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Synthesis of Ti_4O_7 Nanoparticles by Carbothermal Reduction Using Microwave Rapid Heating

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Abstract: The polymer electrolyte fuel cell (PEFC) is an attractive power generation method from the perspective of environmental protection. Carbon is usually used as a catalyst support in PEFC, but it is oxidized under high electrical potential conditions. Ti_4O_7 is expected as a new catalyst support because of its high electrical conductivity and chemical resistivity. Though Ti_4O_7 as a catalyst support must have a high specific surface area for a high performance, it is difficult to synthesize nanostructured Ti_4O_7. In this research, Ti_4O_7 nanoparticles with a size of about 60 nm were synthesized by carbothermal reduction of TiO_2 nanoparticles with polyvinylpyrrolidone (carbon source) using 2.45 GHz microwave irradiation. The experiment condition was at 950 °C for 30 min and the samples synthesized by conventional heating showed a grain growth. The findings of this study suggest that microwave processing can drastically reduce the total processing time for the synthesis of nanostructured Ti_4O_7.

Keywords: Ti_4O_7; nanoparticles; catalyst support; polymer electrolyte fuel cell; microwave heating; carbothermal reduction

1. Introduction

Fuel cells are expected as alternative power generation methods because they are green, high-efficiency power generation methods and are capable of small-scale operations. The polymer electrolyte fuel cell (PEFC) is especially researched as it can operate at relatively low temperatures (~100 °C). PEFC must use catalysts (Pt, Pt-Ru alloy and so on) for the oxidation-reduction reaction on the anode and cathode because of its low temperature operation. Carbon, which has a high electrical conductivity and specific surface area, is usually used as the catalyst support in PEFCs. However, the carbon catalyst support has a problem which is that carbon is oxidized under high electrical potential conditions [1]. The dissipation of the catalyst support causes the catalyst's agglutination and desorption, which are the factors of a low generating efficiency. Therefore, novel catalyst supports are required. Ti_4O_7 has high electrical conductivity (1587 S/cm) [2] and chemical resistivity, and has high potential for applications as a catalyst support in PEFCs. In fact, Ioroi et al. reported that a Pt/Ti_4O_7 cathode catalyst is chemically more stable than Pt/C under high potential conditions [3].

To enhance the performance of Ti_4O_7 as the catalyst support, it is necessary to produce nano-sized Ti_4O_7 with a high surface area. Several methods have been used to synthesize nano-sized reduced titanium oxides. Tominaka et al. used CaH_2 as a reducing agent [4] for the synthesis of titanium oxide nanoparticles. Ti_2O_3 nanoparticles were produced from TiO_2 nanoparticles by heating them at a surprisingly low temperature of 350 °C for 10 days. Furthermore, they synthesized Ti_2O_3 nanorods using $NaBH_4$ at 375 °C for one day [5]. These methods prevented the sintering of the nanoparticles because of the low reaction temperature. However, the method required a strong reducing agent,

and thus had safety- and cost-related issues. Carbothermal reduction is an efficient method for producing reduced titanium oxides because carbon is safe and inexpensive. This method has been used for producing nano-sized reduced titanium oxides by using organotitanium compounds as the raw material [6,7]. Very fine TiO_2 is produced by the decomposition of organotitanium compounds. The resulting TiO_2 has a high surface area; therefore, it can be reduced at lower temperatures as compared to coarse TiO_2 [8]. Pang et al. synthesized 8- to 20-nm-sized Ti_4O_7 particles from titanium ethoxide and polyethylene glycol [9]. The problem of this organotitanium method lies in the fact that the shape control of Ti_4O_7 is difficult because of the difficulty in controlling the shape of raw TiO_2. Thus, to synthesize various shapes of nano-sized Ti_4O_7, it is necessary to have a method to reduce the pre-produced nano-sized TiO_2 [10–12] while also maintaining its morphology. However, the high temperatures and long reaction times required for the reduction of TiO_2 by carbothermal reduction result in the growth and sintering of TiO_2 and submicron-sized Ti_4O_7 is obtained [13–15]. The extent of the reduction is dominated by the holding temperature and time: Ti_4O_7 is synthesized at about 1000 °C by carbothermal reduction [13–16]. On the other hand, the grain growth and sintering of TiO_2 nanoparticles occur at a lower temperature, 700 °C [14]. Therefore, to prevent the grain growth and sintering of nano-sized TiO_2, the total processing time (i.e., the time required for the temperature to rise and fall) should be reduced.

To reduce the total processing time, we used a microwave heating method. Microwaves can heat a target material rapidly to a desired temperature since they transfer their energy to the material directly without thermal conduction. In conventional heating methods (using an electric furnace), the heating rate is about 5 °C/min, whereas it is over 1000 °C/min [17] for microwave heating. The cooling rate in microwave processing is also shorter than that in conventional processing since microwaves heat only the sample, and the furnace temperature remains nearly at room temperature. Hence, microwave processing is effective for producing Ti_4O_7 by carbothermal reduction. It also prevents the grain growth and sintering of TiO_2 nanomaterials.

In this study, we synthesized Ti_4O_7 nanoparticles by the carbothermal reduction of TiO_2 nanoparticles with polyvinylpyrrolidone (carbon source) using microwave heating.

2. Results and Discussion

2.1. Phase and Reduction Behavior

We investigated the effect of the heating temperature and time on the reduction ratio in both the methods used for synthesizing single-phase Ti_4O_7. Figure 1 shows the X-ray diffraction (XRD) patterns of the samples synthesized by microwave irradiation at various temperatures for 30 min (a) and for various holding times at 950 °C (b). The reduction of titanium dioxide was greater at higher temperatures and longer heating times. Only Ti_4O_7 peaks were observed when the microwave irradiation was done at 950 °C for 30 min. Under the microwave processing conditions of 900 °C, 30 min and 950 °C, 10 min, broad peaks were observed (such as that at around $2\theta = 28°$), indicating that a slightly reduced titania phase (Magneli phase Ti_nO_{2n-1}) was present in the samples. Figure 2 shows the XRD patterns of the samples synthesized by conventional heating at various temperatures for 30 min (a) and for various times at 950 °C (b). Like microwave irradiation, in this method, the reduction of TiO_2 was also greater at higher heating temperatures. However, in this case, the phase of the samples did not change when the heating was done for more than 30 min at 950 °C. This indicates that the reduction reaction did not proceed despite of a long heating time. In addition, under the conditions of 950 °C, 60 min and 1000 °C, 30 min, the microwave-irradiated sample showed the Ti_2O_3 phase, while the conventional-heated sample did not. One of the reasons for this was the enhancement in the reduction of titania by microwave irradiation. Fukushima et al. irradiated titania with a microwave to partially reduced titania in a vacuum and found that the reduction reaction occurred at a lower temperature compared to conventional heating [18]. As shown in Figure 1, partially reduced titania was obtained when microwave irradiation was carried out for 10 min at 950 °C. Thus, the Ti_2O_3 phase

was obtained since the partially reduced titania absorbed the microwave energy and the reduction reaction was enhanced in this system. Another reason for the occurrence of the Ti_2O_3 phase only in the microwave-irradiated samples was the presence of impure O_2 in Ar gas in a tube furnace. The samples were heated for longer times in conventional heating because the heating rate in this case was lower than that in microwave heating. In addition, the conventional-heated samples took a longer time to cool because the entire furnace was heated in this case. The conventional-heated samples took about 95 min to cool down to 300 °C after the temperature was held. On the other hand, the microwave-heated samples took only 11 min. It indicates that the synthesized titanium oxides and carbon were oxidized for a longer cooling time after the reduction reaction in the case of conventional heating than that in the case of microwave irradiation. Hence, synthesized Ti_2O_3 was oxidized in the case of conventional heating at 950 °C for 60 min and 1000 °C for 30 min. In the case of microwave irradiation, the reduction was greater when the processing was done at 950 °C for 60 min and at 1000 °C for 30 min. However, it is unclear which condition among these led to a higher reduction.

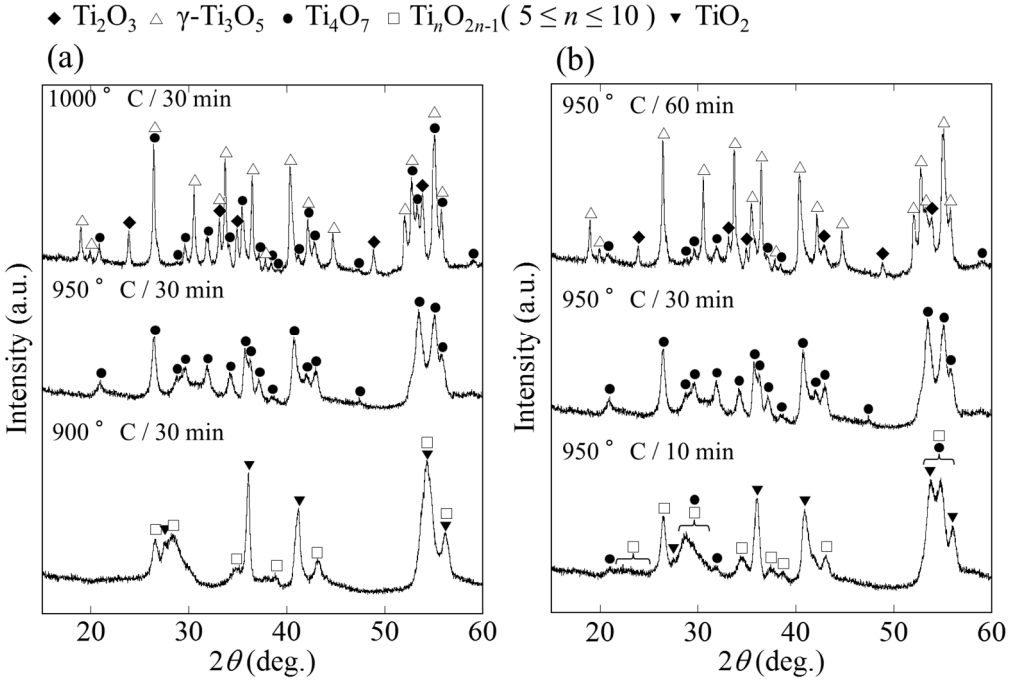

Figure 1. X-ray diffraction patterns of the samples synthesized by microwave irradiation at various heating temperatures (**a**) and times (**b**).

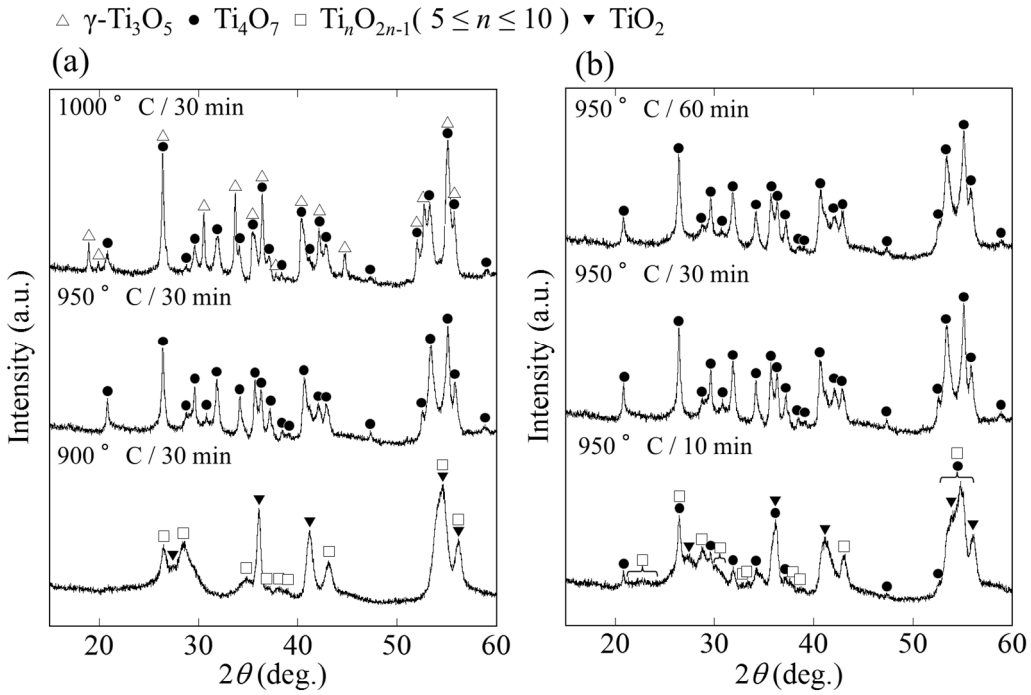

Figure 2. X-ray diffraction patterns of the samples synthesized by conventional heating at various heating temperatures (**a**) and times (**b**).

Although the Ti_4O_7 phase was obtained when the heating was done at 950 °C for 30 min in both the processes, the XRD peaks of the microwave-irradiated sample were broader than those of the conventional-heated sample. Table 1 lists the crystallite diameters (as obtained from the XRD results) of Ti_4O_7 synthesized by both methods. The crystallite diameter was estimated from the Scherrer equation (by using an integral width and $K = 1$). The crystallite diameters of the sample synthesized by microwave processing at 950 °C for 30 min for various Miller indices were smaller than those of the sample synthesized by conventional heating. This result shows that Ti_4O_7 synthesized by microwave irradiation had a smaller particle size than that synthesized by conventional heating.

Table 1. Crystallite diameters of the synthesized samples.

After MW Heating (950 °C, 30 min)	After Conv. Heating (950 °C, 30 min)	After MW Heating (950 °C, 60 min)	Miller Indices	Phase
65(9) Å	151(14) Å	83(17) Å	(1 0 1)	Ti_4O_7
154(9) Å	224(11) Å	225(10) Å	(1 −2 −1)	
143(17) Å	233(21) Å	-	(2 0 6)	
-	-	273(23) Å	(2 2 0)	γ-Ti_3O_5
-	-	330(20) Å	(1 1 −2)	
-	-	297(21) Å	(3 1 0)	

To discuss the crystallinity of the Ti_4O_7 nanoparticles, we show the Field Emission Scanning Transmission Electron Microscope (FE-STEM) image (TE mode) and electron diffraction pattern of microwave-treated sample (950 °C, 30 min.) in Figure 3. The electron diffraction pattern was obtained at a cross-shaped mark. The electron diffraction pattern shows spots clearly and also we can see the periodic lattice fringe in the STEM image, indicating that the sample has good crystallinity at the near-surface region of the particle.

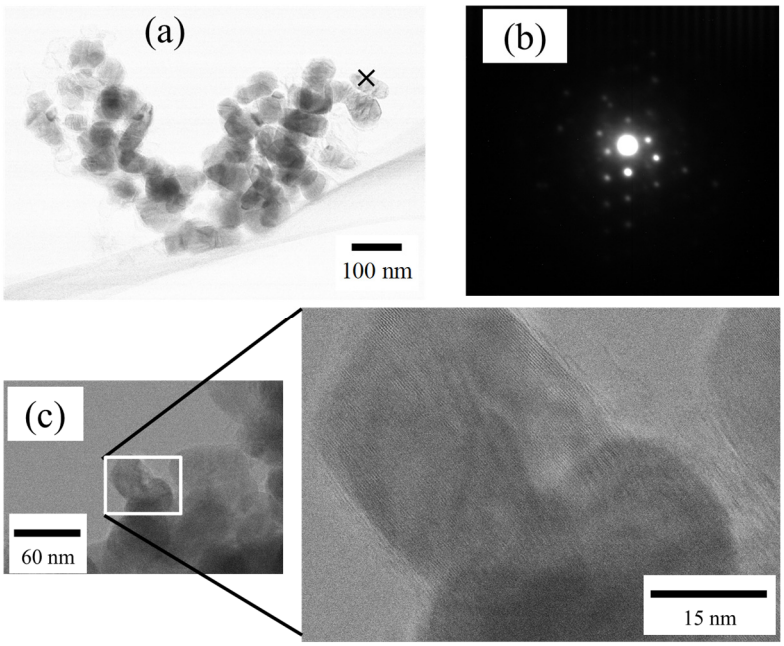

Figure 3. (**a**) Field Emission Scanning Transmission Electron Microscope (FE-STEM) image (TE mode) and (**b**) Electron diffraction pattern of microwave-treated sample (950 °C, 30 min). (**c**) FE-STEM image of microwave-treated sample (950 °C, 30 min) and its high resolution image.

2.2. Size and Morphology of Nanoparticles

As discussed in the previous paragraph, the XRD results suggested that the behavior of crystal growth and sintering was different in both the methods, despite them having the same holding temperature and time. The size and morphology of the obtained nanoparticles were analyzed by Field Emission Scanning Electron Microscope (FE-SEM). The FE-SEM images of the TiO_2 raw material and samples (synthesized by both microwave processing and conventional heating at 950 °C for 30 min) are shown in Figure 4. The particle size of Ti_4O_7 synthesized by microwave irradiation was same as that of the TiO_2 raw material. On the other hand, the sample synthesized by conventional heating showed some coarse Ti_4O_7 particles. In both the samples, Ti_4O_7 particles and residual carbon were observed. The XRD patterns did not show any peak for carbon (Figures 1 and 2) because carbon was present in an amorphous phase. From the BET measurement, the specific surface area of microwave-irradiated sample was 51.2 m^2/g whereas that of the raw TiO_2 powder was 23.2 m^2/g. It is supposed that this residual nano-carbon has a high specific surface area and the specific surface area after microwave processing became large. In future work, we will eliminate the residual carbon electrochemically to measure the electrochemically active surface area, conductivity and other physical and chemical properties of the Ti_4O_7 nanoparticles precisely. Figure 5 shows the histogram of the particle size of the TiO_2 raw material and samples prepared by microwave and conventional heating at 950 °C for 30 min. These histograms were obtained from the diameters of over 100 particles from each FE-SEM image. The mean diameters of the TiO_2 raw material particles and the microwave-synthesized Ti_4O_7 particles were almost the same (about 60 nm). In contrast, some of the Ti_4O_7 particles synthesized by conventional heating were larger than the TiO_2 raw material particles. This increased the mean diameter of the Ti_4O_7 particles synthesized by conventional heating to 81 nm.

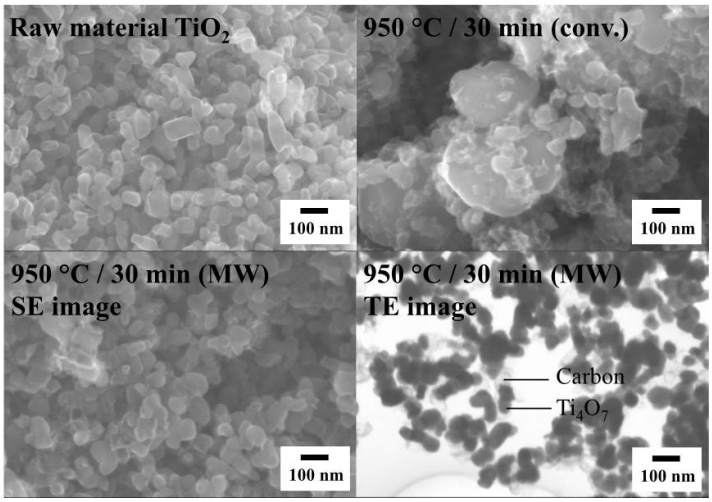

Figure 4. Field Emission Scanning Electron Microscope images of the raw material TiO_2 and samples heated by microwave and conventional heating at 950 °C for 30 min.

We believe that the rapid heating and cooling in the case of microwave irradiation were responsible for the smaller particle size of the microwave-irradiated samples. Microwaves heat a target material directly and the heating rate is very high. In this study, the heating rate of the microwave heating (950 °C for 30 min) was about 260 °C/min and was about 50 times larger than that of conventional heating. In a previous study, TiO_2 nanoparticles grew at temperatures greater than 700 °C. In the present study, the time required to reach temperatures greater than 700 °C by microwave and conventional heating was about 2 and 50 min, respectively. In addition to the heating rate, the cooling rate of the microwave irradiation process was also faster than that of the conventional method. The time required for the microwave-irradiated sample to cool down to 700 °C was about 2 min, while that for the conventional-heated sample was about 18 min. Hence, the total time required for the microwave-irradiated sample to reach temperatures greater than 700 °C and to cool down to 700 °C was about 34 min, while that for the conventional-heated sample was about 98 min. Hence, 64 extra minutes were required in the case of conventional heating. Therefore, it can be stated that sintering occurred in the sample heated by conventional heating.

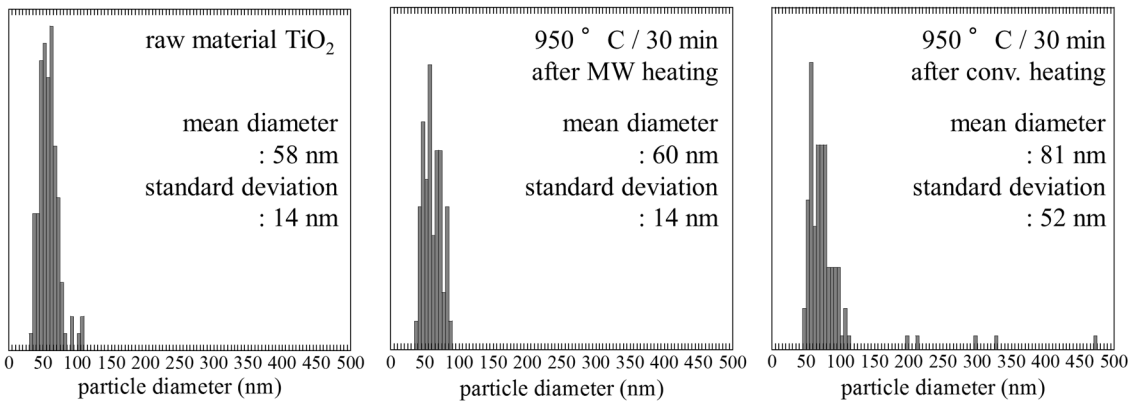

Figure 5. Histograms of particle diameter of the TiO_2 raw material and samples heated by microwave irradiation and conventional heating.

3. Experimental Section

Rutile type TiO_2 (1.21 g, 99.5%, Ionic Liquids Technologies GmbH, Heilbronn, Deutschland) and polyvinylpyrrolidone K30 (5.59 g, Wako Pure Chemical Industries, Ltd., Osaka, Japan) were added

to pure water (80 mL) and mixed by 44.19 kHz ultrasonic irradiation at 100 W for 30 min. After the ultrasonic irradiation, the mixture was dried using a hot plate stirrer. Figure 6 shows the experimental setup of the 2.45 GHz microwave irradiation method used in this study. The raw material powder so obtained (0.15 g) was placed in a silica tube and the tube was surrounded by 1.5 g of carbon, which acted as a heat-supporting agent (susceptor) because of its high microwave absorbance rate. Titanium metal powder (purity 99.9%, 45 μm pass, Kojundo Chemical laboratory Co., Ltd., Saitama, Japan) was used for absorbing oxygen. The raw material was heated at 900–1000 °C for 10–60 min by 2.45 GHz microwave irradiation. The heating rate was 250–320 °C/min. Ar gas (99.998%, TAIYO NIPPON SANSO Co., Tokyo, Japan) was introduced into the furnace at a flow rate of 0.5 L/min. The sample temperature was measured by a thermocouple. For comparison, we also prepared Ti_4O_7 nanoparticle samples using a tube furnace under the conditions same as those used in microwave processing. The heating rate was 5 °C/min, which is maximum rate that can be attained using a tube furnace. The raw material and synthesized samples were analyzed by X-ray diffraction (XRD, RINT-2200/PC, Rigaku Co., Tokyo, Japan), Field Emission Scanning Electron Microscope (FE-SEM, S4800, Hitachi High-Technologies Co. Tokyo, Japan), Field Emission Scanning Transmission Electron Microscope (FE-STEM, HD-2700, Hitachi High-Technologies Co. Tokyo, Japan) and Automatic vapor adsorption measurement apparatus (BELSORP-18, MicrotracBEL Corp., Osaka, Japan). We used transmission electron image (TE image) obtained by FE-SEM for calculating the particle diameters. In the analysis of particle size distribution, we traced each surface of particles in FE-SEM image and used ImageJ to calculate the number average particle diameter from the area of traced particles.

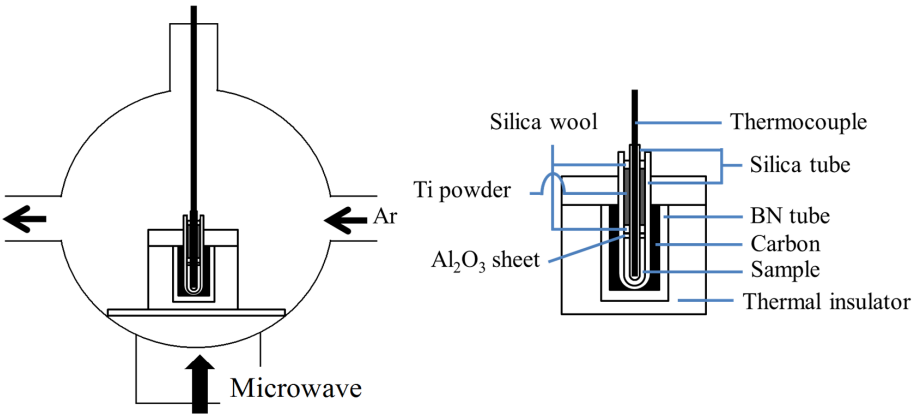

Figure 6. Experimental set up for microwave irradiation.

4. Conclusions

Ti_4O_7 nanoparticles with a particle size of about 60 nm were synthesized by carbothermal reduction using microwave irradiation at 950 °C for 30 min. Microwaves can heat a target material rapidly, thus reducing the total heating time. The short heating and cooling times of the microwave irradiation method restrained the grain growth of the resulting Ti_4O_7 nanoparticles while reducing TiO_2 to Ti_4O_7. The Ti_4O_7 nanoparticles synthesized here are expected to find application as a novel high-performance catalyst support. Microwave processing can be used for synthesizing various Ti_4O_7 nanostructures.

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Conflicts of Interest: The authors declare no conflict of interest.

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