Photocatalytic Activities of $Na_2W_4O_{13}$ with Layered Structure

Akihiko Kudo* and Hideki Kato
Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162

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$Na_2W_4O_{13}$ with a layered structure possessed an energy gap between those of bulky WO_3 and polyacid $[Si(W_3O_{10})_4]^{4-}$ photocatalysts and was active for photocatalytic hydrogen and oxygen evolution reactions in the presence of sacrificial reagents.

Photocatalytic hydrogen and oxygen evolution reactions by tungsten oxides such as WO_3[1-3] and polytungstates[4-7] have been studied. The WO_3 photocatalyst with 2.8 eV of the band gap is responsible for visible light. The valence band level (+3.05 eV vs. NHE) is deep enough to oxidize water to oxygen in the presence of electron scavengers such as Fe^{3+} and Ag^+.[1-3] However, the hydrogen evolution by the reduction of water is unfavorable because the conduction band level is +0.25 eV vs. NHE.[8] The band gap irradiation in the presence of reducing reagents such as alcohol results in the formation of not hydrogen but tungsten bronze. In contrast to the heterogeneous WO_3 photocatalyst, some polytungstates work as homogeneous photocatalysts which show high activities for hydrogen evolution from aqueous alcohol solutions under UV irradiation.[4-7] The polytungstates can be regarded as oxide clusters. However, the homogeneous photocatalysts can not produce oxygen by the oxidation of water.

Layered titanates and niobates show high photocatalytic activities for hydrogen evolution.[9-11] However, the photocatalytic activities of layered compounds consisting of transition metals except for the titanium and niobium have not been reported. $Na_2W_4O_{13}$ with a layered structure has been synthesized.[12-14] This compound consists of the tungsten oxide layers and sodium ions between the layers. The tungsten oxide layers can be regarded as the layers in which tungstate ions are polymerized in the two dimensional form. Therefore, the photocatalytic activities of the layered tungstate is of interest because it is expected to possess the characteristics of the heterogeneous WO_3 catalyst with the high activity for oxygen evolution and the homogeneous polytungstate catalyst with a high activity for hydrogen evolution.

This letter reports the photocatalytic hydrogen and oxygen evolution by $Na_2W_4O_{13}$ with the layered structure in the presence of sacrificial reagents.

$Na_2W_4O_{13}$ was obtained by calcining the mixture of $Na_2WO_4 \cdot 2H_2O$ (Wako Pure Chemicals, purity; 99.0%) and WO_3 (Nacalai Tesque, purity; 99.5%) (1.1:1 in mol mol^{-1}) at 1020 K for 20 h in air using a platinum crucible.[14] The product was washed with distilled water and confirmed by powder X-ray diffraction. H^+-exchanged derivatives were synthesized by suspending 1 g of the $Na_2W_4O_{13}$ powder in 10 ml of 2 mol/l HCl. $H_4[Si(W_3O_{10})_4]$ was purchased from Merck. Absorption and diffuse reflection spectra were measured using a UV-VIS-NIR spectrometer (JASCO, Ubest V-570). Photocatalytic reactions were carried out in a gas-closed circulation system by suspending or dissolving 1 g of the catalyst in aqueous solutions and irradiating with 400 W high pressure mercury lamp. The inner irradiation reaction cell was made of Pyrex. Aqueous methanol and silver nitrate solutions were employed for the hydrogen and oxygen evolution reactions, respectively. The hydrogen and oxygen evolved were determined using a gas chromatography (Ohkura, GC-802 with an MS5A column and a TCD detector).

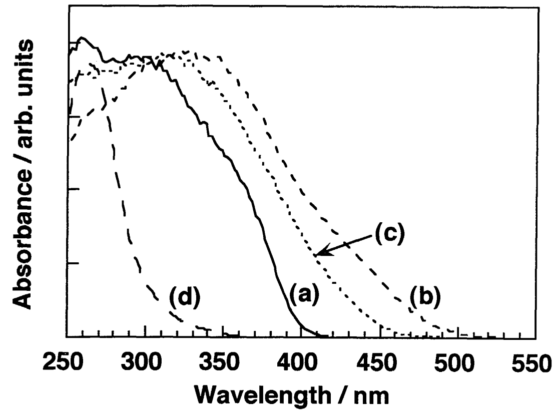

Figure 1. Diffuse reflection spectra of (a) $Na_2W_4O_{13}$, (b) H^+-exchanged $Na_2W_4O_{13}$, and (c) WO_3 powder and the absorption spectrum of (d) an aqueous $[Si(W_3O_{10})_4]^{4-}$ solution (1×10^{-4} mol l^{-1}).

Figure 1 shows the diffuse reflection spectra of $Na_2W_4O_{13}$, H^+-exchanged $Na_2W_4O_{13}$, and WO_3 powder and the absorption spectrum of an aqueous $[Si(W_3O_{10})_4]^{4-}$ solution. The diffuse reflection spectra have been converted by the Kubelka-Munk method. The spectrum of $Na_2W_4O_{13}$ has an onset at 400 nm which is between the onsets of WO_3 and $[Si(W_3O_{10})_4]^{4-}$. This result indicates that $Na_2W_4O_{13}$ is responsible for wider wavelength region than $[Si(W_3O_{10})_4]^{4-}$ and have more negative conduction band level than WO_3. On the other hand, the spectrum of $Na_2W_4O_{13}$ was shifted to longer wavelength by H^+ exchange.

Figure 2 shows photocatalytic activities of layered $Na_2W_4O_{13}$ for hydrogen and oxygen evolution from aqueous solutions with sacrificial reagents. The amounts of hydrogen and oxygen evolved were increased with irradiation time indicating that the reactions proceeded photocatalytically. The photocatalytic activities of $Na_2W_4O_{13}$, H^+-exchanged $Na_2W_4O_{13}$, WO_3, and $[Si(W_3O_{10})_4]^{4-}$ are summarized in Table 1. WO_3 showed the high activity for the oxygen evolution as already reported[1-3] while the hydrogen evolution activity was negligible. In contrast, the homogeneous $[Si(W_3O_{10})_4]^{4-}$ catalyst showed the high activity for the hydrogen evolution[4-7] but it did not for the oxygen evolution at all. $Na_2W_4O_{13}$ can produce hydrogen and oxygen from aqueous solutions with sacrificial reagents. Thus, $Na_2W_4O_{13}$ was found to include the merits of the heterogeneous WO_3 and homogeneous $[Si(W_3O_{10})_4]^{4-}$ photocatalysts. It is noteworthy that $Na_2W_4O_{13}$ of the heterogeneous tungsten oxide

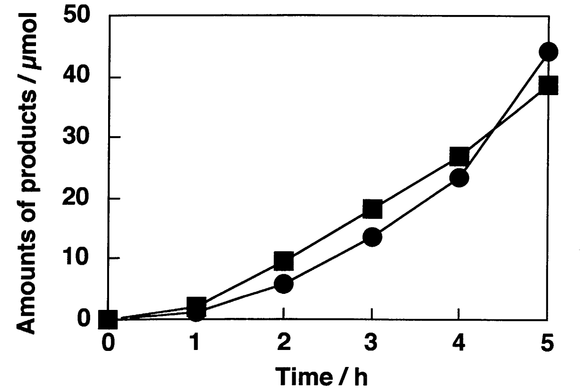

Figure 2. Photocatalytic activities of $Na_2W_4O_{13}$.
● ; H_2 evolution from $CH_3OH_{aq.}$,
■ ; O_2 evolution from $AgNO_{3aq.}$

photocatalyst produced the reasonable amount of hydrogen without co-catalysts such as Pt in contrast to the WO_3 photocatalyst. However, photocatalytic decomposition of pure water into hydrogen and oxygen is not succeeded at the present stage.

The energy diagram can be drawn from the absorption spectra and the photocatalytic activities as shown in Figure 3. The photocatalytic behavior is explained as follows. The conduction band level of $Na_2W_4O_{13}$ is more negative than that of WO_3 as the band gap is larger resulting in the appearance of the hydrogen evolution activity . However, the activity for the hydrogen evolution of $Na_2W_4O_{13}$ is still low compared with that of $[Si(W_3O_{10})_4]^{4-}$. This is probably due to the difference of the conduction band levels. The photocatalytic activities for the hydrogen evolution of layered titanates and niobates are increased by H^+ exchange.[9-11] However, the activity of $Na_2W_4O_{13}$ was almost lost by the H^+ exchange as shown in Table 1 suggesting the conduction band level was shifted more positive by a decrease in the band gap. The hole produced in the homogeneous $[Si(W_3O_{10})_4]^{4-}$ photocatalyst should have possessed the potential energy enough to oxidize water to form oxygen but it does not. This indicates that the $[Si(W_3O_{10})_4]^{4-}$ photocatalyst does not possess the active site for the oxygen evolution. In contrast, the solid surface of $Na_2W_4O_{13}$ would be advantageous for the appearance of the oxygen evolution site. In general, however, H^+-exchanged derivatives of layered oxides are not active for oxygen evolution even if the valence band potentials are enough deep. The oxygen evolution sites would be destroyed by the H^+ exchange.

Table 1. Photocatalytic hydrogen and oxygen evolution from aqueous solutions with sacrificial reagents by tungsten oxide catalysts

Catalyst[a]	Activity / μmol h^{-1}	
	H_2[b]	O_2[c]
$Na_2W_4O_{13}$	21	9
$H^+/Na_2W_4O_{13}$	0.4	---
$H_4[Si(W_3O_{10})]$	156	0
WO_3	0.04	1220

[a] 1 g, [b] from an aqueous methanol solution (H_2O 350 ml+CH_3OH 20 ml), [c] from an aqueous silver nitrate solution (0.05 mol/l, 350 ml). 400 W high pressure mercury lamp, Pyrex inner irradiation cell.

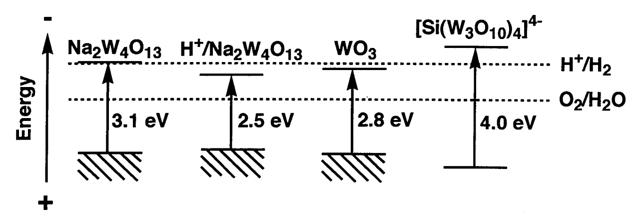

Figure 3. Relative position of energy band levels of $Na_2W_4O_{13}$, H^+-exchanged $Na_2W_4O_{13}$, WO_3, and $[Si(W_3O_{10})_4]^{4-}$ photocatalysts.

The color of all catalysts turned into blue by the photocatalytic reaction in an aqueous methanol solution indicating that the electrons were accumulated in the catalysts. This suggests that the rate determining step in the hydrogen evolution reaction is the reduction of water by the electrons produced under irradiation.

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