

Synthesis of NaTaO₃ Photocatalysts for Efficient Water Splitting From Amorphous Metal-Complex Method

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NaTaO₃ photocatalysts are known to demonstrate high yield of water splitting under UV irradiation. NaTaO₃ has the perovskite-type structure with orthorhombic distortion. Due to the large band gap of 4.0eV, NaTaO₃ can decompose water into H₂ and O₂ without co-catalysts. NaTaO₃ photocatalysts were synthesized by Amorphous Metal-complex Method (AMM) and final synthesis temperature of 800°C. It is 350°C lower than the temperature used in conventional ceramic method. To make a single phase NaTaO₃ photocatalyst excess of sodium was necessary in order to compensate Na evaporation. AMM provided higher surface area of the powder compared to ceramic route or another sol-gel technique based on the Polyvinyl Alcohol (PVA) water solution.

Key words: photocatalyst, Amorphous Metal-complex Method, low temperature synthesis, high-surface area, NaTaO₃

1. INTRODUCTION

Photocatalysts for water decomposition have been studied extensively, and it is reported that some oxides are active in the stoichiometric decomposition of water under UV irradiation [1-5]. Among materials capable for water photodecomposition and having perovskite structure, tantalates are the most promising compounds [6-8]. NaTaO₃ is an example of photocatalyst possessing the perovskite-type structure [8] with orthorhombic distortion. Due to the large band gap of 4.0eV, NaTaO₃ can decompose water into H₂ and O₂ without co-catalysts. The reported quantum yield of 28% for NiO coated NaTaO₃ material is the highest yield ever observed [6]. Taking into account that the fundamental reaction mechanism of photodecomposition involves not only hole-electron pair generation by the absorbed light, but also chemisorption and electron transfer, the crystallinity as well as large surface area become the essential conditions for high performance of photocatalysts [9,10]. Kudo et al. [6] has carried out the synthesis of NaTaO₃ photocatalysts at 1150 °C by conventional ceramic method. Although high synthesis temperature improves grain growth and favors the formation of perfect crystallites, the grain growth itself decreases powders surface area. Therefore utilization of the solution based techniques such as Amorphous Metal-complex Method (AMM) [11-13] or Polyvinyl Alcohol (PVA) aqueous solution sol-gel method [13-15], which provide high homogeneity and normally drastically decrease oxide materials synthesis temperature, should be particularly important for preparation of catalytic materials.

There were several attempts to prepare NaTaO₃ using PVA based technique. However formation of NaCl and its melting at 800°C resulted in the abnormal grain growth of the fine starting precursor. In this paper we report the preparation of NaTaO₃ photocatalyst by AMM without partial melting of by-products, which

allowed control of the powder surface area and improvement of photocatalytic activity.

2. EXPERIMENTAL

2.1 Synthesis of NaTaO₃ photocatalyst

Flowchart of synthesis procedure of NaTaO₃ photocatalysts by Amorphous Metal-complex Method is presented in Fig.1. Tantalum pentachloride (Furuuchi Chemical Co., purity: 99.9%) was dissolved in methanol (Kanto Chemicals Co., Inc., Tokyo, Japan). Citric acid (Wako Pure Chemicals, purity: 98.0%) with molar ratio of [C.A.]/[Ta]=5 was added to the solution. The solution

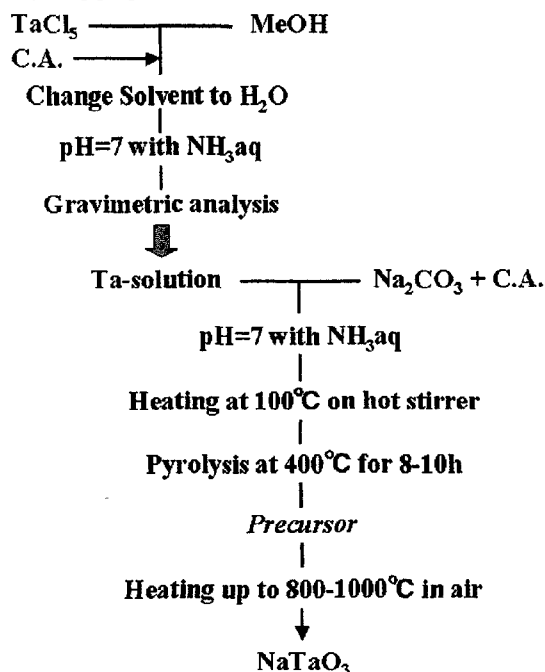


Fig.1 Flow chart for preparing NaTaO₃ by the Amorphous Metal-complex Method

was stirred and heated while gradually adding water to replace methanol. After the solvent has been changed to water the temperature of the solution was raised to 100°C , followed by the addition of an ammonia solution (Kanto Chemicals Co., Inc., Tokyo, Japan, concentration: 28~30 mass %) to adjust pH to 7.0. The obtained stock solution of tantalum citric acid complex was transparent and colorless. The tantalum content was determined by gravimetric analysis [16].

Na_2CO_3 (Wako Pure Chemicals, purity: 99.5%) was added to an aqueous solution of citric acid with $[\text{Na}]/[\text{C.A.}]=1$. Then, this solution was mixed with the tantalum stock solution in a molar ratio of $[\text{Na}]:[\text{Ta}]=1.1:1$. The pH was adjusted to pH=7 by addition of $\text{NH}_3(\text{aq})$. The remaining water has been slowly evaporated at 100°C on a hot stirrer and yielded a yellowish ocher gel. The gel was heat-treated at 400°C for 8-10 hours in mantle heater to eliminate Cl^- by sublimation of NH_4Cl . The obtained gray powder was ground and calcined at $800\text{--}1000^\circ\text{C}$ for 10h in air.

2.2 Characterization of samples

Thermogravimetry-differential thermal analysis (TG-DTA; type-2020, MAC Science Co., Tokyo, Japan) was carried out to follow the decomposition of precursors and crystallization of products using an alumina crucible at a heating rate of $5^\circ\text{C}/\text{min}$ from room temperature to 1200°C in static air. The products after heat treatment between 800°C and 1000°C were characterized by X-ray powder diffraction (XRD) to identify phases formed. A standard X-ray powder diffractometer (Model MXP3VA, MAC Science Co.) was used with $\text{CuK}\alpha$ radiation at 40kV and 40mA and scanning rate of $4^\circ/\text{min}$ in the range of $10\text{--}80^\circ$ (2θ). A specific surface area of sample was determined by B.E.T. adsorption isotherm measurement (ASAP2010, Micromeritic Co.).

3. RESULTS AND DISCUSSIONS

TG-DTA curves of NaTaO_3 photocatalyst precursor are shown in Fig.2. The weight decrease started at about 430°C accompanied by the large exothermic peak with maximum at around 530°C and originates due the oxidation of organic compounds and crystallization of the complex oxide. Note, the endothermic peak at 800°C

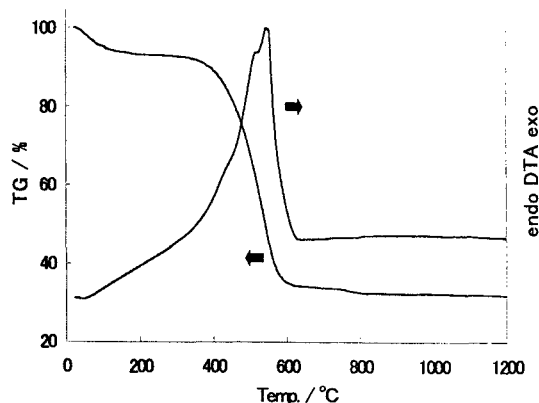


Fig.2 TG-DTA curves obtained by heating the precursor for NaTaO_3 in static air at a heating rate of $5^\circ\text{C}/\text{min}$.

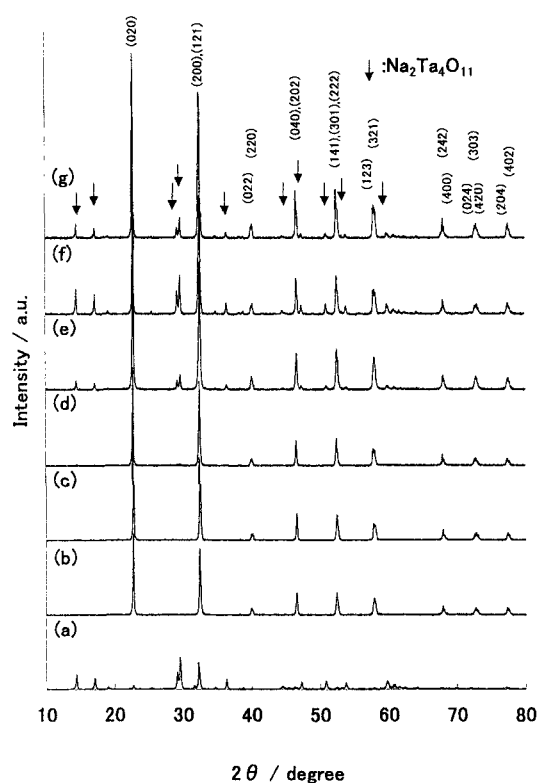


Fig.3 XRD patterns of NaTaO_3 at (a) 600°C (b) 700°C (c) 800°C (d) 850°C (e) 900°C (f) 950°C (g) 1000°C for 10h in air

which should accompany sodium chloride melting (usual problem in PVA method) was not observed in the AMM processing. This indicates that the chloride ions present in the starting solution were removed in the form of ammonium chloride when the sample was treated in mantle heater to eliminate solvent and organic compounds. According to TG-DTA data, the major weight decrease due to the oxidation of organic compounds is accomplished by 700°C . The formation of NaTaO_3 probably takes place till 800°C since one may observe weight loss of approximately 1% in the temperature range of $750\text{--}810^\circ\text{C}$ that we attribute to the decomposition of residual carbonate possibly accompanied by evaporation of NaCl . Note, if all of the sodium excess would be present in form of chloride, one should expect about 2% of weight decrease. Although observed weight loss perfectly matches the estimation of sodium evaporation in the form of Na_2O , we think the temperature range is low for such a process to occur. The minor weight loss of 0.7% between 800°C and 1200°C may be explained purely by the evaporation of sodium. In such a case it should result in the formation of approximately 4% of $\text{Na}_2\text{Ta}_4\text{O}_{11}$. However taking into account that evaporation will occur from the surface of the grains, one should expect formation of impurity phase on the grain surface and, as a consequence, its larger contribution to XRD pattern. These conclusions are in a good agreement with XRD patterns of the samples prepared in the temperature range of $600\text{--}1000^\circ\text{C}$ (Fig. 3) where the highest content of the impurity can be estimated as 10% after 10h annealing at 1000°C . Consequently, we decided to conduct heat

Table I B.E.T. specific surface area of NaTaO₃

Synthesis method	Sintering temp. (°C)	Na:Ta	Specific surface area (m ² /g)
SSR ^{a)}	1150	1:1	0.53
SSR	1150	1.05:1	0.44
PVA ^{b)}	800	1.05:1	1.86
PVA	850	1.05:1	1.51
PVA	900	1.05:1	1.49
PVA	950	1.05:1	1.43
PVA	1000	1.05:1	1.32
AMM ^{c)}	800	1.1:1	3.03
AMM	850	1.1:1	2.75
AMM	900	1.1:1	2.27
AMM	950	1.1:1	2.41
AMM	1000	1.1:1	1.75

a) Solid State Reaction

b) Polyvinyl Alcohol method

c) Amorphous Metal-complex Method

treatment of the precursor in the temperature range of 800-1000°C using the 10% excess of sodium in starting composition to compensate its evaporation.

Samples of NaTaO₃ (hereafter called N-1) and Na_{1.1}TaO₃ (N-1.1) were prepared in the temperature range of 600-1000°C. The XRD patterns of N-1.1 after 10h heat treatment are displayed in Fig.3. One may see that at 600°C the main crystalline phase is Na₂Ta₄O₁₁. After annealing at 700°C, NaTaO₃ appeared as the main phase, and all the peaks can be indexed within orthorhombic room-temperature form of NaTaO₃ with lattice parameters of $a=5.4878(7)\text{\AA}$, $b=7.7876(9)\text{\AA}$ and $c=5.5172(6)\text{\AA}$. Relatively high uncertainty is due to the large peak width, which make it difficult to determine precise reflections positions. Once the temperature rises, peaks become narrower, and starting from 900°C an impurity phase may be detected. In this temperature range lattice parameters of NaTaO₃ and its unit cell volume increase. Even though reflection can be located more accurately for high temperature samples, the difference of lattice parameters for the whole temperature range remains within three standard deviations.

Compared with the specimens prepared at 1150°C by ceramic method, NaTaO₃ photocatalysts synthesized by AMM were obtained as a single phase at lower temperature of 800°C with 10% excess of sodium. As the calcination temperature rose, the diffraction peaks of Na₂Ta₄O₁₁ appeared. These peaks also appeared in N-1 calcined at 800°C. In addition to that, increase of sintering temperature leads to the decrease of the X-ray reflections width, which means that the crystallization is promoted and the crystallinity improves at high temperature.

Table I shows the results of B.E.T. specific surface

area measurements of NaTaO₃ photocatalysts. NaTaO₃ photocatalysts synthesized by AMM have almost six times larger surface area than specimens obtained by conventional ceramic method. This result should be attributed to the small particle size of the sol-gel precursor and 350°C lower synthesis temperature that slows down grain growth. In addition, the specimen prepared by AMM at 800°C has about 1.5 times larger surface area than the one synthesized by PVA method.

4. CONCLUSION

In this paper, we report synthesis of NaTaO₃ materials with perovskite-type structure, which are known to demonstrate high yield for water splitting under UV irradiation, using Amorphous Metal-complex Method and final synthesis temperature of 800°C. To make a single phase NaTaO₃ photocatalyst it was important to utilize excess of sodium compared to the ideal stoichiometry in order to compensate its evaporation. The surface area of NaTaO₃ photocatalysts synthesized by AMM was 5.7 times larger than that of typical samples obtained by ceramic method. Amorphous Metal-complex Method provided higher surface area of the powder compared to another sol-gel technique based on the PVA water solution.

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