Synthesis of $K_3Ta_3B_2O_{12}$ photocatalyst by solution based method and effect of co-catalyst and phase purity to water splitting activity

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$K_3Ta_3B_2O_{12}$ is photocatalyst that exhibit relatively high water splitting activity without co-catalyst, was synthesized by various solution methods. Obtained samples were characterized by X-ray diffraction. Samples synthesized by complex gelation method and polyamide-type polymerizable complex method were single phase $K_3Ta_3B_2O_{12}$. Sample synthesized by complex gelation method was tested for water splitting activity, and this sample has little water splitting activity without co-catalyst. When NiO 0.5 wt% as co-catalyst was loaded to samples, hydrogen generated 1600 $\mu$mol/h.

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1. Introduction

1.1 Photocatalyst for water splitting

Electrical energy currently used in the world is primarily obtained from fossil fuels such as natural gas and coal, as well as some other sources such as nuclear power, that vary countries. However, there are various problems associated with fossil fuels, such as depletion and CO$_2$ emission, as well as with nuclear power, including radioactive waste and environmental effects in the event of an accident. As a solution to these problems, energy from hydrogen has attracted significant recent attention. Hydrogen is easy to handle and is environmentally friendly since only water is generated when it burns. It is a promising substitute to conventional fossil fuel sources and nuclear power for obtaining electrical energy. Currently, hydrogen is primarily obtained by methane steam reforming.

$$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$$

However, this necessitates high-temperature conditions that consume energy and generate CO$_2$ during the synthesis. A number of new energy generation technologies such as solar energy and photocatalysis for splitting water as a method to generate hydrogen are currently being investigated. The focus of the present study was the development of a new photocatalyst for splitting water.

In general, the photocatalyst used for splitting water is a semiconductor which decomposes water by irradiation with sunlight and generates hydrogen and oxygen. Typical materials used as water-splitting photocatalysts include various oxides, nitrides, sulfides, etc., which include metal ions with d$^0$ and d$^{10}$ electronic configuration$^1$: NaTaO$_3$ and GaN/ZnO are representative examples. Among all currently known water-splitting photocatalysts, NaTaO$_3$ doped with lanthanum shows the highest activity, generating 19.8 mmol/h hydrogen in the presence of NiO co-catalyst.$^3$

1.2 Co-catalyst

The co-catalyst promotes the reduction reaction of H$_2$O by excited electron and enhances photocatalytic performance when loaded to the catalyst in small quantities. Loading the surface of a semiconductor photocatalyst with a conductive metal or metal oxide, such as gold, platinum, ruthenium, or nickel oxide, in various ways can effectively move excited electrons in the photocatalyst to the surface and inhibit recombination of electrons and holes.

1.3 $K_3Ta_3B_2O_{12}$

$K_3Ta_3B_2O_{12}$ was investigated by Ikeda et al., and was shown to generate hydrogen at a rate of 2.39 mmol per hour and oxygen at a rate of 1.21 mmol per hour without a co-catalyst.$^5$ It has been suggested that a photocatalyst with the M–O–M bond angle closer to 180 degrees can efficiently move excitons. $K_3Ta_3B_2O_{12}$ has a Ta–O–Ta bond angle of 171.5 degrees, which is close to 180 degrees.$^4$ Also, it shows fluorescence at 77 K which may easily delocalize excitation energy. Thus, it is an intriguing substance as a photocatalyst for water splitting. $K_3Ta_3B_2O_{12}$ is typically synthesized by a conventional solid-state method, its particle can be made smaller in a solution-based method and an increase in photocatalytic activity can be expected. In the present work, we synthesized $K_3Ta_3B_2O_{12}$ using various solution-based methods in this study, with the goal of achieving high activation and also investigated the necessity for the use of a co-catalyst.

2. Experimental

2.1 Complex gelation method

5 mmol TaCl$_3$ (Furuuchi Chemical Co.) was suspended in 30 g H$_2$O$_2$ (Wako Pure Chemical Industries, Ltd.), to which 6 g NH$_3$ aq. (Wako Pure Chemical Industries, Ltd.) was added and the
TaCl₅ was dissolved. White precipitates were obtained when methanol (Wako Pure Chemical Industries, Ltd.) was added; this operation was performed to remove chloride ions. The precipitate was filtered and dissolved again into 30 g H₂O₂ and 6 g NH₃ aq. added. 50 mmol citric acid (Wako Pure Chemical Industries, Ltd.) was added as a complexant agent. To this obtained complex solution was added 5–5.25 mmol KNO₃ (Wako Pure Chemical Industries, Ltd.) and 3–3.3 mmol H₃BO₃. This solution was heated to 80°C with stirring to evaporate water. It was then heated to 350°C and a powder precursor was obtained. The precursor was calcinated at 800°C for 5 h in air to obtain the target material.

2.2 PVA method
5 mmol TaCl₅, 5–5.25 mmol KNO₃, 3–3.3 mmol H₃BO₃, citric acid, and propylene glycol (polyester method) or ethylenediamine (polyamide method) were dissolved in methanol. Evaporation to dryness of the mixed solution was carried out using a hot stirrer at 130°C, and a resinous solid substance was obtained. Thermal decomposition of the solid substance was carried out by heating at 450°C, and the precursor powder was obtained. The precursor was calcinated at 800°C for 5 h under atmosphere conditions to obtain the target material.

2.3 Polymerizable complex method
5 mmol TaCl₅, 5–5.25 mmol KNO₃, 3–3.3 mmol H₃BO₃, citric acid, and propylene glycol (polyester method) or ethylenediamine (polyamide method) were dissolved in methanol. Evaporation to dryness of the mixed solution was carried out using a hot stirrer at 130°C, and a resinous solid substance was obtained. Thermal decomposition of the solid substance was carried out by heating at 450°C, and the precursor powder was obtained. The precursor was calcinated at 800°C for 5 h in air, to obtain the target material.

2.4 Solid state method
Ta₂O₅ (Kanto Chemical Co., Inc.) and K₂CO₃ (Wako Pure Chemical Industries, Ltd.) H₂BO₃ were mixed in an agate mortar for 30 min. The excess amount of potassium (5 mol%) and boron (10 mol%) was added to the mixture to compensate volatilization of these elements. The mixture was calcined in air at 800°C for 5 h using a muffle furnace to obtain the target material.

2.5 Photocatalytic activity test
The photocatalytic reactions were carried out using a gas-closed inner irradiation system. The photocatalyst powder (0.3 g) was dispersed in distilled water 400 ml by a magnetic stirrer. The light source was a 450 W high-pressure mercury lamp (Ushio Inc., UMC-452). The amounts of H₂ and O₂ evolved were determined by gas chromatography (Shimadzu Co., GC-8A, Ar gas carrier, MS-5A Column TCD).

3. Results and discussion
3.1 XRD
XRD (Rigaku Geigerflex RAD-C) patterns of the samples synthesized by the different methods are shown in Fig. 1. In previous report, excess quantities of boron and potassium for the experiment were set to 10 mol% and 5 mol% respectively in the solid state method. In the PVA method, the peroxy-tantalate acid complex was easily decomposed by heat and a white precipitate formed; therefore, it turned out that this method was not suitable for the synthesis of this material. Only the complex gelation method succeeded in synthesizing the target material in the single-phase. A multi-phase target material and K₃Ta₃B₂O₉ were obtained by a polyamide-type polymerizable complex method, and the single-phase of KTaO₃ was obtained by a polyester-type polymerizable complex method. Compared to the polyamide-type polymerizable complex method, all of the boron was volatilized in the polyester-type polymerizable complex method. This suggests that boron and propylene glycol react and generate a highly-volatile substance. In the polyamide method, the ratio of the target material increased when the solvent was changed from methanol to H₂O₂. Peaks due to the target material were also confirmed in the XRD pattern of the samples synthesized by the polyamide-type polymerizable complex method, and it is thus considered that adding more boron can realize a single-phase. Therefore, we conducted the following experiment. The XRD results of the product synthesized by the polyamide-type polymerizable complex method are shown in Fig. 2. Here, H₂O₂ was used as a solvent since methanol is considered to volatilize boron. Making boron exceed 40 mol% in the material led to success in synthesizing a single-phase of the target material. Based on these results, a detailed evaluation of the samples synthesized by the complex gelation method was carried out.
3.2 Diffuse reflectance spectrum

Diffuse reflection spectra were obtained using a UV-vis spectrophotometer (HITACHI, Ltd., U–3000). The absorption spectra obtained by the KUBERUKA–MUNK conversion of the diffuse reflectance spectra of K$_3$Ta$_3$B$_2$O$_{12}$ synthesized by the solid-state method and the complex gelation method are shown in Fig. 3. The band-gap of the sample synthesized by the solid-state method was 4.1 eV, and that of the sample synthesized by the complex gelation method was 4.0 eV. It has been reported that the absorption spectra blue-shift with increasing amount of boron.$^{5}$ Therefore, we considered that the band gap shifted to the short wavelength side as the phase purity increased.

3.3 Scanning electron microscopy

Hitachi, Ltd., S–3200N was used for the observation of the sample. A SEM image of the synthesized K$_3$Ta$_3$B$_2$O$_{12}$ is shown in Fig. 4. The sample synthesized by the complex gelation method showed a plate-like shaped microstructure. This happened presumably because evaporation to dryness of the precursor solution increased its viscosity, thereby generating fine bubbles trapped in the precursor, and the precursor became plate-like form when ground, reflecting a plate-like form even after calcination. Unevenness of the surfaces of the particles was observed because the particles were formed from smaller particles condensed or sintered. It was confirmed that the sample synthesized by the complex gelation method had smaller primary particles compared to the sample synthesized by the solid phase method.

3.4 Photocatalytic activity

The result of the photocatalyst activity test of K$_3$Ta$_3$B$_2$O$_{12}$ synthesized by the complex gel method is shown in Fig. 5. Hydrogen and oxygen were generated at rates of 190 and 100 μmol per hour, respectively. Since the amount of hydrogen and oxygen generated was mostly in a stoichiometric ratio, it was observed that this material can perform complete decomposition of water. Previous reports have suggested that this material shows high activity even if there is no co-catalyst. However, we considered that there could be an effect caused by loading a co-catalyst, and therefore in the present work, NiO was loaded as a co-catalyst and the activity was evaluated. The results are shown in Fig. 6, and indicate that the activity went up markedly by loading the NiO co-catalyst. The highest activity value was 1.6 mmol/h when the amount of co-catalyst was 0.5 wt%. Gas generation increased as the loading amount of the co-catalyst increased up to 0.5 wt%. However, the activity declined when the loading amount exceeded 0.5 wt%. This suggests that the co-catalyst functioned correctly as anticipated, and that K$_3$Ta$_3$B$_2$O$_{12}$ is a material that essentially requires a co-catalyst. However, this experimental
result is contradictory to the result previously reported indicating that high activity is seen without a co-catalyst in the sample synthesized by the solid state method. In the solid-state method, 10 mol% excess amount of HBO₃ and 5 mol% excess amount of K₂CO₃ are used with respect to vaporization of K and B. The remaining K and B, or the shortage of K and B by vaporization, could cause a difference in the water-splitting activity similar to the effect of a co-catalyst. Therefore, in order to investigate this, the following experiment was conducted. The results of water decomposition activity evaluation by loading various additives to the sample are shown in Fig. 7. All the additives loaded at 200°C yielded declining activity. This is presumably because the citrate complex solutions of tantalum used when adding tantalum, which are organic components, were not completely burned off at low temperature. Activity improvement was observed in the catalyst to which both boron and tantalum were added or only boron was added. This activity improvement likely occurred because the added boron filled up defects on boron sites which existed originally and presumably the number of such defects decreased. This suggests that comparatively high activity can be obtained if boron defects can be lessened, even if no co-catalyst was used. Finally, the activities of the samples formed by the complex gelation method and by the solid-state method were compared. The results are shown in Fig. 8. The sample synthesized by the complex gelation method was superior with or without a co-catalyst. This is presumably because particle diameters of the sample synthesized by the complex gelation method are smaller than those for the sample obtained using the solid-state method; thus, the specific surface area of the former sample is larger. The activity did not exceed the previously reported value for the solid-state method. This is presumably because boron is easily volatilized in the solution method, the generated boron defect plays the role of an electron-hole trap site, and the activity declined. In this study of the solution method, loading NiO as a co-catalyst thus promoted charge separation and improved activity.

4. Conclusion

We succeeded in synthesizing a target material with a single-phase by employing the complex gelation method and the polyamide-type polymerizable complex method. The complex gelation method is the most suitable one for synthesis of K₃Ta₃B₂O₁₂ since excess amount of boron is not necessary. The photocatalyst synthesized by the complex gelation method showed very small activity without the co-catalyst. This is presumably because boron defects were generated by the solution method in which boron is easily volatilized, thereby lowering the activity. Loading NiO showed marked improvement in activity, and 1.6 mmol/h hydrogen was generated at 0.5 wt%. In our experiment, the photocatalytic activity of K₃Ta₃B₂O₁₂ improved when loaded with a co-catalyst. Boron addition after synthesis of the photocatalyst showed high activity, even when NiO was not loaded as the co-catalyst, presumably because boron defects were filled up with the added boron. Therefore, we conclude that K₃Ta₃B₂O₁₂ shows high water-splitting activity when there are fewer defects even in the absence of a co-catalyst. In this study, compared to the solid-state method, higher activity was seen for the solution method. We assume that this is because it is possible to synthesize fine particles which have a large surface area by this method.

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References