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Photocatalytic decomposition of organic contaminants by Bi_2WO_6 under visible light irradiation

Junwang Tang[a,*], Zhigang Zou[b,c], and Jinhua Ye[a,**]

[a]*Ecomaterials Center, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*
[b]*Ecoenergy and Ecomaterials Center (EEMC), Nanjing University, Nanjing 210093, China*
[c]*Photoreaction Control Research Center (PCRC), National Institute of Advanced Industrial Science and Technology (AIST),*
Higashi, Tsukuba, Ibaraki 305-8565, Japan

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An oxide photocatalyst Bi_2WO_6 with corner-shared WO_6 octahedral layered structure was synthesized. Its band gap was determined to be 2.69 eV from UV–vis diffuse reflectance spectra. The photocatalyst showed not only the activity for photocatalytic O_2 evolution with the initial evolution rate of 2.0 μmol/h but also the activity of mineralizing both $CHCl_3$ and CH_3CHO contaminants under visible light irradiation. Meanwhile, wavelength dependence of CH_3CHO decomposition was observed, which indicated that the photocatalytic activity of the photocatalyst was in good agreement with its light-absorption ability.

KEY WORDS: Bi_2WO_6 photocatalyst; organic contaminants; visible light irradiation.

1. Introduction

From the viewpoint of the utilization of solar energy, the development of visible light-driven photocatalyst has attracted much attention. Especially in the past 10 years, the scientific interests in the application of photocatalyst have grown exponentially, which involved water splitting and organic contaminants degradation under visible light irradiation [1,2]. Among them, Zou *et al.* have firstly reported water splitting for H_2 and O_2 evolution in a stoichiometric amount over the $NiO_x/In_{0.9}Ni_{0.1}TaO_4$ photocatalyst under visible light irradiation [3]. Furthermore, Khan *et al.* reported the photocatalytic activity of $TiO_{2-x}C_x$ for water splitting with a maximum photoconversion efficiency of 8.35% under visible light irradiation [4]. On the other hand, $TiO_{2-x}N_x$ has been investigated by Asahi *et al.* as an active photocatalyst for organic contaminants decomposition under visible light irradiation [5].

The above-mentioned photocatalysts showed a high activity for water splitting or organic contaminants decomposition under visible light. However, so far few photocatalysts were reported owning the activity both for water splitting and for organic contaminants decomposition under visible light irradiation except the $BiVO_4$ photocatalyst. The latter showed the activity of photocatalytic O_2 evolution from water [6] and photocatalytic 4-*n*-nonylphenol decomposition under visible light irradiation [7]. So the development of a multifunction photocatalyst for water splitting and organic contaminants decomposition is possible and is very attractive. It was reported that Bi_2WO_6 had a suitable valence band (VB) for photocatalytic O_2 evolution from water under visible light irradiation [8]. Here we are interested in the photocatalytic decomposition of organic contaminants by the Bi_2WO_6 photocatalyst. The photocatalyst was synthesized and the photocatalytic decomposition of both $CHCl_3$ and CH_3CHO contaminants were firstly carried out over the photocatalyst under visible light irradiation in the present work.

2. Experimental

The Bi_2WO_6 photocatalyst was prepared by a solid-state reaction method. The high purity chemicals of Bi_2O_3 and WO_3 were mixed with 1 : 1 molar ratio in an ethanol solution. The mixture was dried at 353 K for 5 h and sintered at 1173 K for 12 h in air. The crystal structure of the samples was determined by the X-ray diffraction (XRD) method using Cu Kα radiation (JEOL JDX-3500, Tokyo, Japan). The photophysical property of the photocatalyst was measured by UV–vis spectrometer (UV-2500, Shimadzu, Japan). The surface area of the photocatalysts was determined by BET measurement (Micromeritics-2360, Shimadzu, Japan) on nitrogen adsorption at 77 K after the pretreatment at 573 K for 2 h.

The optical system for the photocatalytic reaction was composed of a 300-W Xe arc lamp, a cutoff filter (providing the visible light of different wavelength) and water filter (removing the IR light irradiation). The

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[*] To whom correspondence should be addressed.
Email: tang.junwang@nims.go.jp
[**] To whom correspondence should be addressed.
Email: jinhua.ye@nims.go.jp

filters were placed between the Xe lamp and the reaction cell. The photocatalytic reaction of $CHCl_3$ decomposition was carried out with 0.5-g powdered Bi_2WO_6 photocatalyst suspended in 100-mL $CHCl_3$ solution ($CHCl_3$ concentration: 12 mmol) in a Pyrex glass cell, and the closed reaction system was filled initially with an atmospheric pressure (atm) of air, which was used to oxidize $CHCl_3$ in the catalytic reaction. The photocatalytic reaction of CH_3CHO decomposition was carried out with 1.5-g powdered Bi_2WO_6 photocatalyst placed at the bottom of a Pyrex glass cell, where the reaction gas was 0.5 atm gaseous mixture that consisted of 837 ppm CH_3CHO, 21% O_2 and Ar balance gas. The photocatalytic reaction for O_2 evolution was conducted with 0.5-g photocatalyst suspended in a 270-mL $AgNO_3$ solution (5-mmol $AgNO_3$ was dissolved in 270-mL H_2O) without any cocatalyst.

All experiments were performed at room temperature. The photocatalytic decomposition of organic contaminants was determined by detecting CO_2 in the evolved gas. The photocatalytic splitting of water was determined by detecting O_2 in the evolved gas. The evolved gases were detected by a gas chromatograph with the TCD (GC-8A, Shimadzu, Japan; AC column for CO_2 detection, 5A molecular sieve column for O_2 detection).

3. Results and discussion

The crystal structure of the Bi_2WO_6 photocatalyst was investigated using XRD and the results are shown in figure 1(a). The XRD analysis of the sample showed that the photocatalyst was well crystallized with the orthorhombic structure (space group $Pca2_1$, $a = 0.5437$ nm, $b = 1.643$ nm, $c = 0.5458$ nm) [9,10]. As shown in figure 2, the orthorhombic structure is constructed by corner-shared WO_6 octahedral layers. Bi atoms layers are sandwiched between WO_6 octahedral layers. Figure 3 represents the UV–vis diffuse reflectance spectra (UV–vis DRS) of the photocatalyst. The steep shape of the spectra indicated that the visible light absorption was not due to the transition from the impurity level but was due to the band-gap transition [11]. The band gap of the photocatalyst was estimated to be 2.69 eV from the onset of the absorption edge. The color of the photocatalyst was yellow, as can be expected from its absorption spectrum.

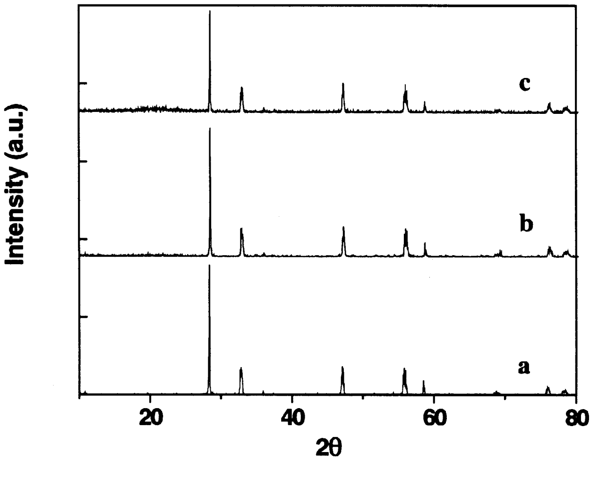

Figure 1. XRD patterns of Bi_2WO_6 before and after the photocatalytic reaction. (a) Before the reaction; (b) after the photocatalytic mineralization of CH_3CHO; (c) after the photocatalytic mineralization of $CHCl_3$.

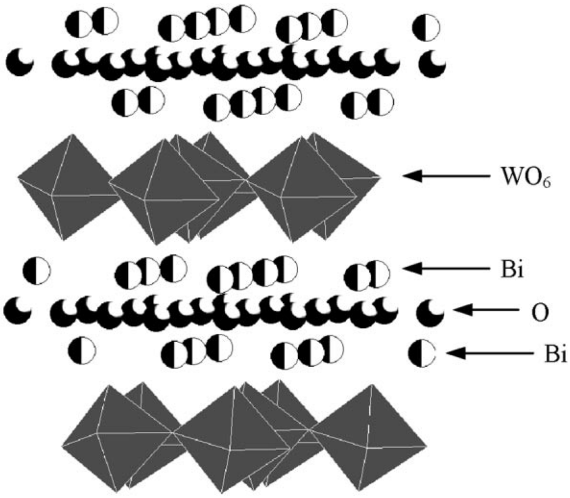

Figure 2. Schematic structure of the Bi_2WO_6 photocatalyst.

First, the photocatalytic O_2 evolution from $AgNO_3$ solution was observed under visible light irradiation ($\lambda > 420$ nm). The initial rate of the O_2 evolution was 2.0 μmol/h under visible light irradiation, in agreement with the results reported by Kudo *et al.* [8]. With increasing reaction time, evolved O_2 increased greatly. After 10 h, the O_2 evolution rate decreased remarkably, which was probably because the metal Ag from the $AgNO_3$ sacrificial reagent shielded the incident light and reduced the surface active sites of the photocatalyst [6].

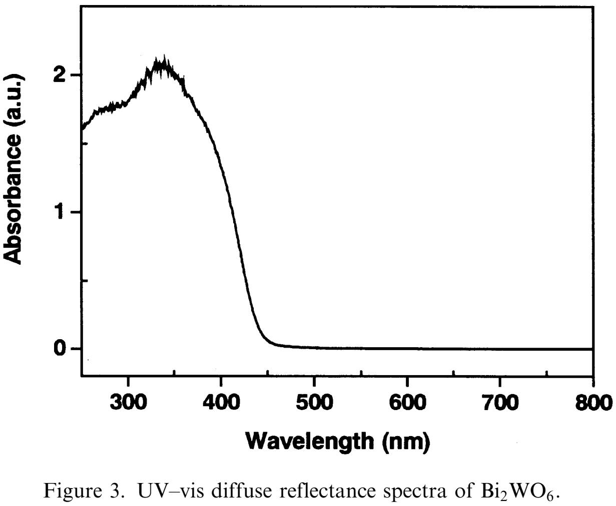

Figure 3. UV–vis diffuse reflectance spectra of Bi_2WO_6.

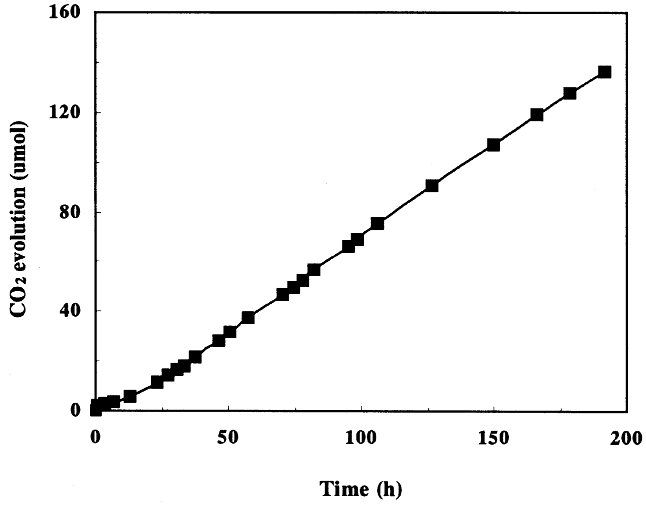

Figure 4. Photocatalytic mineralization of $CHCl_3$ over Bi_2WO_6 under visible light irradiation ($\lambda > 420$ nm) with the initial air pressure of 1 atm. Catalyst: 0.5 g; $CHCl_3$: 12 mmol; water: 100 mL.

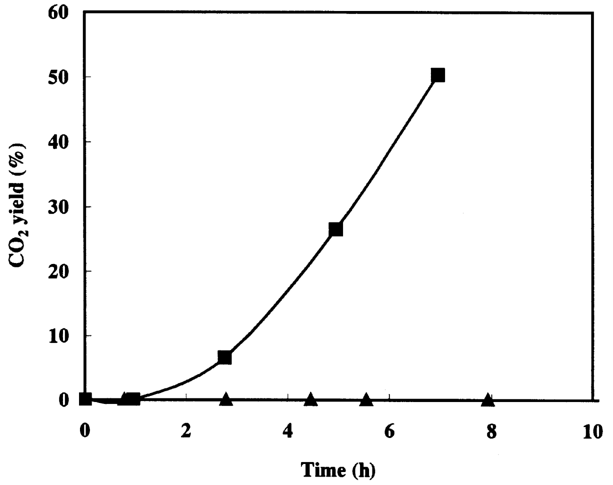

Figure 5. Photocatalytic mineralization of CH_3CHO over Bi_2WO_6 as well as the blank experiment under visible light irradiation ($\lambda > 440$ nm). Catalyst: 1.5 g; gaseous mixture consisted of 837 ppm CH_3CHO, 21% O_2 and Ar balance gas. Bi_2WO_6 (■); blank experiment (▲).

The photocatalytic decomposition of organic contaminants requires that the VB of the photocatalyst must meet the potential level of oxidizing the organic contaminants. The Bi_2WO_6 photocatalyst revealed an activity for O_2 evolution, indicating that its VB is more positive than the O_2/H_2O potential level (1.23 V versus SHE, $pH = 0$). So, the photocatalyst with a strong oxidizing potential was attempted to decompose organic contaminants. The ideal route to decompose the organics is to mineralize the organics thoroughly, where CO_2 was one of the ultimate products. Figure 4 shows the photocatalytic mineralization of a largely used solvent $CHCl_3$ under visible light irradiation ($\lambda > 420$ nm) in the neutral solution. The rate of photocatalytic CO_2 evolution was low at the beginning in figure 4, which was named as the induction period of CO_2 evolution. This process was possibly attributed to the fact that the reactant was firstly converted to intermediates and then to CO_2, or that the yielded CO_2 was firstly dissolved in water and then emitted to the gaseous environment; whereas it was obvious that CO_2 concentration increased linearly with the reaction time except for the initial 10 h. This meant that the photocatalytic mineralization rate of $CHCl_3$ over Bi_2WO_6 kept stable within the total reaction time. To our knowledge, this is the first report of the photocatalytic mineralization of $CHCl_3$ under visible light irradiation, although there were many relevant works reported under UV light irradiation [12,13].

Figure 5 represents the photocatalytic mineralization of CH_3CHO over the Bi_2WO_6 photocatalyst under visible light irradiation ($\lambda > 440$ nm), in which the CO_2 yield (%) was calculated as follows:

$$CO_2(\%) = \frac{M_c}{M_i} \times 100$$

where M_c was the evolved CO_2 (mol) and M_i was the theoretical value of CO_2 formed when CH_3CHO was decomposed totally (mol); namely, if the CO_2 yield is 100%, it means that CH_3CHO is mineralized thoroughly. As a comparison, the blank experiment (without any photocatalyst) was carried out at the same experimental condition. The results are also shown in figure 5. It was evident that there was also an induction period in the photocatalytic reaction. Meanwhile, Bi_2WO_6 revealed a very remarkable activity under visible light irradiation ($\lambda > 440$ nm), while no activity was observed when there was no photocatalyst at the same condition. Asahi *et al.* reported that TiO_2 (anatase), a well-known good photocatalyst under UV light, had a negligible activity for CH_3CHO decomposition under the visible light irradiation ($\lambda > 436$ nm) [5]. Apparently, the activity of the present Bi_2WO_6 photocatalyst is very attractive compared to TiO_2 (anatase) under visible light irradiation.

To investigate the wavelength dependence of the contaminants decomposition over the photocatalyst, which is often used to identify whether a reaction is driven by light irradiation, CH_3CHO conversion to CO_2 was observed with light wavelength variation from full arc to 440 nm (figure 6). The results showed that CO_2 yield decreased relevantly with the increasing of the light wavelength, and the wavelength dependence of CH_3CHO decomposition was in good agreement with the UV–vis DRS of the photocatalyst, indicating that the catalytic reaction was driven by light irradiation. From these results in figures 5 and 6, it is easily seen that CH_3CHO can be mineralized photocatalytically over the Bi_2WO_6 photocatalyst under visible light irradiation. To our knowledge, it is also the first time to report the photocatalytic mineralization of CH_3CHO over a non-TiO_2 and non-ZnO-based photocatalyst

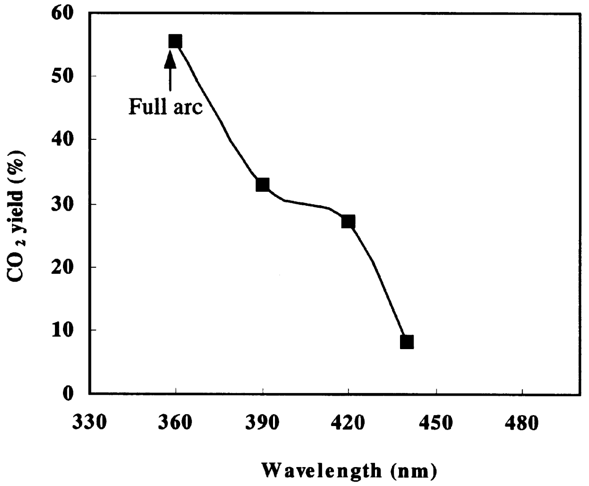

Figure 6. Dependence of CH_3CHO conversion to CO_2 on light wavelength over the Bi_2WO_6 photocatalyst after the photocatalytic reaction for 3 h.

under visible light irradiation [5,14]. The crystal structures of the Bi_2WO_6 photocatalyst were checked again after the photocatalytic reactions of organic contaminants mineralization and the XRD patterns are represented in figure 1(b) and (c). The analysis of the XRD patterns of the sample before and after the photoreactions revealed that the crystal structure of the photocatalyst did not change. So, the photocatalyst was stable in the present photocatalytic reactions.

It is well known that extending the light-absorption region of the photocatalyst and increasing the surface area of the photocatalyst are two of the most important ways to increase the activity of the catalyst. The former is relevant to the electronic structure of the catalyst. The latter is involved in the preparation process of the photocatalyst. BET measurement showed that the surface area of the Bi_2WO_6 photocatalyst was $0.64\,m^2/g$, which is only about 1% of the P-25 ($49.41\,m^2/g$) photocatalyst. This suggested that much higher efficiency of the photocatalyst could be expected from increasing surface area. We are focusing on promoting the photocatalytic activity of the photocatalyst by increasing the surface area of the photocatalyst and modifying the photocatalyst.

In conclusion, we have firstly observed that the Bi_2WO_6 photocatalyst owns activity in mineralizing both $CHCl_3$ and CH_3CHO to CO_2 under visible light irradiation, in addition to the previously reported photocatalytic O_2 evolution from $AgNO_3$ solution by Kudo. The activity of the photocatalyst showed obvious wavelength dependence, which is consistent with the light-absorption property of the photocatalyst. The photocatalyst was also found to be stable during the whole photocatalytic reaction. All these indicated that Bi_2WO_6 is a potential candidate for the practical application in environmental purifications in or outdoors, as long as the activity is enhanced sufficiently by increasing the surface area of the photocatalyst.

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