Highly Efficient Water Splitting over $K_3Ta_3B_2O_{12}$ Photocatalyst without Loading Cocatalyst

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$K_3Ta_3B_2O_{12}$ with pillared structure showed a high photocatalytic activity for water splitting into H_2 and O_2 without assistance of cocatalysts. The bandgap of $K_3Ta_3B_2O_{12}$ was 4.2 eV. $K_3Ta_3B_2O_{12}$ showed blue photoluminescence at 77 K by the bandgap excitation as well as other tantalate photocatalysts for water splitting.

Photocatalyst materials for water splitting have extensively been surveyed aiming at photon-energy conversion. This reaction is expected to be a new process for hydrogen production without consumption of fossil fuels and CO_2 emission in future. Many oxides consisting of d^0 and d^{10} metal cations have been reported.[1–3] Many tantalates show high activities for water splitting.[4–6] NiO/$NaTaO_3$:La gives 56% of a quantum yield at 270 nm.[7] In general, loading of a cocatalyst such as NiO and RuO_2 is indispensable for photocatalysts for water splitting in order to introduce an active site for H_2 evolution and/or enhance charge separation.

There are photocatalyst materials with unique structure such as layered structure for $K_4Nb_6O_{17}$,[8] $K_2La_2Ti_3O_{10}$,[9] and $Sr_2M_2O_7$ (M = Nb and Ta)[10] and tunneling structure for $A_2Ti_6O_{13}$ (A = Na, K, Rb, and Cs)[11] and $BaTi_4O_9$.[12] The present authors have reported $K_3Ta_3Si_2O_{13}$ which consists of pillars formed by corner sharing of three linear TaO_6 chains.[13] The TaO_6 pillars are linked by Si_2O_7 ditetrahedral units. $K_3Ta_3B_2O_{12}$ has the similar crystal structure to $K_3Ta_3Si_2O_{13}$.[14] The TaO_6 pillars in $K_3Ta_3B_2O_{12}$ are linked by BO_3 triangle units as shown in Figure 1. The characteristic structure of $K_3Ta_3B_2O_{12}$ has led us to examine its photocatalytic property.

$K_3Ta_3B_2O_{12}$ was synthesized by calcination of the mixture of K_2CO_3 (Kanto Chemicals, purity; 99.5%), Ta_2O_5 (Wako Pure Chemical, purity; 99.99%), and H_3BO_3 (Kanto Chemicals, purity; 99.5%) in air at 1073–1173 K for 10–20 h using a platinum crucible. Excess amounts of potassium and boron were added in the starting material to compensate the volatilization. The powder was used as prepared. The powder was confirmed by an X-ray diffraction method (Rigaku: MiniFlex). The photocatalytic water splitting was conducted by suspending 0.5–1 g of the catalyst in 350 mL of distilled water in an inner irradiation quartz reaction cell attached to a gas-closed circulation system. The light source was a 450-W high-pressure mercury lamp (Ushio: UM-452). A gas chromatograph (Shimadzu: GC-8A, MS5A column, argon carrier) was used for the determination of H_2 and O_2 evolved. Diffuse reflection and luminescent spectra were obtained using a UV–vis–NIR spectrometer (Jasco: Ubest V-570) and a fluorospectrometer (HORIBA JOBIN YVON: SPEX Fluorolog-3), respectively. The diffuse reflection spectrum was converted to an absorbance mode by means of the Kubelka–Munk method. The powder was observed using a scanning electron microscope (JEOL: JSM-6700F). A surface area was determined by the BET method (Coulter: SA3100).

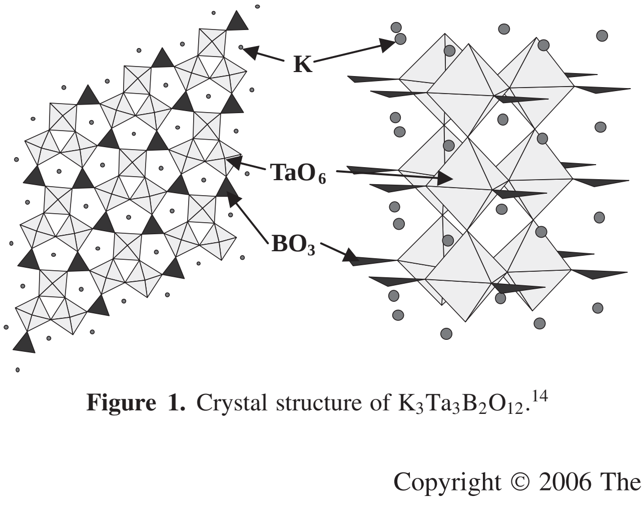

Figure 1. Crystal structure of $K_3Ta_3B_2O_{12}$.[14]

Figure 2 shows a diffuse reflection spectrum at room temperature and photoluminescence spectra at 77 K of $K_3Ta_3B_2O_{12}$. The bandgap was estimated to be 4.2 eV from the onset wavelength. Blue luminescence with a peak at 432 nm was observed. The onset of the excitation spectrum was almost the same as that of the diffuse reflection spectrum indicating that the photoluminescence was due to the bandgap excitation. Most of tantalate photocatalysts for water splitting show photoluminescence at that temperature.[13,15] Therefore, there would be the relationship between photocatalytic activities and luminescent properties for tantalate photocatalysts as suggested for niobate photocatalysts.[16] Showing luminescence indicates that all photogenerated electrons and holes do not recombine nonradiatively: that is advantageous for photocatalysts. The Stokes shift is due to the

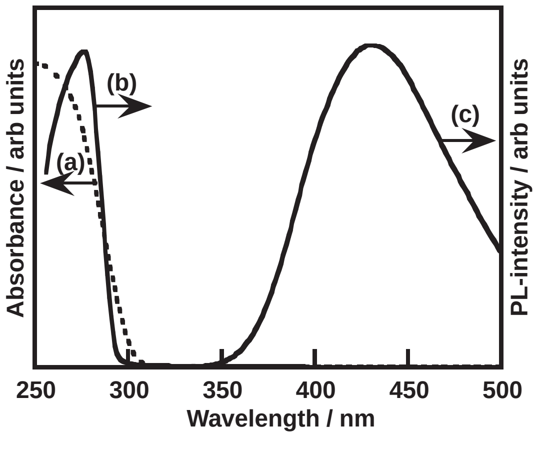

Figure 2. (a) A diffuse reflection spectrum at room temperature, (b) excitation, and (c) emission spectra at 77 K of $K_3Ta_3B_2O_{12}$.

Table 1. Photocatalytic water splitting over $K_3Ta_3B_2O_{12}$[a]

Excess amount in preparation/mol %		Calcination conditions	Activity/mmol h^{-1}	
K	B		H_2	O_2
5	5	1173 K, 10 h	0.54	0.27
5	10	1173 K, 10 h	1.79	0.86
5	15	1173 K, 10 h	1.58	0.77
5	20	1173 K, 10 h	1.13	0.56
5	10	1073 K, 20 h	2.39*	1.21*

[a]Catalyst (1.0 g, *0.5 g), distilled water (350 mL), inner irradiation cell made of quartz, 450-W high-pressure mercury lamp.

degree of delocalization or migration of excited energy.

Photocatalytic water splitting into H_2 and O_2 over $K_3Ta_3B_2O_{12}$ was examined as shown in Table 1. $K_3Ta_3B_2O_{12}$ showed high activity even without cocatalysts. The optimum amounts of excess potassium and boron, and calcination condition were 5%, 10%, and 1073 K–20 h, respectively. SEM observation revealed that the prepared powder had a hexagonal pillared shape reflecting the crystal structure. The width and length were 200–300 and 500–800 nm, respectively. The surface area was 1 $m^2\,g^{-1}$. The excess amount of potassium and boron in the starting material assisted not only the compensation of volatilization but also the crystal growth. Water splitting over the optimized $K_3Ta_3B_2O_{12}$ photocatalyst is shown in Figure 3. The rates of H_2 and O_2 evolution were 2.4 and 1.2 mmol h^{-1}, respectively. The turnover number of reacted electrons to the number of mols of the used catalyst was 41. The XRD pattern was not changed after water splitting. These results indicate that the reaction proceeded photocatalytically. The apparent quantum yield was 6.5% at 254 nm. The activity was considerably high compared with those of other reported photocatalysts without cocatalysts.[8,10,13,15,17] Interestingly, NiO cocatalyst-loading for enhancement of H_2 evolution was not effective for the $K_3Ta_3B_2O_{12}$ photocatalyst. It indicates that the surface possesses highly active sites for H_2 evolution.

The authors have reported that, in $ATaO_3$ (A = Li, Na, and K) photocatalysts, the suitable distortion of the crystal flame work which is derived from the difference in the bond angle of O–Ta–O induced a high photocatalytic activity.[15] The bond angle in $K_3Ta_3B_2O_{12}$ (171.5°)[18] is slightly smaller than that in $K_3Ta_3Si_2O_{13}$ (173.1°).[14] The distortion due to the smaller bond angle of $K_3Ta_3B_2O_{12}$ than that of $K_3Ta_3Si_2O_{13}$ resulted in widening of the bandgap and blue shift in the photoluminescence. Moreover, the photocatalytic activity of $K_3Ta_3B_2O_{12}$ was higher than that of $K_3Ta_3Si_2O_{13}$ and was similar to that of a highly active $NiO/NaTaO_3$ photocatalyst.

In conclusion, $K_3Ta_3B_2O_{12}$ with a pillared structure showed blue luminescence at 77 K and a high photocatalytic activity for water splitting without a cocatalyst. The activity was comparable to that of $NiO/NaTaO_3$.

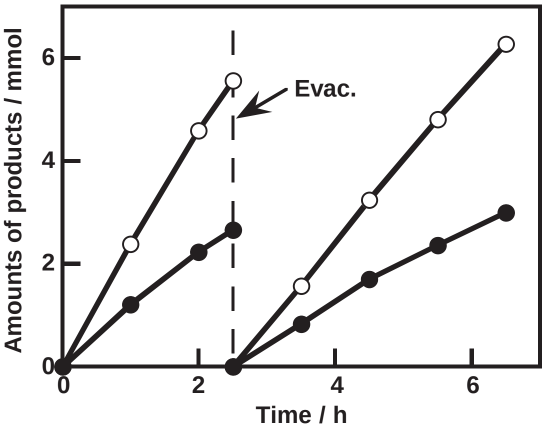

Figure 3. Photocatalytic water splitting over native $K_3Ta_3B_2O_{12}$. Catalyst (0.5 g), distilled water (350 mL), inner irradiation cell made of quartz, 450-W high-pressure mercury lamp. Open marks: H_2 and closed marks: O_2.

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