Mineralization of Phenol and 4-Chlorophenol Induced by Visible Light and Assisted by Semiconducting $\beta$-Bi$_2$O$_3$

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Dedicated to Professor Rolf W. Saalfrank on the occasion of his 70th birthday

Intensely yellow $\beta$-bismuth trioxide in the form of about 41 nm large crystallites has been prepared by thermal decomposition of (BiO)$_2$CO$_3$ at 400 $^\circ$C. From the band gap energy of 2.3 eV obtained under the assumption of an indirect band-to-band transition and the quasi-Fermi level of $-0.28 \pm 0.02$ V (vs. NHE) a valence band edge position of 2.02 V is calculated. This semiconducting oxide assists a Vis light ($\lambda \geq 455$ nm) aerial mineralization of the aqueous model pollutants phenol and 4-chlorophenol exhibiting maximum rates at a bismuth oxide concentration of 2.0 g L$^{-1}$. In the absence of oxygen no degradation occurs indicating that $\beta$-Bi$_2$O$_3$ does not act as oxidizing agent. The mineralization suffers from photocorrosion of $\beta$-Bi$_2$O$_3$ generating a mixture of $\alpha$-Bi$_2$O$_3$ and various bismuth carbonates as observed upon multiple use of the oxide in the mineralization of phenol.

Key words: Bismuth Oxide, Fermi Level, Photocatalysis, Semiconductor, Visible Light

Introduction

Photochemical aerial oxidations catalyzed by semiconductor powders or thin films have moved from basic research to practical application. The most important example is the use of titania for the cleaning of air and water through UV light-induced complete pollutant oxidation by aerial oxygen. Driving such processes by sun light suffers from the fact that only a very small UV part (about 3 %) of the photochemically usable spectrum of solar irradiation can be absorbed by TiO$_2$. Other simple binary semiconductors like CdS undergo photocorrosion [1] or exhibit low activity such as WO$_3$ or Fe$_2$O$_3$ [2]. Attempts to sensitize titania for visible light activity by modification with platinum(IV) or rhodium(III) chloride [3], by “doping” TiO$_2$ with transition metals [4] or non-metals, e.g. N [5 – 19], C [20 – 23] and S [24, 25] were more successful. A different approach has been followed by investigating the photocatalytic properties of more complicated inorganic materials like the ternary and quaternary compounds AgIn$_3$S$_8$ and BiCu$_2$PO$_6$ [26, 27]. However, the challenge has remained to find a binary unmodified semiconductor oxide exhibiting high visible light activity. Previously, Zhang et al. reported that $\alpha$-Bi$_2$O$_3$ enables methyl orange degradation upon irradiation at $\lambda \geq 400$ nm [28]. It is noted, however, that under these experimental conditions not only bismuth oxide, which starts absorbing at 450 – 430 nm, but also methyl orange ($\lambda_{\text{max}} \approx 500$ nm) may absorb the light. And therefore not the semiconductor but the dye may be excited, in which case bismuth oxide only acts as an electron relay preventing charge recombination.

Recently we found that irradiation of the self-prepared $\alpha$-Bi$_2$O$_3$ at $\lambda \geq 455$ nm assists, but not catalyzes, the mineralization of phenol and 4-chlorophenol (4-CP) [29]. Under these experimental conditions only the semiconductor and not the model pollutant absorbed the light. However, upon multiple uses, $\alpha$-Bi$_2$O$_3$ underwent photocorrosion to a mixture of various bismuth carbonates. To find out whether another crystalline phase of bismuth oxide is more photostable, the intensely yellow $\beta$-modification was also investigated. Due to its oxide ion conductivity, $\beta$-Bi$_2$O$_3$ has hitherto predominantly attracted attention in materials science [30, 31]. This modification which is usually a metastable high-temperature phase, undergoes transformation to $\alpha$-Bi$_2$O$_3$ upon cooling to r. t. [32]. However, $\beta$-Bi$_2$O$_3$ could successfully be stabilized by applying a citrate gel preparation method [33], by incor-
poration of rare earth metals or PbF$_2$ [34–36], and by thermal decomposition of basic bismuth carbonate or oxalate [37, 38]. To the best of our knowledge, no report on its photoactivity has appeared in the literature up to now. Herein we report on the preparation of $\beta$-Bi$_2$O$_3$ by thermal decomposition of (BiO)$_2$CO$_3$, on its photoelectrochemical characterization, and on its photostability in the mineralization of 4-CP and phenol induced by visible light ($\lambda \geq 455$ nm).

Results and Discussion

Characterization

Bright-yellow $\beta$-Bi$_2$O$_3$ was obtained by calcination of bismuthyl carbonate at 400 °C. According to XRD analysis only the desired modification was formed, and no lines of $\alpha$-Bi$_2$O$_3$ could be detected (Fig. 1). An average particle size of 41 nm was estimated by applying the Scherrer equation to the main peak at (201).

Fig. 2a displays the diffuse reflectance spectrum of $\beta$-Bi$_2$O$_3$. The band gap energy ($E_g$) was determined by extrapolation of the linear decrease of the modified Kubelka-Munk function as depicted in Fig. 2 assuming b) an indirect or c) a direct band-to-band transition. Values of 2.3 eV were obtained for an indirect and 2.7 eV for a direct transition. For $\beta$-bismuth oxide thin films corresponding values of 1.74 ± 0.05 and 2.6 ± 0.02 eV were reported [39, 40].

The flattened absorption profile of the diffuse reflectance spectrum (Fig. 2a) supports an indirect transition as already proposed [39, 41]. Thus, for the self-prepared $\beta$-Bi$_2$O$_3$ a band gap energy of 2.3 eV is selected. For calculation of the valence band edge potential ($E_{VB}$) it is assumed that the oxide is an n-type semiconductor and that the quasi Fermi level of electrons ($nE_{F^*}$) is equal to the conduction band edge. $E_{VB}$

$$E_{VB} = nE_{F^*} + E_g.$$  

(1)

Determination of $nE_{F^*}$ was performed by measuring the photovoltage generated upon irradiation of a $\beta$-Bi$_2$O$_3$/(DP)Br$_2$ [42] suspension as a function of the corresponding pH value (see Experimental Section) [43]. By increasing the pH value the quasi-Fermi level is shifted cathodically. When it reaches the pH-independent potential of the reversible redox system (DP)Br$_2$ ($-0.27$ V), the voltage increases and the voltage/current curve exhibits an inflection point when
Photovoltage of a $\beta$-Bi$_2$O$_3$ suspension as a function of the pH value.

$E_{\text{F}^{*}} = -0.27$ V. The corresponding pH value, usually labeled as pH$_0$, is located at 6.8 (Fig. 3). $E_{\text{F}^{*}}$ at pH = 7 was calculated according to [44]

$E_{\text{F}^{*}} (\text{pH 7}) = -0.27 + k (\text{pH}_0 - 7)$,  

where the constant $k$ is assumed to be $0.060 \pm 0.005$ V, as found for $\alpha$-Bi$_2$O$_3$ [29], and identical (within experimental error) with the 0.059 V value reported for most metal oxides [45]. Together with the measured band gap energy of 2.3 eV an $E_{\text{VB}}$ value of $2.02 \pm 0.05$ V is finally obtained through Eq. (1).

Visible light degradation of phenol and 4-chlorophenol (4-CP)

Firstly, the dependence of the degradation rate on the amount of $\beta$-Bi$_2$O$_3$ was investigated to ensure maximum light absorption under the given experimental conditions ($\lambda \geq 455$ nm), thus making reaction rates comparable. As expected, after a steep increase, the rate becomes independent of the photocatalyst concentration at about $2 \text{ g L}^{-1}$, which was therefore employed in all experiments (Fig. 4).

Standard irradiation at $\lambda \geq 455$ nm for 2 h in the presence of air induced 94% mineralization of 4-CP (Fig. 5), whereas no reaction occurred when the process was conducted under dinitrogen. This excludes the possibility that bismuth oxide acts as an oxidizing agent. When the experiment was conducted in the dark, only a weak adsorption of 4-CP and no oxidation was observed ($\approx 10\%$).

To investigate if $\beta$-Bi$_2$O$_3$ may also undergo photocorrosion similar to $\alpha$-Bi$_2$O$_3$ [29], a defined amount was re-used in a series of phenol mineralization reactions. Phenol was selected instead of 4-CP since with phenol no hydrogen chloride is produced, which may influence the photoreaction [46, 47]. To minimize substance loss, the usually applied cylindrical irradiation vessel was replaced by a centrifugation tube. This enabled easy separation of the photocatalyst powder by centrifugation. Whereas the activity remained constant during the first three repetitions, it decreased thereafter and completely vanished at the seventh reaction cycle. When the latter was repeated at $\lambda \geq 420$ nm, still no degradation was observed (Fig. 6).
This hitherto unknown photochemical conversion of \( \beta \)-Bi\(_2\)O\(_3\) to \( \alpha \)-Bi\(_2\)O\(_3\) can be rationalized by comparison with the thermal transformation [48]. In the latter it was proposed that molecular oxygen evolution at 445 – 560 \(^\circ\)C originates from the removal of overstochiometric oxide [49] inducing the restructuring to \( \alpha \)-Bi\(_2\)O\(_3\). It seems likely that the photogenerated holes preferentially oxidize these ions to oxygen escaping from the solid. This process destabilizes the crystal structure resulting in a conversion to the more stable, but here inactive, \( \alpha \)-modification. As reported earlier, \( \alpha \)-Bi\(_2\)O\(_3\) exhibits significant photoactivity only when special preparation conditions were followed [29].

**Conclusion**

\( \beta \)-Bismuth trioxide in the form of about 41 nm large crystallites was prepared by thermal decomposition of (BiO)\(_2\)CO\(_3\) at 400 \(^\circ\)C. From the band gap energy of 2.3 eV and the quasi-Fermi level of \(-0.28 \pm 0.02\) V (vs. NHE) a valence band edge position of about 2.02 V was obtained. This semiconducting oxide assists a fast Vis light (\( \lambda \geq 455\) nm) aerial mineralization of phenol and 4-chlorophenol exhibiting maximum rates at bismuth oxide concentrations of at least 2.0 g L\(^{-1}\). However, the reaction is not catalytic since photocorrosion of \( \beta \)-Bi\(_2\)O\(_3\) to \( \alpha \)-Bi\(_2\)O\(_3\) and various bismuth carbonates occurs upon multiple use. In the absence of oxygen no mineralization was observed, excluding the possibility that \( \beta \)-Bi\(_2\)O\(_3\) acts as an oxidizing agent.

**Experimental Section**

**Chemicals and equipment**

All experiments were performed under air. As starting material of the \( \beta \)-Bi\(_2\)O\(_3\) synthesis, (BiO)\(_2\)CO\(_3\) (purum p. a.), 4-chlorophenol (4-CP, purum), and phenol (puriss. p. a.) were purchased from Fluka. 4,5-Dihydro-3a,5a-diazapyrenium dibromide ((DP)Br\(_2\), \( E_{\text{red}} = -0.27\) V vs. NHE) used in quasi-Fermi potential measurements as pH-independent electron acceptor was prepared according to the literature [39].

The photodegradation experiments were performed in a cylindrical Solidex glass vessel which was positioned in the focus of an Osram XBO 150 W xenon lamp installed in a light-focusing lamp housing (AMKO, PTI A 1010S). The beam passed a water IR and a 455 nm cut-off filter (\( P_{\text{tot}} = 950 \pm 100\) W m\(^{-2}\)) before reaching the reaction mixture. For the quasi-Fermi level measurements a similar set up without cut-off filter (full light irradiation, \( \lambda \geq 390\) nm, \( P_{\text{tot}} = 1200 \pm 100\) W m\(^{-2}\) with AM 1.0 filter) was used. Changes in 4-CP concentration were monitored by absorbance measurements on a Varian CARY 50 Conc UV/Vis spectrometer.
(ε₂₅₀μm = 4000 L mol⁻¹ cm⁻¹). Initial rates (r_i) were calculated from the decrease of the 4-CP concentration in one hour. Mineralization of 4-CP was followed by total carbon content (TC) and inorganic carbon content (IC) measurements applying a Shimadzu Total Carbon Analyzer TOC-500/5050 with a NDIR optical detector system. The total organic carbon content (TOC) was calculated by subtraction of the IC values from the corresponding TC values. Intensity of light (Φ_in, λ ≤ 1100 nm) was determined by a MacSolar-E device (Solarc, calibration: IEC904/3). For XRD analysis a Philips X’Pert PW 3040/60 instrument was used. Diffuse reflectance spectra were recorded on a Shimadzu UV-2401PC UV/Vis scanning spectrometer equipped with a diffuse reflectance accessory. For sample preparation a mixture of 50 mg of β-Bi₂O₃ (0.11 mmol) and 2.0 g of BaSO₄ (8.58 mmol, Fluka) was ground homogeneously, pressed to a pellet, and analyzed. The reflectance of pure BaSO₄ served as a reference. The obtained diffuse reflectance was converted to F(R_a) values according to the Kubelka-Munk theory using the instrument software. The band gap energy was acquired from the extrapolation of the linear part of the [F(R_a)E]²/2 or [F(R_a)E]² versus energy (E) plot, assuming an indirect or direct nature of the optical band-to-band transition, respectively.

Preparation of β-Bi₂O₃

The preparation process of β-Bi₂O₃ is based on a method described by Blower and Greaves [37]. First 5.0 g (10 mmol) of Bi₂O₃CO₃ was suspended in 100 mL H₂O and refluxed for three hours. Then the suspension was cooled to r.t. and stirred over night. The colorless powder was filtered off, washed three times with about 100 mL of H₂O and dried at 100 °C. After calcining the colorless crude product at 400 °C for one hour in a tubular furnace the intensely yellow β-Bi₂O₃ was obtained. In ref. [37] (BiO)₂CO₃ was freshly prepared and immediately calcined thereafter at 377 °C for about 1.5 h in an alumina boat.

Degradation experiments

The solidex glass vessel was filled with a mixture of 40 mg of β-Bi₂O₃ (2.0 g L⁻¹, 0.09 mmol) and 20 mL of aqueous 4-CP solution (2.5 × 10⁻⁴ mol L⁻¹). In order to reach a homogeneous suspension the mixture was kept for 30 s in an ultrasonic bath before it was irradiated with visible light (λ ≥ 455 nm) under vigorous stirring. Samples were taken shortly before the illumination was started, and continuously every 30 min during the experiment. After two hours the experiment was stopped. The photoactive material was filtered off with a nanopore filter (Rotilabo, 0.22 µm) and the carbon content of the filtrate was determined by TOC measurements.

Quasi-Fermi level measurements

The quasi-Fermi level of electrons (ε_F*) was obtained by measuring the photovoltage as a function of the pH value, based on a method developed by Roy et al. [3, 40]. The experimental set-up consisted of an electrochemical cell (pH-meter, Pt working electrode, Ag/AgCl reference electrode), which was filled with a mixture of 50 mg of β-Bi₂O₃, 15 mg of (DP)Br and 50 mL of aqueous KNO₃ solution (0.1 mol L⁻¹). The resulting suspension was first acidified to pH = 3 with diluted HNO₃ and purged with nitrogen for about one hour under full light irradiation. Thereafter the procedure was as follows: (1) The photocurrent and pH values were noted, (2) diluted NaOH (0.01 and 0.001 mol L⁻¹) was dropped into the mixture to attain a pH change of 0.2 – 0.4 units, and (3) after two minutes the photocurrent and pH values were noted, and diluted NaOH was added again similar to step 2. This procedure was repeated until a pH value of about 10 was reached.

Photocorrosion test

In a centrifugation tube 50 mg of β-Bi₂O₃ (2.5 g L⁻¹) was suspended in a mixture of 20 mL of aqueous phenol solution (3.13 × 10⁻⁴ M) and 5 mL of H₂O to reach an overall phenol concentration of 2.5 × 10⁻⁴ M. The reaction mixture was centrifuged, and 5 mL of the supernatant were taken out and analyzed by TC and IC measurements. The residual suspension was irradiated for two hours using either a 455 nm or a 420 nm cut-off filter. After each experiment the suspension was centrifuged, and 15 mL of the supernatant were removed and again analyzed. To the remaining bismuth trioxide suspension in the centrifugation tube 20 mL of aqueous phenol solution was added. After centrifugation, 5 mL of the supernatant was taken out and analyzed. Then the remaining 20 mL of the reaction mixture were irradiated again for two hours. This procedure was repeated several times until mineralization became negligible.

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