

Photocatalytic decomposition of water with $\text{Bi}_2\text{InNbO}_7$

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Received 17 March 2000; accepted 20 June 2000

We report the observation of the photocatalytic property of the $\text{Bi}_2\text{InNbO}_7$ compound for the first time. A polycrystalline sample of $\text{Bi}_2\text{InNbO}_7$ was synthesized by the solid state reaction and characterized by powder X-ray diffraction and Rietveld structure refinement. The H_2 and CO evolutions were obtained from $\text{Pt}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution and O_2 evolution was generated from an aqueous cerium sulfate solution. H_2 was evolved from pure H_2O under UV irradiation. A magnetic susceptibility measurement indicated that the O_2 formed from pure H_2O is photoadsorbed on the surface of the $\text{Bi}_2\text{InNbO}_7$ particles.

Keywords: $\text{Bi}_2\text{InNbO}_7$, photocatalyst, decomposition of water, magnetic susceptibility

1. Introduction

Since the discovery of the photocatalytic splitting of water on Pt/TiO_2 electrodes [1], the study of photolysis of water with a semiconductor as the catalyst has attracted much interest. Such studies are often related to electron transfer and energy transfer processes in photocatalytic reactions. To date, the research efforts mainly focused on understanding fundamental processes and on enhancing the photocatalytic efficiency of TiO_2 [2–4]. Later advances in materials fabrication led to the discovery that metal oxide semiconductors with tunnel or layered perovskite structures have the possibility to decompose water with higher activity [5,6]. Recently, a number of reports have shown that compounds consisting of three linear TaO_6 chains could decompose water into H_2 or O_2 [7]. Unfortunately, most photocatalysts need a co-catalyst to decompose water. Even though, the number of photocatalyst materials is yet limited. There is an urgent need to develop new types of photocatalyst materials with higher activity. In addition, it is well known that the generation of O_2 evolution is very difficult in the photocatalytic decomposition of water. However, the origin is not so clear.

In this letter, we report the preparation and characterization of a new photocatalyst, $\text{Bi}_2\text{InNbO}_7$. A comparison of the photocatalytic property of $\text{Bi}_2\text{InNbO}_7$ to that of a TiO_2 photocatalyst is made.

2. Experimental

The polycrystalline sample of $\text{Bi}_2\text{InNbO}_7$ was prepared by a solid state reaction method using high-purity grade chemicals In_2O_3 , $\text{Bi}_2(\text{CO}_3)_3$ and Nb_2O_5 . In_2O_3 was dried

at 700 °C and Nb_2O_5 at 600 °C before use. Stoichiometric amounts of the precursors were mixed and pressed into small columns. The columns were reacted on an aluminum crucible in air for three times. At the final process, the column samples were reacted for two days at 1100 °C.

The chemical composition of the samples before and after reactions was determined by scanning electron microscope X-ray energy dispersion spectroscopy (SEM-EDS) with accelerating voltage of 25 kV. The crystal structure of $\text{Bi}_2\text{InNbO}_7$ was decided by powder X-ray diffraction (Rigaku RINT-2000 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$)). Magnetic susceptibility measurement was performed in the temperature range 5–300 K and at an applied field of 1.0 T using a superconducting quantum interference device (SQUID) magnetometer. The UV-vis diffuse reflectance spectrum of $\text{Bi}_2\text{InNbO}_7$ was measured by using an UV-vis spectrometer (MPS-2000). The conductivity measurement was made using direct current and four-probe technique. Au wires and silver electrodes were used. The surface area was determined by BET measurement (Micromeritics, Shimadzu, FlowPrep 060).

The photocatalytic reaction was examined using a gas closed circulation system and an inner-irradiation type quartz cell with 400 W high-pressure Hg lamp. The gases evolved were determined with a TCD gas chromatograph, which was connected with a circulating line. In order to obtain high activity, it is essential to load a metal or metal oxide on the surface of the photocatalyst. The Pt was found to be the most effective for the TiO_2 photocatalyst [8]. The photocatalytic reaction was performed in an aqueous $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution (1.0 g powder catalyst, 50 ml CH_3OH , 350 ml H_2O and 0.1 wt% Pt (Pt loading instead of a H_2PtCl_4)) and in pure water (1.0 g powder catalyst, 400 ml H_2O). The O_2 evolution reaction was performed in an aqueous cerium sulfate solution (1.0 g powder

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catalyst, 1.0 mmol $\text{Ce}(\text{SO}_4)_2$, 400 ml H_2O) since this solution is more stable than an aqueous silver nitrate under UV irradiation [9].

3. Results and discussion

SEM analysis of the $\text{Bi}_2\text{InNbO}_7$ compound indicated that the crystalline grains of the sample have a maximum size of 6.0 μm . The chemical composition of the $\text{Bi}_2\text{InNbO}_7$ compound was determined using characteristic X-rays of In $L\alpha$, Bi $M\alpha$, and Nb $L\alpha$. The composition content was decided using the ZAF quantification method. The SEM-EDS analysis showed that the compound has a homogeneous atomic distribution with no other additional elements. An average atomic ratio of Bi:In:Nb = 2.00(1):1.95(3):1.05(2) was obtained from measurements made at several different points. Oxygen content was calculated from the EDS results [10].

X-ray powder diffraction intensity data (see figure 1) of $\text{Bi}_2\text{InNbO}_7$ were collected at room temperature. Full-profile structure refinement of the collected powder diffraction data was performed using the Rietveld program REITAN [11]. The details of the investigations on structure will be published elsewhere [12]. The final refinement result revealed that the $\text{Bi}_2\text{InNbO}_7$ compound has the pyrochlore type crystal structure, cubic system with space group $\text{Fd}\bar{3}\text{m}$ and the lattice parameter is $a = 10.7793(2)$ Å. All the diffraction peaks could be indexed with the space group, showing that the sample is a single phase of $\text{Bi}_2\text{InNbO}_7$.

Figure 2(a) shows the H_2 and CO evolutions from Pt/ $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution. The reaction stopped when the light was turned off in this experiment, showing the obvious light response. The result shows that the photocatalytic reaction is induced by the absorption of UV irradiation. The formation rate of H_2 evolution was estimated to be $170 \mu\text{mol h}^{-1}$ in the first 10 h. The total amount of H_2 /catalyst (mol) was beyond 1.0 at 10 h, indicating that

the reaction seems to occur catalytically. The H_2 production continued even after 100 h, but the formation rate of H_2 evolution decreased after 10 h. Even so, the total volume of evolved H_2 was attained to $12 \text{ mmol g-cat}^{-1}$ when this reaction achieved 100 h, the value corresponded to 9.3 mol ratio of H_2 evolution to catalyst.

The CO evolution (see figure 2(a)) was observed in this reaction from Pt/ $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution as the oxidation product. The formation rate of CO evolution was estimated to be $5 \mu\text{mol h}^{-1}$. The CO evolution increases with illumination time as does the H_2 evolution. However, the formation rate of CO evolution is much lower than that of H_2 evolution. The CO arises probably from decomposition of the formaldehyde, which decomposes slower than

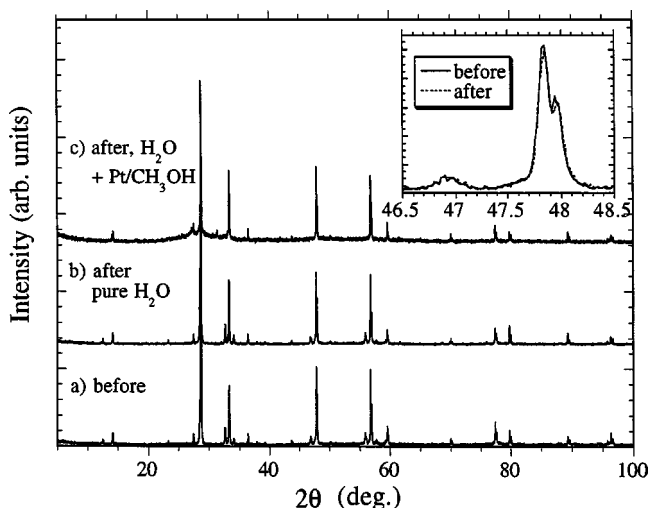


Figure 1. X-ray powder diffraction patterns of samples before and after reactions. Inset: a comparison of patterns before and after reactions.

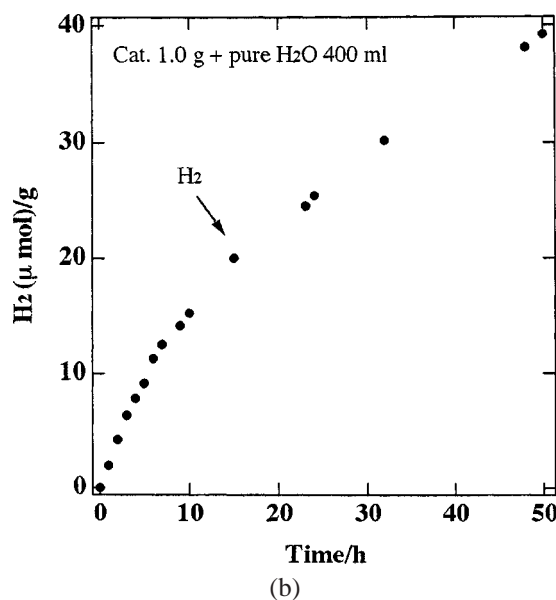
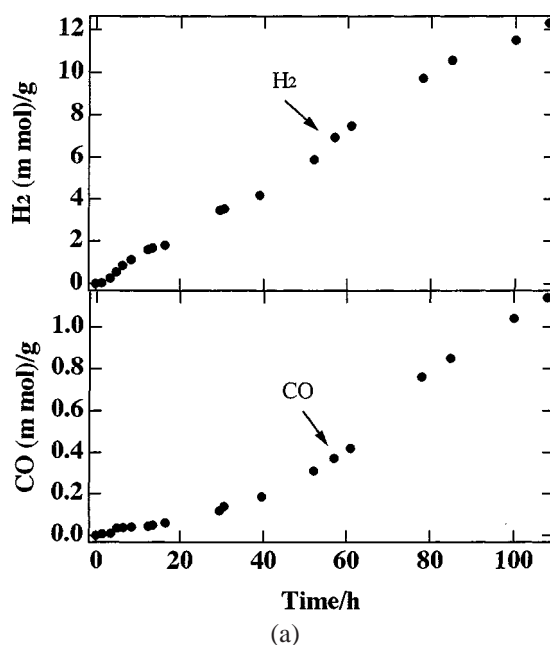


Figure 2. (a) Photocatalytic H_2 and CO evolutions on the $\text{Bi}_2\text{InNbO}_7$ compound from Pt/ $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution. (b) Photocatalytic H_2 evolution on the $\text{Bi}_2\text{InNbO}_7$ compound from pure water.

Table 1
Rates of gas evolution and physical properties of photocatalysts.

Catalyst	Type of structure	Band gap (eV)	Surface area (m ² /g)	Rates of gas evolutions (μmol h ⁻¹)			
				Pt/CH ₃ OH/H ₂ O		Ce(SO ₄) ₂ /H ₂ O	Pure H ₂ O
				H ₂	CO	O ₂	H ₂
Bi ₂ InNbO ₇	Pyrochlore	2.7	0.52	170	5	7	1.5
TiO ₂ -P25	Anatase + rutile	3.2	53.8	550	15	17	1.0

methanol dehydrogenates. On the other hand, the ratios of non-stationary and non-stoichiometry evolutions between H₂ and CO might result from generation of CO₂ and other evolutions. It is well known that when CH₃OH is added to a Pt/TiO₂ aqueous suspension, sustained H₂ production is observed under UV irradiation and the alcohol molecules are oxidized to final productions of CO₂, CO, CH₄, etc. [13]. The presence of oxygen vacancy defects strongly enhances such interaction due to electron back-donation from surface Ti³⁺ into the π* orbital of molecular CO [13].

The O₂ evolution reaction was performed in an aqueous cerium sulfate solution and the following stoichiometric reaction occurred: 4Ce⁴⁺ + 2H₂O → 4Ce³⁺ + O₂ + 4H⁺. The aqueous Ce(SO₄)₂ solution is more stable than an aqueous silver nitrate under UV irradiation since photodeposition of Ce³⁺ did not occur after illumination [9]. The formation rate of O₂ evolution is about 7 μmol h⁻¹. This means that the photocatalyst has potential for O₂ evolution from aqueous solution.

It is known that the TiO₂ photocatalyst has very high photocatalytic activity under UV light irradiation. In order to compare Bi₂InNbO₇ to TiO₂ photocatalyst, the TiO₂ photocatalyst (TiO₂-P25) was tested by the same method. The result is shown in table 1. The formation rates of H₂ and CO evolutions were estimated to be 550 and 15 μmol h⁻¹ in the first 10 h from Pt/CH₃OH/H₂O solution under UV light irradiation, respectively. The formation rate of O₂ evolution is about 17 μmol h⁻¹ from an aqueous cerium sulfate solution. It is noted that the formation rate of evolutions using Bi₂InNbO₇ is slower than that of the TiO₂ photocatalyst (TiO₂-P25). This means that the activity of Bi₂InNbO₇ is lower than that of the TiO₂ photocatalyst. BET measurement showed that the surface area of Bi₂InNbO₇ is 0.52 m² g (see table 1). This is about 1% of the value for the TiO₂ photocatalyst (53.8 m² g⁻¹). This means that the surface area of Bi₂InNbO₇ is much smaller than that of the TiO₂ photocatalyst. Since an efficient photocatalytic reaction process occurs on the photocatalyst surface, the smaller surface area of the Bi₂InNbO₇ photocatalyst might lead to the decrease in effective photocatalytic reaction of the photocatalyst. The study for effects of surface area on effective photocatalytic reaction and on photocatalytic activity is in progress, which is believed to lead to further understanding of the new photocatalysts.

Figure 2(b) shows the H₂ evolution from pure water with photocatalyst suspension under UV irradiation. The formation rate of H₂ evolution was about 1.5 μmol h⁻¹ in the first 10 h. The total volume of evolved H₂ was

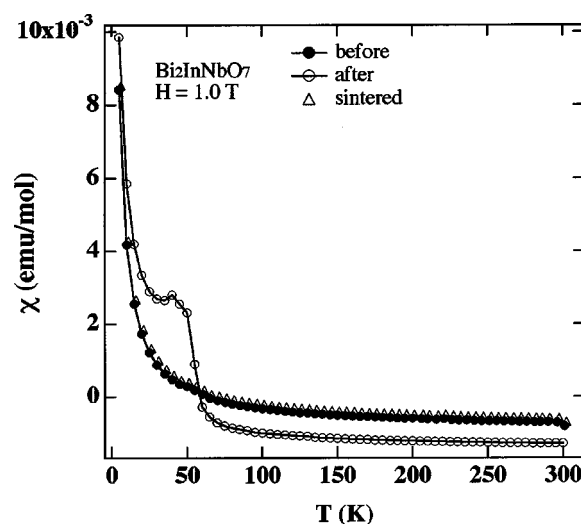


Figure 3. Temperature dependence of susceptibilities of samples before and after reactions.

attained to 40 μmol g-cat⁻¹ when this reaction achieved 50 h. The TiO₂ photocatalyst (TiO₂-P25) was tested by the same method. The formation rate of H₂ evolution was about 1.0 μmol h⁻¹ in the first 10 h. It is interesting to notice that the TiO₂ photocatalyst shows lower activity than that of Bi₂InNbO₇. This means that although the photocatalytic activity of TiO₂ photocatalyst is very high under UV light irradiation in an aqueous solution, its photocatalytic activity is very small in pure water.

Oxygen evolution was not observed from pure water in this experiment using both Bi₂InNbO₇ and TiO₂. It is commonly accepted that free holes in TiO₂ particles can generate OH radicals either on the surface or even at the aqueous interface [14,15]. Extensive research found that there are both physisorbed and chemisorbed oxygen molecules in the TiO₂ surface by low-energy photon irradiation [16,17]. The physisorbed O₂ molecules are produced through the neutralization of chemisorbed O₂⁻ species by photo-generated holes. Amy et al. found a similar result for a TiO₂ photocatalyst namely that the produced oxygen can be photoadsorbed on the surface of the photocatalyst [18]. Very recently, Ishibashi et al. found that under UV light illumination O₂⁻ was formed on the order of 10¹⁴ cm⁻² at the TiO₂ surface during photocatalytic reaction. This indicates a photogenerated electron is mainly trapped by adsorbed oxygen resulting in the formation of O₂⁻ [19]. The photoadsorption of oxygen in the sample after pure water decomposition was investigated by measurements of magnetic susceptibility (χ). The result is shown in figure 3. The magnetic

susceptibility of oxygen adsorbed on a solid surface was studied by many authors and it was shown that adsorbed oxygen undergoes an antiferromagnetic transition around 50 K [20,21]. The susceptibility is different between two samples before and after reaction. The sample after reaction shows an obvious broad peak around 50 K. However, the sample before reaction does not have any anomaly around 50 K. Measurements under zero field and field cooled conditions revealed that the susceptibility is independent of the applied magnetic field. The fact suggests that the origin of this anomaly is unlikely from a spin-glass-like behavior. To understand further the origin of this anomaly, the sample after reaction was sintered at 600 °C using an electric furnace to deoxidation. The sintered sample showed the same result as that of the sample before reaction (see figure 3), the broad peak around 50 K was disappeared after sintering. The anomaly seen around 50 K might arise from the antiferromagnetic ordering of adsorbed oxygen in the sample. The similar result was also observed in other compounds containing niobium, such as in compounds $\text{K}_7\text{Nb}_{14.13}\text{P}_{8.87}\text{O}_{60}$ and BaNb_2S_5 [22,23]. Although it is not clear whether the O_2 molecules physisorbed on the surface of the photocatalysts are in physisorbed and/or chemisorbed molecule states, we speculate that the phenomenon as in TiO_2 takes place on the surface of our photocatalysts. Further study of the photoadsorption of oxygen on these samples under UV irradiation is in progress, which is believed to supply more concrete information.

It is known that the photooxidation/photodissolution of a catalyst might consume oxygen. However, the reactions generally lead to changes of crystal structure and chemical composition of the photocatalyst. We examined the atomic ratio and the crystal structure of these photocatalysts before and after reactions. The chemical composition and the crystal structure of these samples after reactions were examined. We can observe from figure 1 that these samples after reactions have not only the same crystal structure, but also the same lattice parameter (see figure 1 inset). The chemical composition of these samples after reactions is also the same as that of samples before reactions. From these experimental results we confirmed that these samples before and after reactions have not changed in both the crystal structure and the chemical composition.

The UV-vis diffuse reflectance spectrum of the $\text{Bi}_2\text{InNbO}_7$ compound is shown in figure 4. The band gap of the $\text{Bi}_2\text{InNbO}_7$ compound was estimated to be about 2.7 eV. The inset shows the conductivity of the $\text{Bi}_2\text{InNbO}_7$ compound in the temperature range 250–650 K. The conductivity decreases rapidly with decreasing temperature, showing semiconducting behavior. The activation energy (E_a) is 2.62(5) eV, according to the function $\sigma = \sigma_0 \exp(E_a/KT)$, where σ is the conductivity of the $\text{Bi}_2\text{InNbO}_7$ compound. The activation energy is in good agreement with the value estimated from UV-vis diffuse reflectance spectrum measurement. This means the $\text{Bi}_2\text{InNbO}_7$ compound may be a direct gap semiconductor. Furthermore, the value of the band gap of $\text{Bi}_2\text{InNbO}_7$ sug-

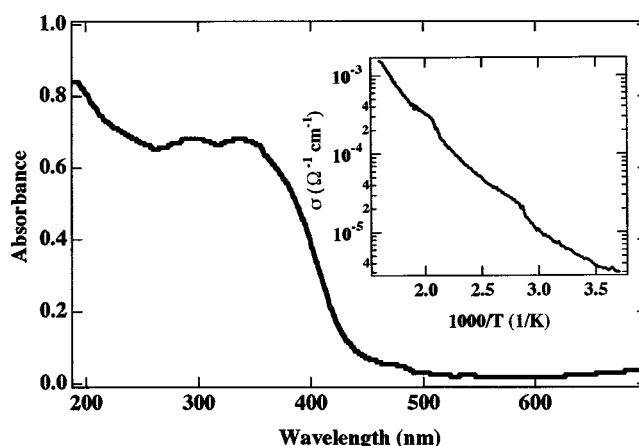


Figure 4. Diffuse reflectance spectrum of the $\text{Bi}_2\text{InNbO}_7$ compound. Inset: the conductivity in temperature range of 250–650 K.

gests that the compound has ability to generate H_2 evolution from water with visible light. However, the compound does not work under visible light irradiation to directly decompose pure water, even $\text{Pt}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution. It is known that the process for photocatalysis of semiconductors is the direct absorption of a photon by the band gap of the materials and generates electron–hole pairs in the semiconductor particles. The excitation of an electron from the valence band to the conduction band is initiated by light absorption with energy equal to or greater than the band gap of the semiconductor. Upon excitation of the photon the separated electron and hole can follow surface of solid. However, it is found that direct absorption of photons by band gap oxides can generate electron–hole pairs in the solid and, generally, this is more than twice the energy gap of the material and such excess energy requirement is common for many oxides [24].

In summary, we have presented the evidence for photocatalytic decomposition of an aqueous solution and pure water on the $\text{Bi}_2\text{InNbO}_7$ photocatalyst. Our experimental results show that the $\text{Bi}_2\text{InNbO}_7$ compound is sensitive to UV irradiation and that it is possible to obtain H_2 from both $\text{Pt}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution and pure water. Although $\text{Bi}_2\text{InNbO}_7$ has a suitable band, the compound does not work under visible light irradiation to directly decompose pure water, even $\text{Pt}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution. Modification of the surface of the compound may be needed to increase the responding wavelength range.

Acknowledgement

The authors would like to thank Dr. K. Sayama for his valuable discussion and appreciate the contributions of Dr. K. Kawaguchi, and K. Hara.

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