H_2 or O_2 Evolution from Aqueous Solutions on Layered Oxide Photocatalysts Consisting of Bi^{3+} with $6s^2$ Configuration and d^0 Transition Metal Ions

Akihiko Kudo* and Satoshi Hijii

Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601

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$Bi_2W_2O_9$, Bi_2WO_6, and Bi_3TiNbO_9 consisting of layered structure with perovskite slabs interleaved with Bi_2O_2 layers showed photocatalytic activities for H_2 evolution from an aqueous methanol solution and O_2 evolution from an aqueous silver nitrate solution. Bi_2WO_6 with the Aurivillius structure and a 2.8 eV band gap was active for the O_2 evolution reaction under visible light irradiation (λ>420 nm).

Bismuth mixed oxides with the Aurivillius structure represented by $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ (A=Ba, Bi, Pb, etc., B=Ti, Nb, W, etc.) possess unique layered structures in which perovskite slabs of $(A_{n-1}B_nO_{3n+1})^{2-}$ are sandwiched between $(Bi_2O_2)^{2+}$ layers.[1-6] Dielectric,[1,6-9] ion conductive,[10,11] luminescent[12] and catalytic[13] properties of this material family have attracted attention. One of the authors has recently reported that $BiVO_4$ is a new photocatalyst working under visible light irradiation.[14] Therefore, photocatalytic properties of the bismuth mixed oxides with the Aurivillius structure and the relative compounds are of interest. In the present paper, photocatalytic activities of oxides consisting of Bi^{3+} with $6s^2$ configuration, and Ti^{4+}, Nb^{5+}, W^{6+}, and Mo^{6+} with d^0 were investigated in order to find new photocatalysts based on bismuth mixed oxides with structural regularities. Bi-W oxides were especially paid attention in the present study.

Samples were synthesized in air using alumina crucibles by conventional solid state reactions. Starting materials used were as follows: Bi_2O_3 (Kanto Chemical, purity; 99.9%), WO_3 (Nacalai tesque, purity; 99.5%), TiO_2 (Kanto Chemical, purity; 99.0%), Nb_2O_5 (Kanto Chemical, purity; 99.95%), $BaCO_3$ (Kanto Chemical, purity; 99.0%). The calcination temperature and time were as follows: 1023 K for 5 h and 1123 K for 10 h for $Bi_2W_2O_9$, 1023 K for 5 h and 1073 K for 20 h for $Bi_{14}W_2O_{27}$,[15] 1023 K for 5 h and 1073 K for 24 h for Bi_2WO_6, 1123 K for 5 h and 1473 K for 10 h for $Bi_2Ti_2O_7$ (a small amount of $Bi_4Ti_3O_{12}$ was detected by XRD in the product), 1073 K for 6 h and 1373 K for 10 h for $Bi_4Ti_3O_{12}$, 1073 K for 5 h and 1373 K for 10 h for Bi_3TiNbO_9, 1073 K for 5 h and 1323 K for 10 h for $BaBi_4Ti_4O_{15}$. All samples were ground once between the calcinations. Bi_2MoO_6 (Kojundo Chemical, purity; 99.9%) was purchased and used as received.

The photocatalytic reactions were carried out in a closed gas circulation system. H_2 evolution from aqueous methanol solutions (H_2O 350 ml + CH_3OH 20 ml) and O_2 evolution from aqueous silver nitrate solutions (0.05 mol/l, 350 ml) were investigated as test reactions to evaluate the photocatalytic properties. When the H_2 evolution reaction was carried out, Pt was photodeposited on photocatalysts from H_2PtCl_6 during the reaction. The catalyst powder (1 g) was dispersed in aqueous solutions by a magnetic stirrer in an inner irradiation Pyrex cell. The light source was a 450 W high pressure mercury lamp (USHIO; UM452). The amounts of H_2 and O_2 evolved were determined by using a gas chromatograph (Shimadzu; GC-8A, TCD, Ar carrier). Photocatalytic reactions under visible light irradiation were carried out by using an external irradiation Pyrex cell, a 300 W Xe illuminator (CERMAX; LX300), and a cut-off filter (L42). Diffuse reflection spectra were obtained by using a UV-VIS-NIR spectrometer (JASCO; Ubest-570) and was converted from reflection to absorbance by the Kubelka-Munk method.

Figures 1 and 2 show diffuse reflectance spectra of Bi-(W, Mo) and Bi-(Ti, Nb) oxides, respectively. All spectra possessed steep absorption edges. The diffuse reflectance spectra revealed that Bi_2WO_6, $Bi_7W_2O_{27}$, and $Bi_2Ti_2O_7$ absorbed visible light.

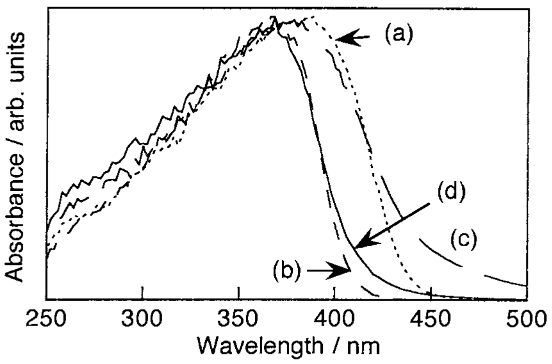


Figure 1. Diffuse reflectance spectra of Bi-W and Bi-Mo oxides. (a): Bi_2WO_6, (b): $Bi_2W_2O_9$, (c): $Bi_7W_2O_{27}$, (d): Bi_2MoO_6.

Figure 2. Diffuse reflectance spectra of Bi-Ti-Nb oxides. (a): $Bi_2Ti_2O_7$, (b): $Bi_4Ti_3O_{12}$, (c): Bi_3TiNbO_9, (d): $BaBi_4Ti_4O_{15}$.

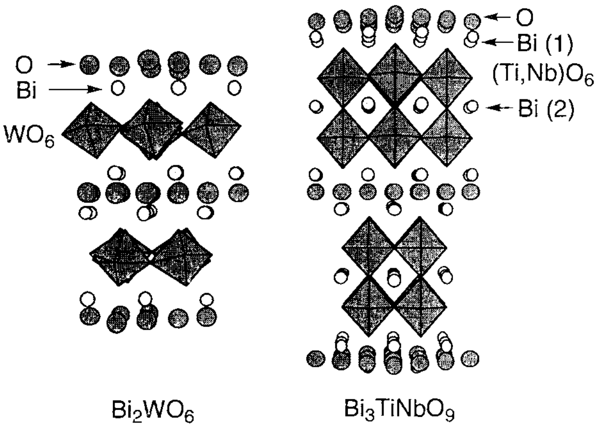
Table 1 shows band gaps estimated from the diffuse reflectance spectra and photocatalytic activities for H_2 or O_2 evolution from aqueous solutions in the presence of sacrificial reagents. $Bi_2W_2O_9$, Bi_2WO_6, and Bi_3TiNbO_9 showed relatively high activities among oxides listed in Table 1. Bi_2WO_6 and Bi_3TiNbO_9 possess the Aurivillius structure as shown in Figure 3 while $Bi_2W_2O_9$[3,6] has the layered structure in which bismuth ions

Table 1. Photocatalytic activities for H_2 evolution from aqueous methanol solutions and O_2 evolution from aqueous $AgNO_3$ solutions on layered oxides consisting of Bi^{3+}

Catalyst	Band gap /eV	Activity / μmol/h	
		H_2 [a]	O_2
$Bi_2W_2O_9$	3.0	18	281
Bi_2WO_6	2.8	1.6	34
$Bi_{14}W_2O_{27}$	2.8	0	0.7
$Bi_2Ti_2O_7$	2.9	0	0.7
$Bi_4Ti_3O_{12}$	3.1	0.6	3.0
Bi_3TiNbO_9	3.1	33	31
Bi_2MoO_6	3.0	0.01	2.1
$BaBi_4Ti_4O_{15}$	3.3	8.2	3.7

Catalyst; 1 g, light source; 450 W high pressure mercury lamp, reaction cell; inner irradiation cell made of Pyrex.

[a] 1 wt% of Pt was loaded.



Bi_2WO_6 Bi_3TiNbO_9

Figure 3. Structure of Bi_2WO_6 and Bi_3TiNbO_9.[4]

(Bi(2) in Figure 3) are taken away from A sites in the perovskite slab of Bi_3TiNbO_9 with 2-layers thickness. Namely, the tungstate layers of $Bi_2W_2O_9$ have ReO_3 structure as well as WO_3. The corner-sharing structure seems to contribute to the high photocatalytic activity of $Bi_2W_2O_9$ for the O_2 evolution.

H_2 was evolved on $Bi_2W_2O_9$ even if Bi_2O_3 and WO_3 of the starting materials did not have such an activity. The band gaps suggest that the activity for the H_2 evolution is due to the high conduction band level of $Bi_2W_2O_9$ compared with that of Bi_2O_3 and WO_3. The dependence of the photocatalytic H_2 evolution over $Bi_2W_2O_9$ upon the amount of Pt loaded was investigated. When Pt was not loaded the activity was very low (1.3 μmol/h). The maximum activity (55 μmol/h) was obtained when 0.1 wt% of Pt was loaded. Bi_3TiNbO_9 with 2-layers thickness also showed the H_2 evolution activity. In contrast, the activity of $Bi_4Ti_3O_{12}$ with 3-layers thickness was negligible even if the band gap of $Bi_4Ti_3O_{12}$ was similar to that of Bi_3TiNbO_9.

Among Bi_2WO_6, $Bi_2W_2O_9$, and Bi_3TiNbO_9 with reasonable photocatalytic activities, only Bi_2WO_6 can absorb visible light. Bi_2WO_6 showed the O_2 evolution activity under visible light irradiation (λ>420 nm) as shown in Figure 4. The initial rate of the O_2 evolution was 3 μmol/h.

WO_3 is a well-known photocatalyst which shows a high activity for photocatalytic O_2 evolution.[16] However, among metal tungstates, only $Na_2W_3O_{10}$ in which the tungstate layer consists of corner and edge-sharing WO_6 units[17] shows the photocatalytic activities for H_2 or O_2 evolution under UV irradiation.[18] In the present study, $Bi_2W_2O_9$ has arisen as one of novel tungstate photocatalysts which are active for H_2 or O_2 evolution from aqueous solutions. Domen and co-workers have extensively investigated the photocatalytic activities of layered perovskite oxides.[19,20] The perovskite slabs of the photocatalysts reported so far consist of TiO_6 and NbO_6 units as seen in $K_2La_2Ti_3O_{10}$ and $KCa_2Nb_3O_{10}$. In contrast to them, the perovskite slabs of Bi_2WO_6 and $Bi_2W_2O_9$ photocatalysts consist of WO_6 units corner-shared. Thus, the Bi-W oxide with the Aurivillius and its relative structure was found to be a new group of photocatalyst materials from the view point of the component and the structure.

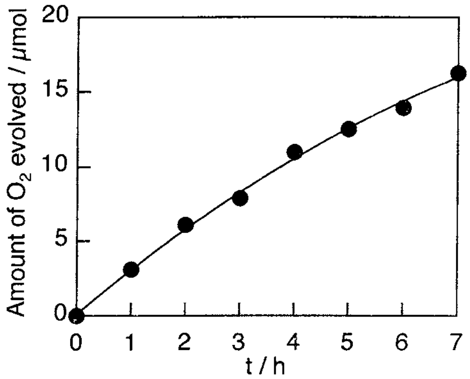


Figure 4. O_2 evolution from an aqueous $AgNO_3$ solution (0.05 mol/l) under visible light irradiation (λ>420 nm) over a Bi_2WO_6 photocatalyst.

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References

1 R. E. Newnham, R. W. Wolfe, and J. F. Dorrian, *Mater. Res. Bull.*, **6**, 1029 (1971).
2 J. L. Hutchison, J. S. Anderson, and C. N. R. Rao, *Proc. R. Soc. Lond. A.*, **355**, 301 (1977).
3 Y. Bando, A. Watanabe, Y. Sekikawa, M. Goto, and S. Horiuchi, *Acta Crystallogr. Sect. A*, **35**, 142 (1979).
4 B. Frit and J. P. Mercurio, *J. Alloys Compd.*, **188**, 27 (1992).
5 M.T. Montero, P. Millán, P. Durán-Martín, B. Jiménez, and A. Catro, *Mater. Res. Bull.*, **33**, 1103 (1998).
6 A. Watanabe and M. Goto, *J. Less-Common Met.*, **61**, 265 (1978).
7 S. E. Cummins and L. E. Cross, *J. Appl. Phys.*, **39**, 2268 (1968).
8 M. Hamada, H. Tabata, and T. Kawai, *Thin Solid Films*, **306**, 6 (1997).
9 T. Hirose, M. Kawaminami, K. Obara, M. Arakawa, and H. Takeuchi, *J. Phys. Soc. Jpn.*, **62**, 1758 (1993).
10 N. Baux, R. N. Vannier, G. Mairesse, and G. Nowogrocki, *Solid State Ionics*, **91**, 243 (1996).
11 M. S. Islam, S. Lazure, R.N. Vannier, G. Nowogrocki, and G. Mairesse, *J. Mater. Chem.*, **8**, 655 (1998).
12 O. M. Bordun, *Inorg. Mater.*, **34**, 1270 (1998).
13 P. K. Sinhamahapatra, S. Sinhamahapatra, and S. K. Bhattacharyya, *Kris. Tech.*, **12**, 1205 (1977).
14 A. Kudo, K. Ueda, H. Kato, and I. Mikami, *Catal. Lett.*, **53**, 229 (1998).
15 A. Watanabe, N. Ishizawa, and M. Kato, *J. Solid State Chem.*, **60**, 252 (1985).
16 J. R. Darwent and A. Mills, *J. Chem. Soc., Faraday Trans. 2*, **78**, 359 (1982).
17 K. Viswanathan, *J. Chem. Soc., Dalton Trans.*, **1974**, 2170.
18 A. Kudo and H. Kato, *Chem. Lett.*, **1997**, 421.
19 K. Domen, Y. Ebina, T. Sekine, A. Tanaka, J. Kondo, and C. Hirose, *Catal. Today*, **16**, 479 (1993).
20 T. Takata, Y. Furumi, K. Shinohara, A. Tanaka, M. Hara, J. N. Kondo, and K. Domen, *Chem. Mater.*, **9**, 1063 (1997).