Mineralization of Phenol and 4-Chlorophenol Induced by Visible Light and Assisted by Semiconducting β-Bi_2O_3

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

Intensely yellow β-bismuth trioxide in the form of about 41 nm large crystallites has been prepared by thermal decomposition of $(BiO)_2CO_3$ at 400 °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 ± 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 β-Bi_2O_3 does not act as oxidizing agent. The mineralization suffers from photocorrosion of β-Bi_2O_3 generating a mixture of α-Bi_2O_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_2O_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 $AgIn_5S_8$ and $BiCu_2PO_6$ [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 α-Bi_2O_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 ($\lambda_{max} \approx 500$ 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 α-Bi_2O_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, α-Bi_2O_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 β-modification was also investigated. Due to its oxide ion conductivity, β-Bi_2O_3 has hitherto predominantly attracted attention in materials science [30, 31]. This modification which is usually a metastable high-temperature phase, undergoes transformation to α-Bi_2O_3 upon cooling to r. t. [32]. However, β-Bi_2O_3 could successfully be stabilized by applying a citrate gel preparation method [33], by incorporation 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 β-Bi_2O_3 by thermal decomposition of $(BiO)_2CO_3$, 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 β-Bi_2O_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 α-Bi_2O_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 β-Bi_2O_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 β-bismuth oxide thin films corresponding values of 1.74 ± 0.05 and 2.6 ± 0.02 eV were reported [39, 40].

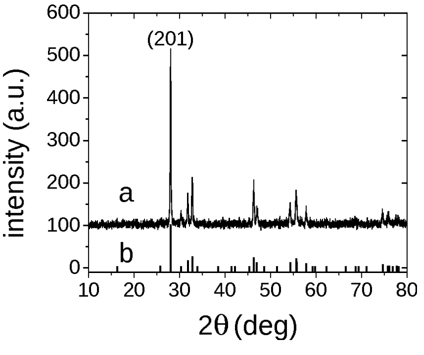

Fig. 1. a) XRD spectrum of β-Bi_2O_3 and b) the reference signals from the JCPDS file 27-50 (β-Bi_2O_3).

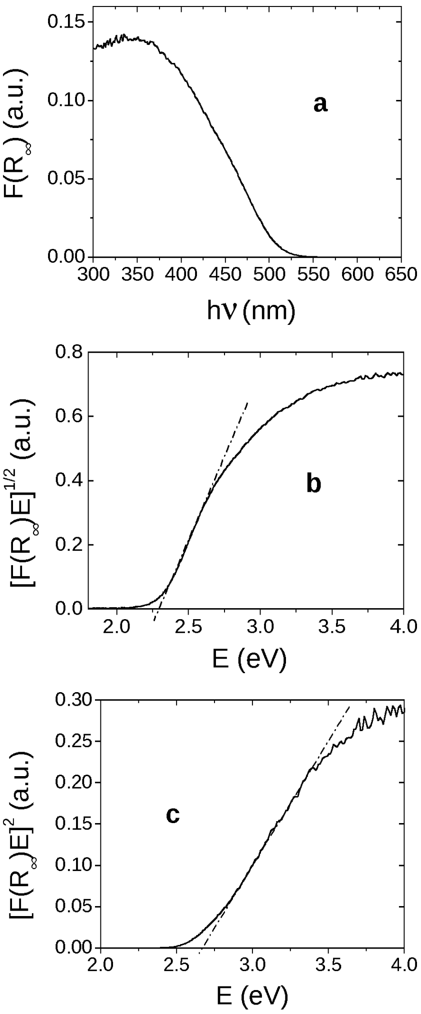

Fig. 2. (a) Diffuse reflectance spectrum of β-Bi_2O_3. The Kubelka-Munk function $F(R_\infty)$ is equivalent to absorbance. Plot of the modified Kubelka-Munk function *vs.* light energy to obtain the band gap energy for the case of an indirect (b) and a direct (c) band-to-band transition.

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 β-Bi_2O_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} is obtained by using

$$E_{VB} = {}_nE_F{}^* + E_g. \qquad (1)$$

Determination of ${}_nE_F{}^*$ was performed by measuring the photovoltage generated upon irradiation of a β-Bi_2O_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

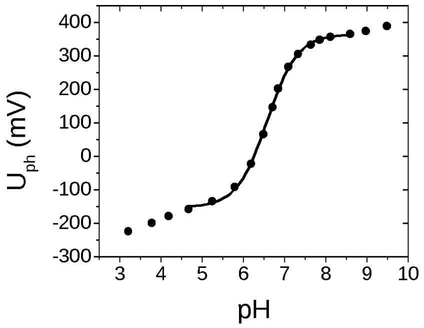

Fig. 3. Photovoltage of a β-Bi_2O_3 suspension as a function of the pH value.

${}_{n}E_F{}^* = -0.27$ V. The corresponding pH value, usually labeled as pH_0, is located at 6.8 (Fig. 3). ${}_{n}E_F{}^*$ at pH = 7 was calculated according to [44]

$$ {}_{n}E_F{}^* \,(\mathrm{pH}\,7) = -0.27\,\mathrm{V} + k\,(\mathrm{pH}_0 - 7), \qquad (2) $$

where the constant k is assumed to be 0.060 ± 0.005 V, as found for α-Bi_2O_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_{VB} value of 2.02 ± 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 β-Bi_2O_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 g L^{-1}, which was therefore employed in all experiments (Fig. 4).

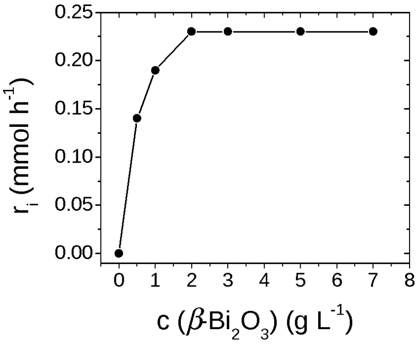

Fig. 4. Dependence of the initial rate r_i of the 4-CP disappearance on the β-Bi_2O_3 concentration, $\lambda \geq 455$ nm.

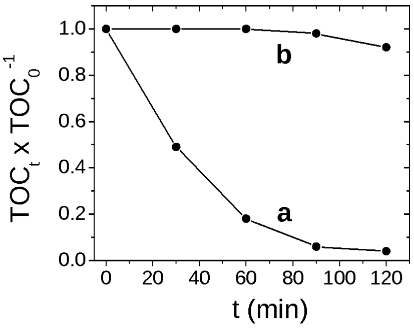

Fig. 5. Variation of relative TOC values with irradiation time in the presence of β-Bi_2O_3; (a) with and (b) without irradiation ($\lambda \geq 455$ nm).

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 (≈ 10 %).

To investigate if β-Bi_2O_3 may also undergo photocorrosion similar to α-Bi_2O_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).

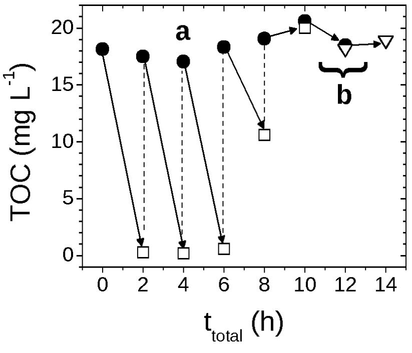

Fig. 6. Sequential mineralization of phenol assisted by β-Bi_2O_3; (a) $\lambda \geq 455$ nm or (b) $\lambda \geq 420$ nm.

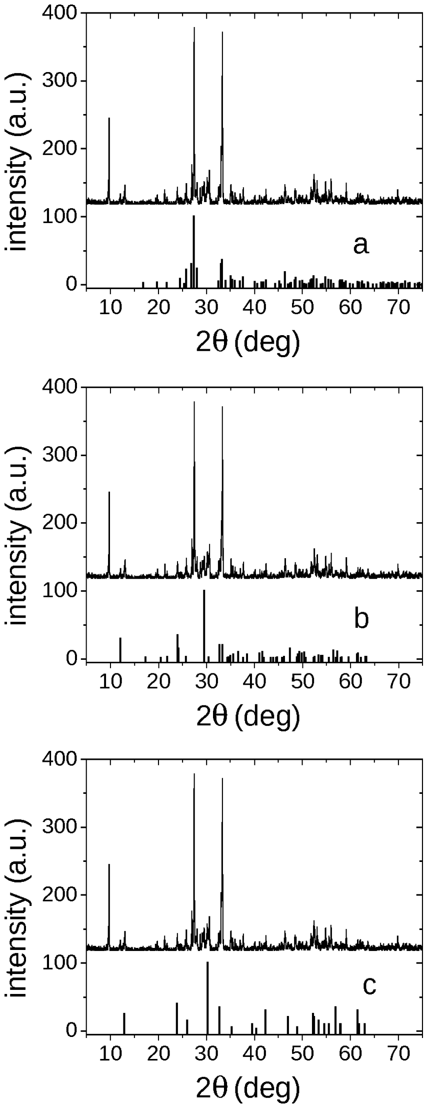

Fig. 7. XRD patterns of β-Bi_2O_3 photocorrosion products. Line patterns correspond to the ASTM data files (a) 71-2274 (α-Bi_2O_3), (b) 38-0579 ($(BiO)_2CO_3(OH)_2$), and (c) 41-1488 ($(BiO)_2CO_3$).

At the end of this multiple use experiment the color of β-Bi_2O_3 had changed from bright-yellow to beige. XRD analysis of the residue revealed the presence of α-Bi_2O_3 (Fig. 7a) and small amounts of $(BiO)_4CO_3(OH)_2$ (Fig. 7b) and $(BiO)_2CO_3$ (Fig. 7c). Unfortunately, the intense line at 10° could not be assigned. Formation of the carbonates originates from carbon dioxide generated during phenol mineralization. Similar carbonate peaks were observed in the α-Bi_2O_3 photocorrosion products [29].

This hitherto unknown photochemical conversion of β-Bi_2O_3 to α-Bi_2O_3 can be rationalized by comparison with the *thermal* transformation [48]. In the latter it was proposed that molecular oxygen evolution at 445 – 560 °C originates from the removal of overstoichiometric oxide [49] inducing the restructuring to α-Bi_2O_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, α-modification. As reported earlier, α-Bi_2O_3 exhibits significant photoactivity only when special preparation conditions were followed [29].

Conclusion

β-Bismuth trioxide in the form of about 41 nm large crystallites was prepared by thermal decomposition of $(BiO)_2CO_3$ at 400 °C. From the band gap energy of 2.3 eV and the quasi-Fermi level of -0.28 ± 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 β-Bi_2O_3 to α-Bi_2O_3 and various bismuth carbonates occurs upon multiple use. In the absence of oxygen no mineralization was observed, excluding the possibility that β-Bi_2O_3 acts as an oxidizing agent.

Experimental Section

Chemicals and equipment

All experiments were performed under air. As starting material of the β-Bi_2O_3 synthesis, $(BiO)_2CO_3$ (purum *p. a.*), 4-chlorophenol (4-CP, purum), and phenol (puriss. *p. a.*) were purchased from Fluka. 4,5-Dihydro-3a,5a-diazapyrenium dibromide ($(DP)Br_2$, $E_{red} = -0.27$ 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_{tot} = 950 ± 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_{tot} = 1200 ± 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

($\varepsilon_{225\text{nm}}$ = 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 (P_{tot}, $\lambda \leq 1100$ nm) was determined by a MacSolar-E device (Solarc, calibration: IEC904/3). For XRD analysis a Phillips 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-Bi_2O_3 (0.11 mmol) and 2.0 g of $BaSO_4$ (8.58 mmol, Fluka) was ground homogeneously, pressed to a pellet, and analyzed. The reflectance of pure $BaSO_4$ served as a reference. The obtained diffuse reflectance was converted to $F(R_\infty)$ 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 $[F(R_\infty)E]^{1/2}$ or $[F(R_\infty)E]^2$ *versus* energy (E) plot, assuming an indirect or direct nature of the optical band-to-band transition, respectively.

Preparation of β-Bi$_2$O$_3$

The preparation process of β-Bi_2O_3 is based on a method described by Blower and Greaves [37]. First 5.0 g (10 mmol) of $(BiO)_2CO_3$ was suspended in 100 mL H_2O 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 H_2O 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-Bi_2O_3 was obtained. In ref. [37] $(BiO)_2CO_3$ 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-Bi_2O_3 (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 ($\lambda \geq 455$ 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 ($_nE_F{}^*$) 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-Bi_2O_3, 15 mg of $(DP)Br_2$ and 50 mL of aqueous KNO_3 solution (0.1 mol L^{-1}). The resulting suspension was first acidified to pH = 3 with diluted HNO_3 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-Bi_2O_3 (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 H_2O 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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