

Photocatalytic Degradation of 4-n-Nonylphenol under Irradiation from Solar Simulator: Comparison between BiVO_4 and TiO_2 Photocatalysts

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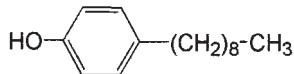
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A toxic endocrine disruptor, 4-n-nonylphenol, was degraded using a well-known TiO_2 and a visible-light-driven BiVO_4 photocatalyst under irradiation from a solar simulator. The degradation rates for both BiVO_4 and TiO_2 are comparable in air-saturated solution though surface area of BiVO_4 is much smaller than that of TiO_2 . This fact indicates that BiVO_4 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 CO_2 and H_2O using TiO_2 ,^{8,9} the photocatalysis of which works only under UV light. On the other hand, BiVO_4 photocatalyst has been recently found to evolve O_2 gas by oxidation of H_2O in silver nitrate solution under visible light.^{10,11} BiVO_4 is therefore expected to possess high oxidation activity for degradation of organic pollutants under solar light.

In this letter, we report photocatalytic activity of BiVO_4 for degradation of linear alkyl 4-n-nonylphenol (NP) under visible and solar light. Comparison between BiVO_4 and TiO_2 is investigated for the following points: (1) photodegradation rates of NP, (2) CO_2 mineralization yields, and (3) O_2 concentration effects on the photocatalysis.



Structure of 4-n-nonylphenol (NP)

NP (Kanto Chemical, purity 99.5%) and TiO_2 powder (Degussa P25) were used as received. BiVO_4 powder was synthesized in an aqueous medium.¹² X-ray diffraction patterns of the synthesized BiVO_4 indicate a monoclinic scheelite structure as reported.^{10,11} BET surface areas of BiVO_4 and TiO_2 are 0.2 and 54 m^2/g , respectively. The surface area of TiO_2 is 270 times larger than that of BiVO_4 .

Figure 1 shows diffuse reflectance spectra of BiVO_4 and TiO_2 powders. It is obvious that BiVO_4 absorbs visible light (400–

525 nm) whereas TiO_2 absorbs only UV light (<400 nm). For the monoclinic scheelite BiVO_4 , the visible absorption band of BiVO_4 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 O_2 evolution from an aqueous AgNO_3 solution is accompanied with photoexcitation of this visible band.^{10,11}

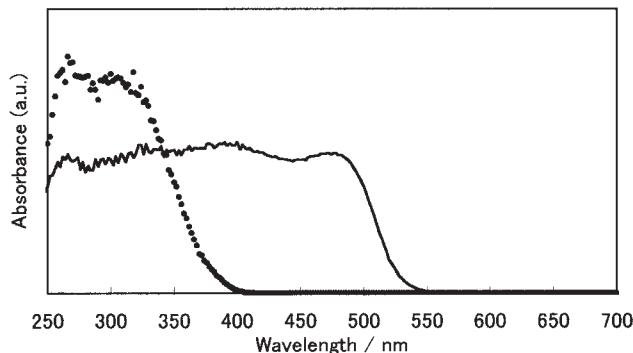


Figure 1. Diffuse reflectance spectra of BiVO_4 (solid) and TiO_2 (dotted).

NP sample solutions ($2 \times 10^{-4} \text{ mol}/\text{dm}^3$) were prepared by adding BiVO_4 or TiO_2 powder (0.2 g) to 25 cm^3 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 (Oriel 81192) equipped with an AM2DB air mass filter was employed as the light source. The intensity was 24 mW/cm^2 , 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 BiVO_4 and TiO_2 in air- and O_2 -saturated alkaline solutions under irradiation from the solar simulator. In air-saturated solution, NP is almost degraded within 1 h for both BiVO_4 and TiO_2 . The NP degradation rate for BiVO_4 is coincident with that for TiO_2 . A control experiment in the absence of semiconductor powders shows that the NP degradation was not observed within 1 h. In O_2 -saturated solution, the degradation rate for BiVO_4 is faster than that for TiO_2 as shown in Figure 2. BiVO_4 is thus more useful in the presence of sufficient amount of O_2 in solution. In the dark with the presence of BiVO_4 or TiO_2 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 BiVO_4 under visible light irradiation (>400 nm) was also examined in N_2 -, air-, and O_2 -saturated alkaline solutions.¹³ The degradation is also observed in

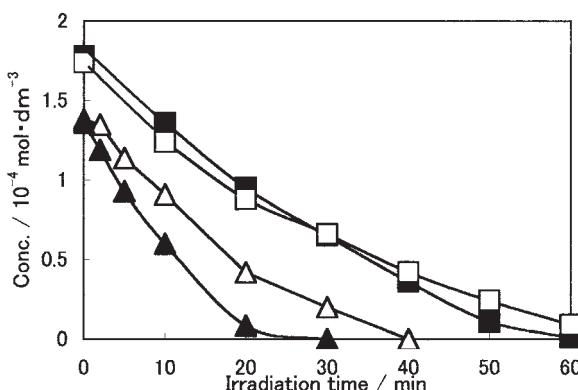


Figure 2. Photocatalytic degradation of NP in air- and O_2 -saturated alkaline solutions under irradiation from a solar simulator (24 mW/cm^2): BiVO_4/air (■), TiO_2/air (□), BiVO_4/O_2 (▲), and TiO_2/O_2 (△). NP concentrations were determined by a reverse-phase HPLC system equipped with Supelco TPR-100 column (4.6 mm i.d. \times 150 mm, at 308 K). The mobile phase was an acetonitrile/water (3 : 1) at a flow rate of $0.5\text{ cm}^3/\text{min}$. A chromatogram was monitored at 280 nm. Valerophenone was used as an internal standard.

air- and O_2 -saturated solutions. The photocatalytic activity is thus ascribed to photoexcitation of the visible absorption band of BiVO_4 . Assuming that the NP degradation follows pseudo-first order kinetics, rate constants in air- and O_2 -saturated solution are determined to be 0.72 and 1.62 h^{-1} , respectively. The value in O_2 -saturated solution is 2.3 times faster than that in air saturated solution. On the contrary, the rate constant in N_2 -saturated solution (0.04 h^{-1}) becomes very small compared to those in air- and O_2 -saturated solutions. These results indicate that the photodegradation of NP using BiVO_4 is sensitive to the concentration of O_2 dissolved in solution.

CO_2 and CO evolution under irradiation from the solar simulator was investigated.¹⁴ CO_2 mineralization yields for TiO_2 are monotonically increased and reached 24% (total amount of evolved CO_2 is 0.40 cm^3) after 5 h irradiation. The CO evolution is thus efficient for TiO_2 as reported by Pelizzetti et al.⁸ and Horikoshi et al.⁹ In addition, a small amount of CO evolution (ca. 0.02 cm^3) was also observed from the TiO_2 solution. However neither CO_2 nor CO gas was detected in BiVO_4 suspended solution within 5 h irradiation. This result is explained in terms of valence band position of BiVO_4 . Since the conduction band edge of BiVO_4 is located at ca. 0 V vs NHE (pH 0), the valence band edge of BiVO_4 is predicted to be at ca. $+2.4\text{ V}$ vs NHE, which is considerably negative potential compared to the valence band edge of TiO_2 (ca. $+3\text{ V}$ vs NHE at pH 0).¹⁰ Therefore, photooxidation power of BiVO_4 is lower than that of TiO_2 so that mineralization to CO_2 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 BiVO_4 solution, photoproducts have not yet been identified. Formic and acetic acids were identified as intermediates in an irradiated TiO_2 solution.⁹ However neither formic nor acetic acid was detected in the BiVO_4 solution by means of indirect photometric ion chromatography.¹⁵ Experimental endeavors to identify photoproducts are in progress.

In conclusion, three remarkable properties of BiVO_4 are clarified on the photocatalytic degradation of NP. (1) The NP

degradation occurs upon photoexcitation of the visible band of BiVO_4 , which is strongly affected by O_2 concentration in the solution. (2) CO_2 mineralization is efficient in TiO_2 suspended solution but not observed for BiVO_4 because the potential of the valence band edge of BiVO_4 is more negative than that of TiO_2 . (3) Surface area of our synthesized BiVO_4 is much smaller than that of TiO_2 . Nevertheless, BiVO_4 shows comparable photocatalytic activity for degradation of NP under irradiation from the solar simulator. This photocatalytic activity of BiVO_4 can be improved by expanding surface area, calcinations, and loading co-catalysts.

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- 12 Aqueous equimolar $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NH_4VO_3 solutions (0.4 mol/dm^3) containing HNO_3 (1.84 mol/dm^3) were prepared separately. After these two 100 cm^3 solutions were mixed, 7.5 g of urea was added. The mixed solution was then stirred at 363 K for 8 h . The BiVO_4 precipitation formed by the hydrolysis was washed by water, filtered, and dried at 318 K .
- 13 A 500-W Xenon arc lamp with a Toshiba L42 glass filter was used as visible light source (9 mW/cm^2).
- 14 The CO_2 and CO evolution during irradiation was followed by gas chromatography. After irradiation from the solar simulator, 0.25 cm^3 of 2.5 mol/dm^3 sulfuric acid was added to the sample through the rubber septum by use of a syringe. When thermal equilibrium was reached at 298 K , CO_2 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 N_2 as the carrier gas.
- 15 K. Hayakawa and M. Miyazaki, *Bunseki* (in Japanese), **1991**, 47. The anion exchange MCI GEL SCA02 column (6.0 mm i.d. \times 50 mm) was used at 298 K . The mobile phase was a potassium hydrogen phthalate aqueous solution (0.5 mol/dm^3) at a flow rate of $1\text{ cm}^3/\text{min}$. A chromatogram was monitored as negative peaks at 280 nm .