

# 論文内容の要旨

## Introduction

Porous materials having accessible pores and a large surface area, including activated carbon, silica gel, metal oxides, zeolites, and metal–organic frameworks (MOFs), are promising functional materials such as gas storage and separation, energy storage, drug delivery, catalysis, and catalyst supports. In particular, metal oxides are intriguing materials because of their intrinsic properties of semi-conductive behavior, catalytic activity, high temperature stability, durability, easiness of handling, and cost. In order to improve the performance of materials, it is extremely important to control the size, morphology, crystallinity, and stoichiometry according to the specific application. Therefore, considerable effort has been devoted to developing new methods for the synthesis of porous materials. Among them, hydrothermal and solvothermal methods have received much attention because of their simplicity, low cost, and ability to make new porous nanomaterials.<sup>1</sup> In this thesis, solvothermal conditions for controlling the morphology and crystal structure of porous nanomaterials are focused.

## 1. Porous niobia spheres with large surface area: alcohothermal synthesis and controlling of their composition and phase transition behavior

Niobia ( $\text{Nb}_2\text{O}_5$ ), and  $\text{Nb}_2\text{O}_5$  and titania ( $\text{TiO}_2$ ) composite materials have been used as photocatalysts, solid acid, catalyst supports, and anode materials for rechargeable batteries, and fuel cells. Several preparation methods are available for these materials, but simpler preparation methods should be developed for further acceleration of their practical uses. On the other hand, we have successfully synthesized porous spherical nanocrystal assemblies, namely MARIMOs (mesoporously architected roundly integrated metal oxides), by our original one-pot solvothermal method (alcohothermal method) using alcohol as a solvent.<sup>2</sup> This synthetic method is an extremely simple method of heating a precursor solution consisting of metal compounds and additives in alcohol at a high temperature for a short time in a pressurized vessel. The obtained MARIMOs with micro- and meso-pores have a large surface area and nano concave–convex surface structure. Therefore, these MARIMOs can be useful materials as catalysts and catalyst supports.<sup>3,4</sup> In this chapter, the simple synthesis of  $\text{Nb}_2\text{O}_5$  MARIMO,  $\text{TiO}_2$ – $\text{Nb}_2\text{O}_5$  composite MARIMO, and  $\text{TiNb}_2\text{O}_7$  MARIMO with large surface area by applying alcohothermal method are described.

Simple heating of a methanol solution of  $\text{Nb}(\text{OEt})_5$  and formic acid at 300 °C for 10 min afforded perfectly monodisperse  $\text{Nb}_2\text{O}_5$  MARIMO in high yield (>90%, Figure 1a). The obtained  $\text{Nb}_2\text{O}_5$  MARIMO showed a high specific surface area (302 m<sup>2</sup>/g) and porous structure whose pore size was less than 10 nm-sized. However, the obtained  $\text{Nb}_2\text{O}_5$

MARIMO was not crystalline but amorphous. The crystal phases significantly affect the activity of the photocatalyst and solid acid. Thus, it is important to control of the crystal phase formation in the obtained Nb<sub>2</sub>O<sub>5</sub> MARIMO. The easiest method to improve the crystallinity is further heating. When the heating time of the precursor solution was prolonged to 60 min, the crystal phase dramatically changed from amorphous to the hexagonal phase of Nb<sub>2</sub>O<sub>5</sub>. This was concomitant with a drastic morphology change from spherical to rod-shaped (Figure 1b). Although the crystallinity was successfully improved, the porosity was lost due to the morphology change, and the specific surface area was greatly reduced. Calcination of the as-synthesized amorphous Nb<sub>2</sub>O<sub>5</sub> MARIMO was used as an alternative method to change the crystal phase. Calcination of the as-synthesized amorphous Nb<sub>2</sub>O<sub>5</sub> MARIMO yielded a hexagonal phase while maintained the spherical morphology at 500 °C.

Next, TiO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> composite MARIMOs were synthesized by heating of a methanol solution of Ti(O<sup>i</sup>Pr)<sub>4</sub>, Nb(OEt)<sub>5</sub>, and formic acid at 300 °C for 10 min. The molar ratio of Ti to Nb in the product MARIMO was easily controlled by changing the ratio in the corresponding precursor solution. As shown in STEM/EDX mappings in Figure 1c, Ti and Nb atoms were equally distributed at the nano-level. In addition, the TiO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> composite MARIMOs were highly porous with specific surface areas larger than 200 m<sup>2</sup>/g.

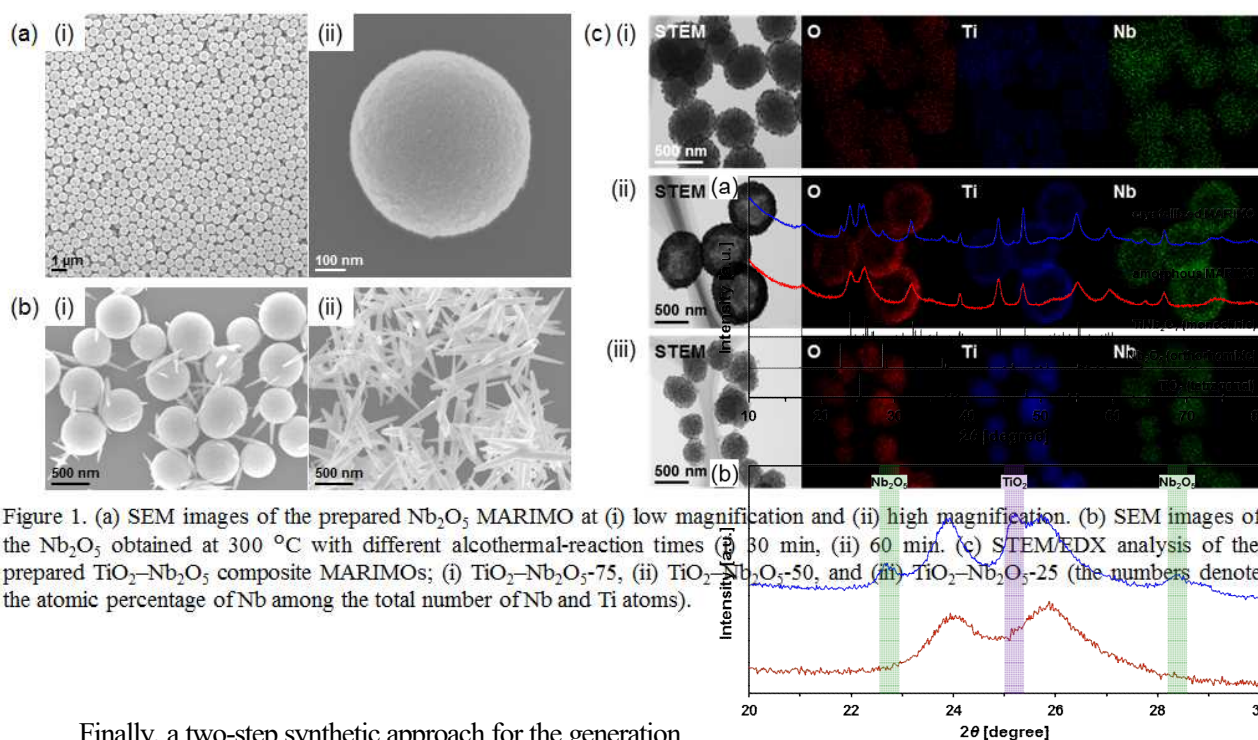


Figure 1. (a) SEM images of the prepared Nb<sub>2</sub>O<sub>5</sub> MARIMO at (i) low magnification and (ii) high magnification. (b) SEM images of the Nb<sub>2</sub>O<sub>5</sub> obtained at 300 °C with different alcohothermal-reaction times (i) 30 min, (ii) 60 min. (c) STEM/EDX analysis of the prepared TiO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> composite MARIMOs; (i) TiO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub>-75, (ii) TiO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub>-50, and (iii) TiO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub>-25 (the numbers denote the atomic percentage of Nb among the total number of Nb and Ti atoms).

Finally, a two-step synthetic approach for the generation of TiNb<sub>2</sub>O<sub>7</sub> porous spheres being a significant anode material for ion batteries was developed *via* an alcohothermal treatment of a 1:2 (molar ratio) mixed solution of Ti(O<sup>i</sup>Pr)<sub>4</sub> and Nb(OEt)<sub>5</sub> in methanol followed by simple calcination. First step, a similar alcohothermal treatment afforded a precursor composite MARIMO with tetragonal TiO<sub>2</sub> and amorphous Nb<sub>2</sub>O<sub>5</sub>. The second step involved calcination of the precursor MARIMO at 700 °C for 2 h and yielded monoclinic TiNb<sub>2</sub>O<sub>7</sub>

Figure 2. XRD patterns of the TiNb<sub>2</sub>O<sub>7</sub> MARIMO obtained by calcination of different precursor MARIMOs (blue, crystallized MARIMO; red, amorphous MARIMO). The 2θ range: (a) 10–80°, (b) 20–30°.

MARIMO. However, the XRD patterns showed that the calcined MARIMO contained mainly monoclinic  $\text{TiNb}_2\text{O}_7$  with a small amount of tetragonal  $\text{TiO}_2$  and orthorhombic  $\text{Nb}_2\text{O}_5$  (Figure 2). This indicates that a pure  $\text{TiNb}_2\text{O}_7$  MARIMO was not afforded by the calcination of the as-synthesized  $\text{TiO}_2\text{-Nb}_2\text{O}_5$  MARIMO obtained at 300 °C. Therefore, amorphous  $\text{TiO}_2\text{-Nb}_2\text{O}_5$  composite MARIMO was selected as an alternative precursor. As shown in Figure, calcination of the amorphous  $\text{TiO}_2\text{-Nb}_2\text{O}_5$  composite MARIMO at 600 °C for 2 h produced the desired  $\text{TiNb}_2\text{O}_7$  MARIMO with a pure monoclinic phase. The specific surface area of the obtained monoclinic  $\text{TiNb}_2\text{O}_7$  MARIMO was not so large (50  $\text{m}^2/\text{g}$ ) as compared to that of before calcination (497  $\text{m}^2/\text{g}$ ), however the number 50  $\text{m}^2/\text{g}$  was the largest one to our best knowledge.

### 3. Rapid one-pot synthesis of ultrafine titania nanocrystals and their conversion into transparent mesoporous thin layer films

Controlling the size and morphology of inorganic nanocrystals is an important aspect of improving certain intrinsic characteristics, such as electronic, magnetic, photophysical, and catalytic properties. Especially, nanocrystals less than 10 nm in size show unique properties. However, synthesis of such ultrafine nanoparticles is quite difficult, since sintering or agglomeration of primary particles occur easily in their preparation process. Herein, a simple one-pot approach to producing ultrafine  $\text{TiO}_2$  nanocrystals using a rapid heating technique in conjunction with a solvothermal reaction using aliphatic carboxylic acid are described. This rapid heating method enhances the nucleation and crystal growth of the nanocrystals, thus avoiding undesired sintering during the high temperature solvothermal reaction and ensuring sub-5 nm sized nanocrystals.

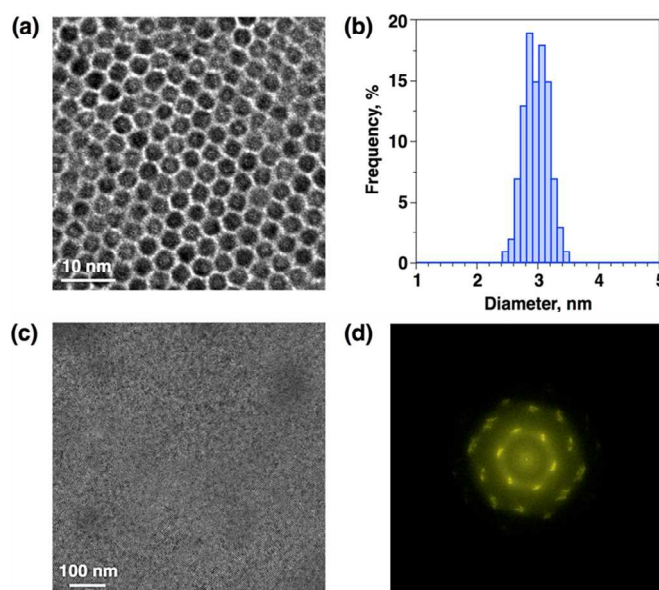


Figure 3. (a) TEM image and (b) size distribution histogram of the  $\text{TiO}_2$  nanocrystals. The size distribution was evaluated by statistical analyses ( $N = 100$ ) using selected TEM images. (c) Low magnification TEM image of the periodically aligned  $\text{TiO}_2$  nanocrystals. (d) The FFT image derived from the image in (c).

Ultrafine  $\text{TiO}_2$  nanocrystals were synthesized by rapid heating solvothermal method using liquid mixtures of titanium alkoxide and oleic acid as precursor solutions. The important point of this method is to heat rapidly (500 °C/min). The obtained  $\text{TiO}_2$  nanocrystals have extremely small size and narrow distribution ( $3.0 \pm 0.4$  nm), resulting in the periodic nanostructures with hexagonal symmetry (Figure 3). These results show that the present method yields extremely fine and uniformly sized  $\text{TiO}_2$  nanocrystals. To confirm the role of the oleic acid in the formation of these  $\text{TiO}_2$

nanocrystals, a detailed characterization of the products using FT-IR spectroscopy and TG analysis were performed. These results show that the surfaces of the nanocrystals are covered with oleate anions. The surface covering of oleate anion on the nanocrystals may also contribute the hexagonal periodic alignment of the nanocrystals through the lipophilic interaction between unsaturated aliphatic chains.

The nanocrystals can also be re-dispersed stably in a non-polar solvents such as *n*-hexane and toluene. The *n*-hexane dispersion was easily converted into porous TiO<sub>2</sub> thin layer transparent film through drop-casting and calcination process. The optical properties of the resultant mesoporous TiO<sub>2</sub> film were also assessed. As shown in Figure 4a, the film had good optical transparency even after three cycles of drop-casting and calcination. In order to evaluate the catalytic ability of the mesoporous TiO<sub>2</sub> thin layer film, the transient photocurrent measurements were performed. The use of the mesoporous TiO<sub>2</sub> film electrode prepared from our ultrafine TiO<sub>2</sub> nanocrystals afforded 2.7 times higher photocurrent than that of the commercial TiO<sub>2</sub> nanoparticles film electrode (Figure 4b).

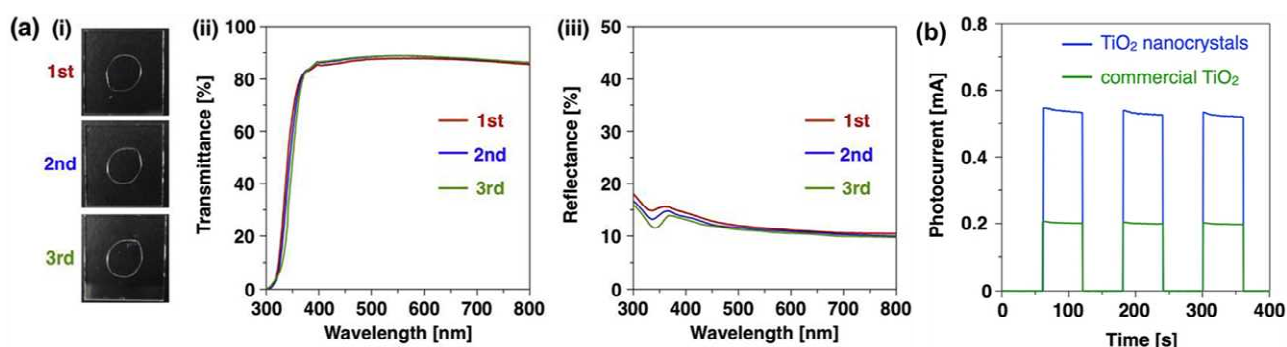


Figure 4. (a) Optical image (i), transmittance spectra (ii), and reflectance spectra (iii) of deposited TiO<sub>2</sub> thin films on glass substrates prepared from dispersions of TiO<sub>2</sub> nanocrystals. (b) Transient photocurrent responses of semiconducting thin layer electrodes prepared from ultrafine 3-nm TiO<sub>2</sub> nanocrystals (blue line) and commercial TiO<sub>2</sub> nanoparticles (green line) under ON-OFF cycles of UV irradiation (< 350 nm).

#### 4. Selective synthesis of Ti-based nanocrystals *via* hydrothermal method using squaric acid

TiO<sub>2</sub> is known as a promising material used in a wide area of applications in energy storage, photocatalysts, solar cells, and other optoelectronic devices. Controlling the crystal structure and exposing desired crystal face are important for improving performance. Three types of TiO<sub>2</sub> crystal structures were known: rutile, anatase, and brookite. Stability of the TiO<sub>2</sub> phases depends on their particle sizes. Rutile is the most stable phase for particles above 35 nm, anatase is the most stable phase for nanoparticles below 11 nm, and brookite is found to be the most stable for nanoparticles of 11–35nm.<sup>5</sup> Although anatase of TiO<sub>2</sub> with large surface area has been well studied, few studies have been reported on the synthesis of rutile-type TiO<sub>2</sub> with a specific surface area over 100 m<sup>2</sup>/g. In this chapter, hydrothermal synthesis of TiO<sub>2</sub> nanocrystal assemblies with rutile crystal phase was studied using squaric acid having quite strong acidity (pK<sub>a1</sub> = 0.54) as an organic acid as well as unique square molecular structure with various coordination modes to metal cation.

Ti(O<sup>i</sup>Pr)<sub>4</sub> was mixed with water to form a white suspension. Squaric acid was added to the suspension and the suspension was sonicated. Then, the white suspension changed to a homogeneous red solution. Next, the precursor aqueous solutions with different concentrations of squaric acid were heated at 150 °C for 3 h in a Teflon autoclave. Hexagonal plates (Figure 5a) and urchin-like submicron sized particles (Figure 5b) were obtained from high and low concentrations of squaric acid, respectively. XRD patterns of the obtained hexagonal plates were totally different from the known crystal phases of TiO<sub>2</sub> (Figure 5c, red line). In addition, the TG data of the hexagonal plates demonstrate weight-loss of approximately 40% in the temperature range from 300 to 400 °C, indicating the inclusion of organic materials. These results strongly suggest that the hexagonal plate is MOF consisting of titanium ions and squarate ligands. On the other hand, XRD patterns of urchin-like particles demonstrated the presence of a rutile phase (Figure 5c, blue line). The urchin-like particles showed a high specific surface area (122 m<sup>2</sup>/g).

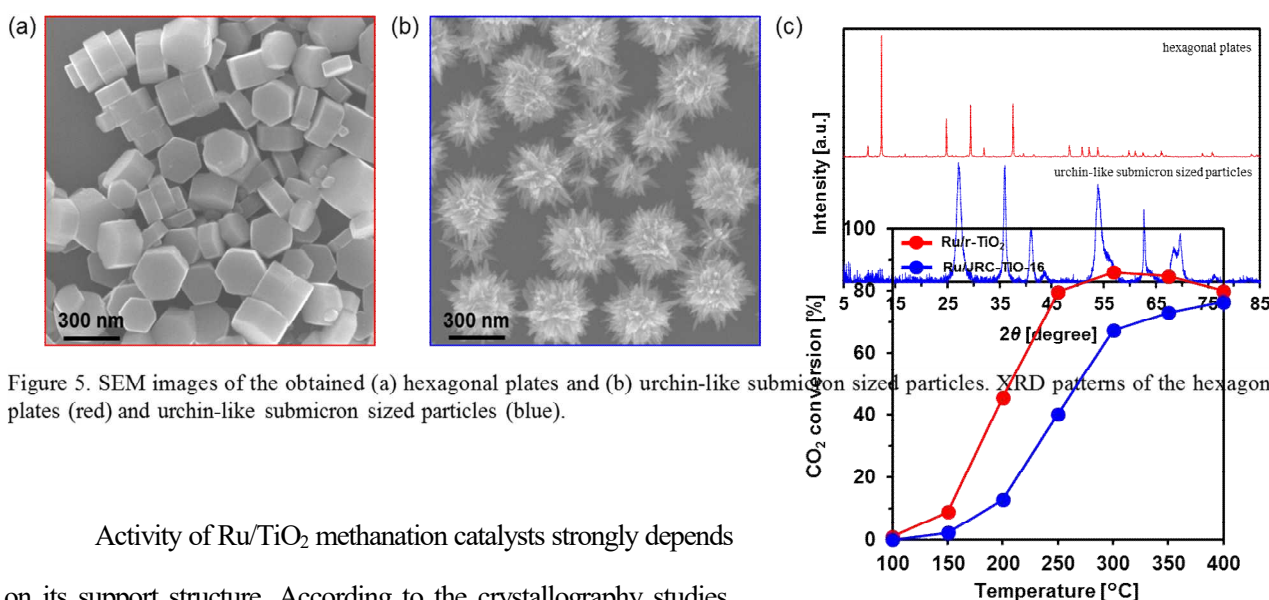


Figure 5. SEM images of the obtained (a) hexagonal plates and (b) urchin-like submicron sized particles. XRD patterns of the hexagonal plates (red) and urchin-like submicron sized particles (blue).

Figure 6. CO<sub>2</sub> conversion obtained at different reaction temperature of CO<sub>2</sub> methanation using Ru/r-TiO<sub>2</sub> (red line) and Ru/JRC-TiO-16 (blue line).

Activity of Ru/TiO<sub>2</sub> methanation catalysts strongly depends on its support structure. According to the crystallography studies, RuO<sub>2</sub> possesses not only the same crystalline structure to rutile-type TiO<sub>2</sub>, but also has a high degree of lattice matching with rutile-type TiO<sub>2</sub> owing to their close lattice parameters. Therefore, this strong interaction can promote the dispersion of RuO<sub>2</sub> nanoparticles on the TiO<sub>2</sub> support to a great extent and it can prevent RuO<sub>2</sub> nanoparticles aggregation. Ru/TiO<sub>2</sub> catalysts with Ru amount of 2 wt% were prepared by the wet impregnation method using the obtained urchin-like rutile TiO<sub>2</sub> assemblies (Ru/r-TiO<sub>2</sub>). Actually CO<sub>2</sub> methanation using Ru/r-TiO<sub>2</sub> as a catalyst showed better performance than reference standard catalyst, Ru/JRC-TiO-16 (Figure 6). To obtain direct evidence for Ru dispersion on the TiO<sub>2</sub> supports, quantitative evaluation was performed by CO pulse experiment. The Ru dispersion of Ru/r-TiO<sub>2</sub> and Ru/JRC-TiO-16 were 16.5% and 4.7%, respectively. Thus, Ru/r-TiO<sub>2</sub> obtained by hydrothermal synthesis using squaric acid resulted in highly efficient dispersion of Ru and acceleration of the CO<sub>2</sub> methanation.



## Summary

Porous metal oxide nanomaterials with controlled crystal structures were prepared by changing several experiment parameters, including solvent, additive, reaction temperature, and heating rate, in solvothermal method. Nb<sub>2</sub>O<sub>5</sub> MARIMO, TiO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> composite MARIMO, and TiNb<sub>2</sub>O<sub>7</sub> MARIMO with large surface area were successfully synthesized using alcohothermal method at high temperature. Ultrafine TiO<sub>2</sub> nanocrystals were obtained by a rapid heating technique in conjunction with a solvothermal reaction using aliphatic carboxylic acid. These nanoparticles were easily converted into porous TiO<sub>2</sub> thin layer transparent film through drop-casting and calcination process, showing not only anti-reflection properties but also high photocatalytic activity. The rutile-type urchin-like TiO<sub>2</sub> obtained by hydrothermal synthesis using squaric acid exhibited an excellent ability as a support for Ru-supported catalyst.

## Reference

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