

Photocatalytic Degradation of 4-n-Nonylphenol under Irradiation from Solar Simulator: Comparison between BiVO₄ and TiO₂ Photocatalysts

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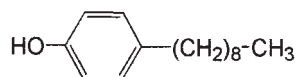
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A toxic endocrine disruptor, 4-n-nonylphenol, was degraded using a well-known TiO₂ and a visible-light-driven BiVO₄ photocatalyst under irradiation from a solar simulator. The degradation rates for both BiVO₄ and TiO₂ are comparable in air-saturated solution though surface area of BiVO₄ is much smaller than that of TiO₂. This fact indicates that BiVO₄ has a great ability to degrade alkylphenols in wastewater under solar light.

Non-ionic surfactant alkylphenolpolyethoxylates (APOEs) have been used in a wide variety of industrial, household, and commercial applications. It should be noted that bio-degradation of APOEs in sewage treatment may generate alkylphenols such as nonyl- and octylphenols¹ which are toxic to freshwater species² and have properties of weak estrogenic activities.³ Alkylphenols have been widely distributed in rivers and lakes in some countries.⁴

In order to remove organic pollutants from environments, photocatalytic degradations have been extensively studied.^{5–7} It has been demonstrated that nonylphenol and its ethoxylated surfactants are efficiently degraded and finally mineralized to CO₂ and H₂O using TiO₂,^{8,9} the photocatalysis of which works only under UV light. On the other hand, BiVO₄ photocatalyst has been recently found to evolve O₂ gas by oxidation of H₂O in silver nitrate solution under visible light.^{10,11} BiVO₄ is therefore expected to possess high oxidation activity for degradation of organic pollutants under solar light.

In this letter, we report photocatalytic activity of BiVO₄ for degradation of linear alkyl 4-n-nonylphenol (NP) under visible and solar light. Comparison between BiVO₄ and TiO₂ is investigated for the following points: (1) photodegradation rates of NP, (2) CO₂ mineralization yields, and (3) O₂ concentration effects on the photocatalysis.



Structure of 4-n-nonylphenol (NP)

NP (Kanto Chemical, purity 99.5%) and TiO₂ powder (Degussa P25) were used as received. BiVO₄ powder was synthesized in an aqueous medium.¹² X-ray diffraction patterns of the synthesized BiVO₄ indicate a monoclinic scheelite structure as reported.^{10,11} BET surface areas of BiVO₄ and TiO₂ are 0.2 and 54 m²/g, respectively. The surface area of TiO₂ is 270 times larger than that of BiVO₄.

Figure 1 shows diffuse reflectance spectra of BiVO₄ and TiO₂ powders. It is obvious that BiVO₄ absorbs visible light (400–

525 nm) whereas TiO₂ absorbs only UV light (<400 nm). For the monoclinic scheelite BiVO₄, the visible absorption band of BiVO₄ is assigned to the transition from a valence band formed by Bi_{6s} or a hybrid orbital of Bi_{6s} and O_{2p} to a conduction band of V_{3d}.¹⁰ The photocatalytic activity for O₂ evolution from an aqueous AgNO₃ solution is accompanied with photoexcitation of this visible band.^{10,11}

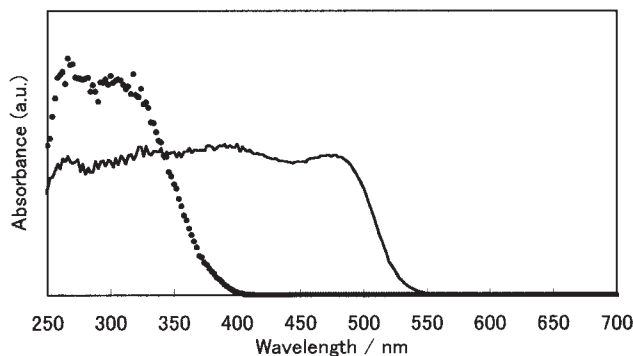


Figure 1. Diffuse reflectance spectra of BiVO₄ (solid) and TiO₂ (dotted).

NP sample solutions (2×10^{-4} mol/dm³) were prepared by adding BiVO₄ or TiO₂ powder (0.2 g) to 25 cm³ of NaOH aqueous solution (pH 13) and sealed in a cylindrical quartz cell (45 mm i.d. \times 50 mm) with a rubber septum. A solar simulator (Oriol 81192) equipped with an AM2DB air mass filter was employed as the light source. The intensity was 24 mW/cm², measured by a thermopile sensor (Coherent 210). Prior to irradiation, the samples were kept stirring for 1 h in the dark.

Figure 2 indicates time courses of NP photodegradation by BiVO₄ and TiO₂ in air- and O₂-saturated alkaline solutions under irradiation from the solar simulator. In air-saturated solution, NP is almost degraded within 1 h for both BiVO₄ and TiO₂. The NP degradation rate for BiVO₄ is coincident with that for TiO₂. A control experiment in the absence of semiconductor powders shows that the NP degradation was not observed within 1 h. In O₂-saturated solution, the degradation rate for BiVO₄ is faster than that for TiO₂ as shown in Figure 2. BiVO₄ is thus more useful in the presence of sufficient amount of O₂ in solution. In the dark with the presence of BiVO₄ or TiO₂ powder, NP concentrations were slightly decreased (about 10%) after 3.5 h, which is probably due to adsorption of NP on semiconductor surface.

The NP photodegradation using BiVO₄ under visible light irradiation (>400 nm) was also examined in N₂-, air-, and O₂-saturated alkaline solutions.¹³ The degradation is also observed in

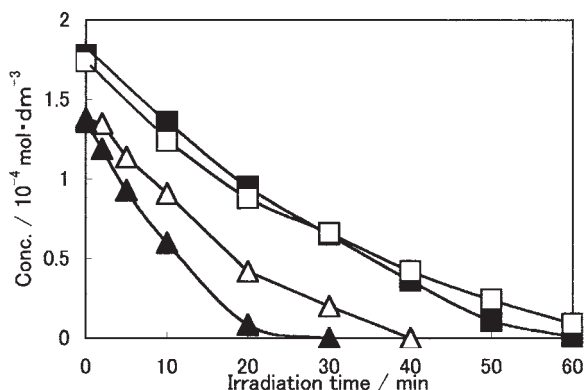


Figure 2. Photocatalytic degradation of NP in air- and O₂-saturated alkaline solutions under irradiation from a solar simulator (24 mW/cm²): BiVO₄/air (■), TiO₂/air (□), BiVO₄/O₂ (▲), and TiO₂/O₂ (△). NP concentrations were determined by a reverse-phase HPLC system equipped with Supelco TPR-100 column (4.6 mm i.d. × 150 mm, at 308 K). The mobile phase was an acetonitrile/water (3 : 1) at a flow rate of 0.5 cm³/min. A chromatogram was monitored at 280 nm. Valerophenone was used as an internal standard.

air- and O₂-saturated solutions. The photocatalytic activity is thus ascribed to photoexcitation of the visible absorption band of BiVO₄. Assuming that the NP degradation follows pseudo-first order kinetics, rate constants in air- and O₂-saturated solution are determined to be 0.72 and 1.62 h⁻¹, respectively. The value in O₂-saturated solution is 2.3 times faster than that in air saturated solution. On the contrary, the rate constant in N₂-saturated solution (0.04 h⁻¹) becomes very small compared to those in air- and O₂-saturated solutions. These results indicate that the photodegradation of NP using BiVO₄ is sensitive to the concentration of O₂ dissolved in solution.

CO₂ and CO evolution under irradiation from the solar simulator was investigated.¹⁴ CO₂ mineralization yields for TiO₂ are monotonically increased and reached 24% (total amount of evolved CO₂ is 0.40 cm³) after 5 h irradiation. The CO₂ evolution is thus efficient for TiO₂ as reported by Pelizzetti et al.⁸ and Horikoshi et al.⁹ In addition, a small amount of CO evolution (ca. 0.02 cm³) was also observed from the TiO₂ solution. However neither CO₂ nor CO gas was detected in BiVO₄ suspended solution within 5 h irradiation. This result is explained in terms of valence band position of BiVO₄. Since the conduction band edge of BiVO₄ is located at ca. 0 V vs NHE (pH 0), the valence band edge of BiVO₄ is predicted to be at ca. +2.4 V vs NHE, which is considerably negative potential compared to the valence band edge of TiO₂ (ca. +3 V vs NHE at pH 0).¹⁰ Therefore, photooxidation power of BiVO₄ is lower than that of TiO₂ so that mineralization to CO₂ was not observed in the present study.

Although complete ring-opening cleavage of the NP aromatic ring is confirmed by UV absorption change in the irradiated BiVO₄ solution, photoproducts have not yet been identified. Formic and acetic acids were identified as intermediates in an irradiated TiO₂ solution.⁹ However neither formic nor acetic acid was detected in the BiVO₄ solution by means of indirect photometric ion chromatography.¹⁵ Experimental endeavors to identify photoproducts are in progress.

In conclusion, three remarkable properties of BiVO₄ are clarified on the photocatalytic degradation of NP. (1) The NP

degradation occurs upon photoexcitation of the visible band of BiVO₄, which is strongly affected by O₂ concentration in the solution. (2) CO₂ mineralization is efficient in TiO₂ suspended solution but not observed for BiVO₄ because the potential of the valence band edge of BiVO₄ is more negative than that of TiO₂. (3) Surface area of our synthesized BiVO₄ is much smaller than that of TiO₂. Nevertheless, BiVO₄ shows comparable photocatalytic activity for degradation of NP under irradiation from the solar simulator. This photocatalytic activity of BiVO₄ can be improved by expanding surface area, calcinations, and loading co-catalysts.

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- Aqueous equimolar Bi(NO₃)₃·5H₂O and NH₄VO₃ solutions (0.4 mol/dm³) containing HNO₃ (1.84 mol/dm³) were prepared separately. After these two 100 cm³ solutions were mixed, 7.5 g of urea was added. The mixed solution was then stirred at 363 K for 8 h. The BiVO₄ precipitation formed by the hydrolysis was washed by water, filtered, and dried at 318 K.
- A 500-W Xenon arc lamp with a Toshiba L42 glass filter was used as visible light source (9 mW/cm²).
- The CO₂ and CO evolution during irradiation was followed by gas chromatography. After irradiation from the solar simulator, 0.25 cm³ of 2.5 mol/dm³ sulfuric acid was added to the sample through the rubber septum by use of a syringe. When thermal equilibrium was reached at 298 K, CO₂ and CO evolved in head space were collected by a gas-tight syringe through the rubber septum and analyzed using a gas chromatograph equipped with a Porapak Q column, a methanizer, and a flame-ionized detector with N₂ as the carrier gas.
- K. Hayakawa and M. Miyazaki, *Bunseki* (in Japanese), **1991**, 47. The anion exchange MCI GEL SCA02 column (6.0 mm i.d. × 50 mm) was used at 298 K. The mobile phase was a potassium hydrogen phthalate aqueous solution (0.5 mol/dm³) at a flow rate of 1 cm³/min. A chromatogram was monitored as negative peaks at 280 nm.