Photocatalytic O_2 evolution under visible light irradiation on $BiVO_4$ in aqueous $AgNO_3$ solution

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$BiVO_4$ with a 2.3 eV band gap showed an activity for O_2 evolution from aqueous solutions containing Ag^+ as an electron scavenger under visible light irradiation ($\lambda > 520$ nm). The quantum yield was 0.5% at 450 nm.

Keywords: photocatalyst, $BiVO_4$, visible light response, O_2 evolution

1. Introduction

It is important to develop new visible-light-driven photocatalysts for achieving artificial photosynthesis. Well-known heterogeneous photocatalysts with reasonable activities under visible light irradiation are only CdS and WO_3 at the present stage. CdS, which possesses a 2.4 eV band gap, can efficiently produce H_2 from aqueous solutions including sacrificial reagents with assistance of a Pt co-catalyst [1], although there are problems of photocorrosion and harm. WO_3 with a 2.8 eV band gap shows an activity for O_2 evolution from aqueous solutions, when including electron scavengers such as Ag^+ and Fe^{3+} [2,3]. $RbPb_2Nb_3O_{10}$ powder with a layered perovskite structure shows photocatalytic activities for H_2 and O_2 evolution reactions under visible light irradiation ($\lambda > 420$ nm) from aqueous solutions with sacrificial reagents [4]. Domen and co-workers have recently reported visible-light-induced water splitting into H_2 and O_2 on Cu_2O powder [5]. However, the number of photocatalyst materials for H_2 and O_2 evolution under visible light irradiation is still limited. Therefore, surveying materials is indispensable for the development of new photocatalysts. Large band gaps of stable oxide semiconductor photocatalysts such as TiO_2 are due to the deep valence band formed by an O_{2p} orbital. The authors have directed their attention to mixed oxides consisting of Bi^{3+} as candidates of new visible-light-driven photocatalyst materials because the 6s orbital of Bi^{3+} may form the valence bands in the mixed oxides containing Bi^{3+}, instead of the O_{2p} orbital [6].

This paper reports the photocatalytic O_2 evolution from aqueous solutions containing Ag^+ as an electron scavenger under visible light irradiation on $BiVO_4$ with a 2.3 eV band gap.

2. Experimental

$BiVO_4$ was synthesized by calcining mixtures of starting materials of Bi_2O_3 (Kanto Chemical, purity 98%) and NH_4VO_3 (Kanto Chemical, purity 99%) at 970 or 1170 K for 5 h in air using an alumina crucible. The synthesized materials were confirmed by X-ray diffraction (Rigaku, LINT-1400). The particle size and surface area were determined by SEM observation and BET measurement, respectively. A diffuse reflection spectrum was obtained by using a UV-vis-NIR spectrometer (JASCO, Ubest-570) and was converted from reflection to absorbance by the Kubelka–Munk method. The photocatalytic O_2 evolution was carried out in a gas-closed circulation system. The photocatalytic activity of $BiVO_4$ was compared with that of WO_3 powder (Nacalai tesque, purity 99.5%) which is a well-known photocatalyst working under visible light irradiation. The catalyst powder (1 g) was dispersed by a magnetic stirrer in an aqueous $AgNO_3$ solution (0.05 mol/l, 300 ml) in a reaction cell made of Pyrex glass. The light source was an ozone-free 300 W Xe illuminator (CERMAX, LX300). Cut off and band pass filters (Kenko, Y42, Y44, Y48, Y52, R56 and BP-45) were employed for visible light irradiation. The quantum yield was determined at 450 nm using a band pass filter (half width 11.5 nm) by a chemical actinometry employed potassium ferrioxalate [7]. The amount of O_2 evolved was determined by using a gas chromatograph (Shimadzu, GC-8A, TCD, Ar carrier).

3. Results and discussion

Figure 1 shows a diffuse reflection spectrum of $BiVO_4$. The onset was around 540 nm, showing that the band gap was ca. 2.3 eV. The color was orange-yellow. The crystal structure was monoclinic. The particle size and surface area were 1–10 μm and ca. 0.7 m^2/g, respectively.

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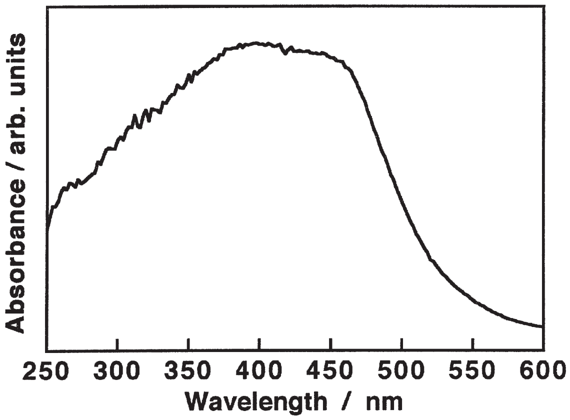

Figure 1. A diffuse reflection spectrum of $BiVO_4$ powder prepared at 970 K.

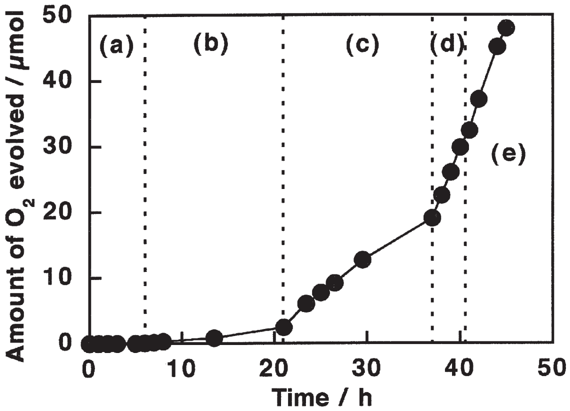

Figure 2. Visible light response for photocatalytic O_2 evolution on $BiVO_4$ powder prepared at 970 K from an aqueous $AgNO_3$ solution. (a) $\lambda >$ 560 nm, (b) $\lambda >$ 520 nm, (c) $\lambda >$ 480 nm, (d) $\lambda >$ 440 nm, (e) $\lambda >$ 420 nm.

Figure 2 shows the yield of photocatalytic O_2 evolution from an aqueous $AgNO_3$ solution for visible light irradiation in the different wave length regions. When a cut-off filter of $\lambda > 560$ nm was used, the activity was negligible. In contrast, O_2 evolution was observed when a cut-off filter of $\lambda > 520$ nm was employed. This action spectrum agreed well with the diffuse reflection spectrum, indicating the reaction proceeding photocatalytically. Thus, it was found that the valence band of $BiVO_4$ has a potential for water oxidation to form O_2. This result suggests that $BiVO_4$ is expected to be available for an O_2 evolution photocatalyst in a two-photon system of a Z scheme. On the other hand, although H_2 evolution from an aqueous methanol solution was attempted in the presence of a Pt co-catalyst, the activity was not obtained, suggesting that the conduction band level of this material was not high enough for the H_2 evolution by H_2O reduction.

Figure 3 shows photocatalytic O_2 evolution on $BiVO_4$ and WO_3 from aqueous $AgNO_3$ solution under visible light irradiation ($\lambda > 420$ nm). The obtained maximum activity of $BiVO_4$ synthesized at 1170 K was 31 μmol/h. The activity of WO_3 was 65 μmol/h when the reaction was carried out in the present experimental condition. The degradation of the activity in both photocatalysts is due to photodeposition of Ag on the surface. This behavior is usually observed for this reaction. The XRD pattern of $BiVO_4$ was not changed after a prolonged reaction (50 h), indicating the catalyst being stable during the reaction. The quantum yield, defined as the number of holes consumed for O_2 evolution of $BiVO_4$ per that of incident photons, was 0.005 at 450 nm. The quantum yield of WO_3 has been reported to be 0.02 under monochromatic irradiation at 405 nm [3]. Although the activity of $BiVO_4$ was lower than that of WO_3 at the present stage, it is noteworthy that the wavelength region of available photon for $BiVO_4$ is wider than that for WO_3.

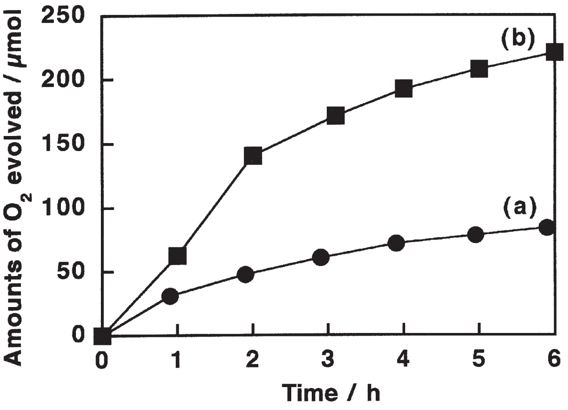

Figure 3. Photocatalytic O_2 evolution on $BiVO_4$ and commercial WO_3 from aqueous $AgNO_3$ solution under visible light irradiation ($\lambda >$ 420 nm). (a) $BiVO_4$ prepared at 1170 K, (b) WO_3.

Thus, $BiVO_4$ was found to be an active photocatalyst for O_2 evolution under visible light irradiation.

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