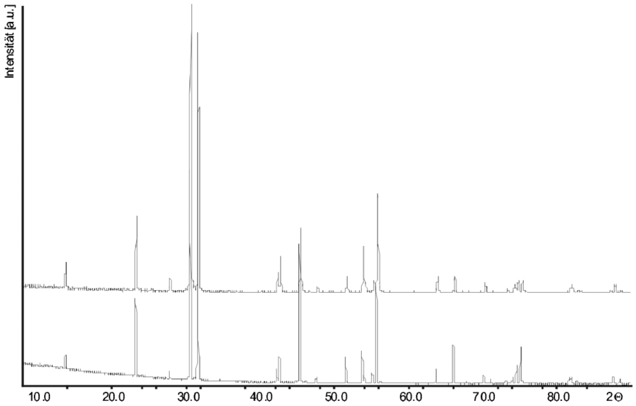


Fig. 5 X-Ray powder diffraction patterns of $PbBiO_2Br$ before (upper) and after catalysis (lower).

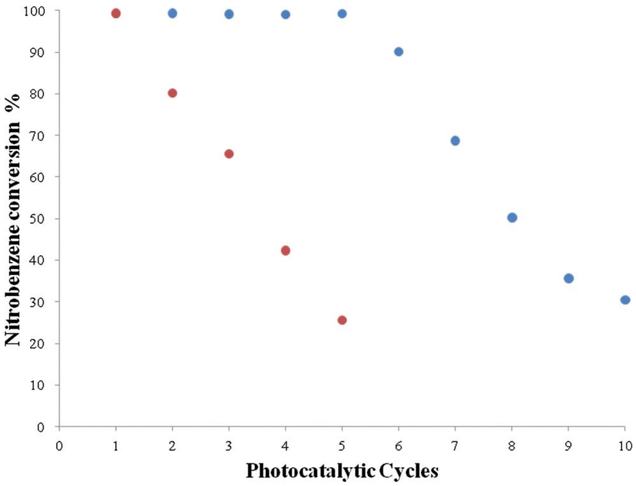


Fig. 6 Photocatalyst recycling experiments of $PbBiO_2Br$ (a) with sonication of the catalyst before reuse (blue) and (b) reuse without sonication (red).

Conclusions

Semiconductors of composition $PbBiO_2X$ (X = Cl, Br) selectively photoreduce nitrobenzenes to anilines in the presence of triethanolamine if irradiated with blue light of low intensity. The photocatalysts are easy to prepare by established solid state chemistry techniques, and allow the complete and clean conversion of substrates. Structural studies have explained the differences in catalytic activity for related Bi^{3+} and Sb^{3+} compounds. The missing photocatalytic activity of the iodide-containing materials may be due to redox quenching and surface effects, as indicated by the decrease of photocatalytic activity in $PbBiO_2Br_nI_m$ and $PbBiO_2Cl_nI_m$ with increasing iodide content, and an inhibited nitrobenzene photoreduction with TiO_2 in presence of iodide. The detection of dihydrogen finally explains the exclusive selectivity for nitrobenzene reductions. Recycling experiments revealed a high stability of the photocatalyst over several reuses, but sonication to remove passivations is essential.

The investigations provide a more detailed mechanistic description of this class of heterogeneous semiconductor photocatalysts, which will facilitate the design and prediction of properties of the next generation of photocatalysts of this type.

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