Synthesis of Spherical Photocatalyst LiTaO\textsubscript{3} Particles for Overall Water-splitting

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In this study, we developed a new solution method, Peroxide Sol-Gel (PSG) method to obtain the LiTaO\textsubscript{3} photocatalytic powder. This method uses the peroxo tantalum complex as a starting material. The precursor powders prepared by PSG method by spray-drying, formed spherical and hollow shaped particles and crystallized above 500 °C. When the precursor was annealed at 700°C, the sample with the highest photocatalytic activity (H\textsubscript{2}: 539 µmol/h and O\textsubscript{2}: 253 µmol/h) was produced. The activity of this sample exceeded the activity of solid state reaction (SSR) method’s sample. By use of the PSG method together with spray drying, the high-performance photocatalytic powders of LiTaO\textsubscript{3} having large specific surface areas and small primary particle sizes have been obtained.

Key words: LiTaO\textsubscript{3}, photocatalyst, water-splitting, solution method, tantalum complex

1. INTRODUCTION

LiTaO\textsubscript{3} was reported as a photocatalyst for overall water-splitting without co-catalyst under ultraviolet irradiation [1]. Its photocatalytic activity was H\textsubscript{2}: 430 µmol/h and O\textsubscript{2}: 220 µmol/h for 1 g of catalyst [2]. It is the highest reported activity among the alkali tantalate double oxides without a co-catalyst. This sample was prepared by solid-state reaction, which needed annealing at 1147 °C for 10 h to obtain a single phase LiTaO\textsubscript{3}. As a result this sample had a small surface area and large particle sizes, due to grain growth at such a high temperature and long heating. The surface area decrease is disadvantageous for a photocatalyst, because the photocatalytic activity depends strongly on the size of surface area and surface state. Generally, to synthesize complex oxide materials solution methods are more favorable than the SSR to achieve temperature reduction. The Pechini-type polymerizable complex (PC) method [3] and a co-precipitation method [4, 5] were used for synthesis of LiTaO\textsubscript{3} powders. PC method is superior to other techniques since it can yield an extremely homogeneous precursor. However, this method uses a lot of organic compounds to make the precursor powders. On the other hand, for co-precipitation method one has to use a lot of HF to prepare the precursor powders. Therefore, both PC and co-precipitation methods are not desirable approaches from the environmental view point.

In this study we developed a new solution technique, Peroxide Sol-Gel (PSG) method to obtain a high-performance LiTaO\textsubscript{3} photocatalytic powders, which have small particle sizes and large specific surface areas. When peroxo tantalum complex [Ta(O\textsubscript{2})\textsubscript{4}]\textsuperscript{3-} [6] is used as a starting material, organic compounds and HF are not necessary.

2. EXPERIMENTAL

The photocatalytic powder samples of LiTaO\textsubscript{3} were synthesized by PC method and PSG method as schematically described in Fig. 1. 1.5 mmol of 99.9 % TaCl\textsubscript{5} powders (Furuuchi Chemical Corporation, Tokyo, Japan) and 1 g of 28 % NH\textsubscript{3} aq. (Kanto Chemical, Tokyo, Japan) were added to 10 g of 30 % H\textsubscript{2}O\textsubscript{2} (Kanto Chemical, Tokyo, Japan). After that, 10 g of methanol was added to the solution, to obtain tantalum oxide hydrate (Ta\textsubscript{2}O\textsubscript{5}· nH\textsubscript{2}O) precipitate, which was washed to eliminate Cl ions. After filtration, the precipitate was dissolved into 10 g of H\textsubscript{2}O\textsubscript{2} aq., and then peroxo tantalum complex solution was obtained. To prepare the precursor solution for PSG method, 1.575 mmol of 95 % LiOH H\textsubscript{2}O (Wako Pure Chemicals, Osaka, Japan) was added to the peroxo tantalum complex solution. This precursor solution was evaporated to dryness by two different methods (type 1 and type 2) to form precursor powders. In the type 1, the precursor solution in a beaker was dried by heating at 280 °C. In the type 2, the precursor solution was sprayed by 200 °C air and dried to form a fine powder. The powder samples of LiTaO\textsubscript{3} were obtained after the annealing the precursor powders.

LiTaO\textsubscript{3} powder samples were synthesized also by PC method. 15 mmol of 98 % citric acid (Wako Pure Chemical Industries, Osaka, Japan), 1.575 mmol of 95% LiOH H\textsubscript{2}O and 60 mmol of 99.0 % propylene glycol (Wako Pure Chemical Industries, Osaka, Japan) were added to the peroxo tantalum complex solution. This solution was kept at 180 °C for 24 hours to promote polymerization to obtain a polymeric gel. The gel was decomposed at 450°C to form powder precursor. The LiTaO\textsubscript{3} powder samples were obtained by calcining these precursor powders.

All LiTaO\textsubscript{3} samples were characterized by X-ray diffraction (XRD, Rigaku Geigerflex RAD-C diffractometer) for phase identification, and by transmission electron microscopy (Hitachi HF-2200TU, accelerating voltage 200 kV) using scanning mode. Differential
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Thermal analysis of all samples was conducted by TG-DTA (Bruker AXS 2020SA-TU19). Specific surface areas of samples were measured by the gas adsorption method with a SHIMADZU, ASAP2010. Nitrogen gas was used as adsorption gas. Photocatalytic reactions were carried out in a closed system. The powdered photocatalysts (0.1g or 0.3g) were magnetically suspended in 400 ml of distilled water in an inner irradiation quartz cell. The photodecomposition of water was then carried out under irradiation of light from a high-pressure 450-W Hg lamp (USHIO, UM-452). The evolved gases were measured by Hg manometer, and analyzed by gas chromatography (Shimadzu, GC-8A, Ar gas carrier, MS-5A Column, TCD).

H$_2$O$_2$ aq. \[ \text{TaCl}_5 \] \[ \text{NH}_3 \text{aq.} \] \[ [\text{Ta(O}_2\text{)}_5]^{4+} + \text{NH}_4^+ + \text{Cl}^- \] \[ \text{filtrate contains NH}_4^+, \text{Cl}^- \] \[ \text{filtration} \] \[ \text{methanol} \] \[ \text{Ta}_2\text{O}_5 \cdot \text{n(H}_2\text{O)} \] \[ \text{H}_2\text{O}_2 \text{aq.} \] \[ \text{citric acid} \] \[ \text{LiOH-H}_2\text{O} \] \[ \text{LiOH-H}_2\text{O} \text{precursor solution} \] \[ \text{estersification} \] \[ \text{precursor solution} \] \[ \text{precursor powder} \] \[ \text{calcination} \] \[ \text{sample} \] (a) PC method (b) PSG method

Fig. 1 Flow chart of LiTaO$_3$ powder preparation by the (a) PC method and (b) PSG method (type 1: drying in beaker, type 2: spray drying)

3. RESULTS AND DISCUSSION
3.1 Synthesis
PSG precursor powders (both type 1 and type 2) needed 500 °C annealing to crystallize single phase LiTaO$_3$. The PSG method referred to the metal-alkoxide method in which hydrolysis and polymerization of metal-alkoxides were carried out. In this study, we obtained the homogeneous precursor powder, decomposed the peroxo tantalum complex and dried the precursor solution simultaneously. Decomposition of the peroxo tantalum complex led to formation of Ta-O-Ta bonds, and kept uniformity of Li ions achieved in the precursor solution. However, segregation of Ta or Li was possible because of different chemical properties of Li and Ta ions during drying. The DTA curves of type 1 and 2 precursors were compared in Fig. 2. Type 1 precursor powders have a sharp DTA peak; it means there is an endothermic reaction that seemed to be related to a segregation of Ta. In contrast type 2 precursor powders have no DTA peak, therefore this precursor is more homogeneous than type 1 precursor. In the spray drying the time of solvent removal is extremely short. Moreover surface area of the precursor powder increased compared to usual drying in a beaker due to aerosol formation during spray drying. The PC method precursor powders needed heating above 700°C to crystallize the single phase LiTaO$_3$. This can be explained by the large amount of organics used in the PC method which require relatively high temperature to be removed.

3.2 Photocatalytic activity
Table 1 compares the photocatalytic activity of LiTaO$_3$ powder samples synthesized by PC method and PSG method (type 1 and type 2). The samples were calcined at 600 ~ 900 °C. Surface areas of the samples, which have the highest photocatalytic activity in each method were measured and the photocatalytic activity per the unit surface areas are shown in Fig. 3. PSG method type 2 LiTaO$_3$ powder samples photocatalytic activity per the unit surface area was higher than that of PC method which is close to the activity of PSG type 1 sample. It means that photocatalytic activity of PSG sample is higher than activity of PC method, and the difference between type 1 and type 2 samples is due to the different of surface areas.

The sample prepared by PSG method type 2 calcined at 700°C exhibited the highest photocatalytic activity (H$_2$: 539μmol/h, O$_2$: 253μmol/h). The ratio of evolved H$_2$ to O$_2$ is 2 : 1, and it was stable for 5 hours as shown in Fig. 4. Turnover number for this sample in 5 hour activity test was 3.11, therefore this reaction is catalytic. The photocatalytic activity of this sample exceeded the value.
of the activity shown by SSR method sample even when smaller amount of catalyst was used. 80% of this activity was kept in second and third run by the same sample indicating that this catalyst does not deteriorate.

Table 1 Photocatalytic activity (H$_2$ evolution: μmol/h) of LiTaO$_3$ powders

<table>
<thead>
<tr>
<th>Method</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>600 700 800 900</td>
</tr>
<tr>
<td>PC</td>
<td>- 12.1 30.7 6.8</td>
</tr>
<tr>
<td>PSG-1</td>
<td>17.4 18.2 16.9 26.1</td>
</tr>
<tr>
<td>PSG-2</td>
<td>52.3 136.4 92.3 61.1</td>
</tr>
</tbody>
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Catalyst: 0.1 g, distilled water: 400ml, inner irradiation cell made of quarts, 450W high-pressure mercury lamp.

Fig. 3 Photocatalytic activities of LiTaO$_3$ samples. Catalyst: 0.1 g, distilled water: 400ml, inner irradiation cell made of quarts, 450W high-pressure mercury lamp.

Fig. 4 Photocatalytic decomposition of water (○, H$_2$; ●, O$_2$) over spherical LiTaO$_3$ particles. Catalyst: 0.1 g, distilled water: 400ml, inner irradiation cell made of quarts, 450W high-pressure mercury lamp.

3.3 Microstructures of LiTaO$_3$ samples
Shape of the particles prepared by spray-drying method was spherical and hollow (Fig. 5). The particles calcined above 800 °C have unevenness on its surface and loose the spherical shape above 900 °C. It was observed that each a spherical particle was composed of small primary particles as seen in STEM images in Fig. 6. The primary particles on the surface. Primary particle sizes became larger as annealing temperature increases. So the sample calcined at 900 °C composed of 500 nm primary particles, and some layers could not act as the photocatalytic surface because the layers are not exposed on the surface. Moreover, all primary particles are in contact with surrounding primary particle. For this reason, there is a large area of grain boundary among the primary particles and the grain boundary acts as a recombination center for free electrons and holes. So these photocatalytic powders loose photocatalytic activity because of the grain boundary and unexposed particles on the surface. Primary particle sizes became larger as annealing temperature increases. So the sample calcined at 900 °C composed of 500 nm primary particles, and the fraction of grain boundaries is reduced while it become difficult to keep the spherical and

Fig. 5 SEM images of photocatalytic particles prepared by PSG method type 2 annealed at (a) 700 °C, (b) 800 °C, (c) 900 °C, and (d) PSG method type 1 at 900, and (e) PC method at 800°C

particle size was about 50 nm, which was calcined at 600°C. Under this condition, the thickness of the particles was about 150 nm. These facts mean that a several primary particles layers constitute the wall of hollow particles, and some layers could not act as the photocatalytic surface because the layers are not exposed on the surface. Moreover, all primary particles are in contact with surrounding primary particle. For this reason, there is a large area of grain boundary among the primary particles and the grain boundary acts as a recombination center for free electrons and holes. So these photocatalytic powders lose photocatalytic activity because of the grain boundary and unexposed particles on the surface. Primary particle sizes became larger as annealing temperature increases. So the sample calcined at 900 °C composed of 500 nm primary particles, and the fraction of grain boundaries is reduced while it become difficult to keep the spherical and

Fig. 6 STEM images and section models of LiTaO$_3$ particles made by PSG method, Method 2 ((a): 600°C and (b): 800°C) ○: photocatalytic surface, ●: hidden by the photocatalytic surface
hollow shape. On the other hand, the sample calcined at 700 °C has primary particle of 150 nm, the size is almost the same as the thickness of hollow particles. Under these annealing conditions it was possible to reduce the grain boundary contribution keeping the spherical shape of particles. As a result, this sample has the highest photocatalytic activity. These results mean that preserving the spherical and hollow particles and reducing the grain boundaries are effective for the enhancing the photocatalytic activity of LiTaO₃ material.

The photocatalytic activity of PSG sample was compared with the activity of SSR sample. When the activity per the unit surface area is observed, the value for SSR method is H₂: 1.47 mmol/m² while for PSG method type 2 it is H₂:0.26 mmol/m². This result means that, samples prepared by PSG method have much more extended grain boundary than SSR method’s sample. On the other hand, the activity per gram of SSR is 0.44 mmol/g and PSG method type 2 is 1.88 mmol/g. This result is because of the peculiar shape of the particles and small primary particle sizes of photocatalysts prepared by PSG method type 2. As a result, for the same amount of samples the photocatalytic activity of the PSG method type 2 powder has higher value than that of SSR method.

![Graph](image.png)

Fig. 7 H₂ evolution of standardized photocatalytic surface (mmol/m²) and weight (mmol/g)

4. Conclusion
In this study, we developed a new solution method, Peroxide Sol-Gel (PSG) method to obtain the LiTaO₃ photocatalyst powder. Applying spray drying in the combination with the PSG method precursor solution, it was able to obtain the high-performance photocatalyst powders, which had large surface areas, small primary particle sizes, spherical and hollow shape.

5. References

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