Fabrication of nanometer-sized anatase particles by a pulsed laser ablation method

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TiO_2 particles of <10 nm have been prepared by ablating a rutile target rod with a pulsed laser beam, which was assisted by the synchronized injection of an $Ar-O_2$ mixture. By controlling the wavelength of laser beam, injecting pressure (p) and O_2 concentration in the gas mixture, ultrasmall anatase particles could be obtained. In the present work, $\lambda = 532$ nm, $p = 5 \times 10^5$ Pa and O_2 concentration $<5\%$ resulted in anatase particles of <6 nm.

TiO_2 has been used in various optical materials including semiconductor photocatalysts since the pioneering work by Honda and Fujishima.[1] Nanometer-sized TiO_2 particles show size dependence on optical properties ('quantum size effect'), which corresponds to a shift of optical absorption spectrum.[2–4] The bandgap shift (ΔE_g) relates to the radius (R) of nanometer-sized particles as follows;[3,5]

$$\Delta E_g = \frac{h^2}{8R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{4\pi\varepsilon R} \qquad (1)$$

where h is Planck's constant, m_e and m_h are the effective mass of the electron and hole, e is the electron charge, and ε is the relative permittivity of the semiconductor. Ultrasmall TiO_2 particles are useful materials for highly activated photocatalysts. Anpo *et al.*[2] reported that the photocatalytic activity of TiO_2 particles become stronger with decrease in particle size, and rutile particles below 12 nm and anatase particles below 8.5 nm result in a large blue shift and large quantum yield. There have been many studies concerning other ultrasmall semiconductor particles. For example, CdS and ZnS crystalline[5–8] and colloidal[9] nanoparticles of <10 nm have attracted particular interest owing to the large blue shift of their absorption spectra and photoluminescence.

Nanometer-sized particles have been mainly prepared by sol–gel techniques, and TiO_2 particles have been prepared by hydrolysis of $TiCl_4$.[2–4] Other methods such as laser induced reactions, pyrolysis of titanium isopropoxide[10] and titanium alkoxide,[11] and ignition of $TiCl_4-H_2-O_2$,[12] have also been reported. In these studies, a low photon energy CO_2 laser ($\lambda = 10.6$ µm) has been used to provide heat for reactant gases to produce a very high reaction temperature over a short time which prevents dissociation of gas molecules.

To discuss the quantum size effect more clearly, nanometer-sized particles require high purity since impurities lead to a serious influence on the bandgap of the semiconductor. Laser ablation is a novel technique for fabrication of homogeneous nanometer-sized particles incorporated with ultrahigh vacuum systems. The technique is to evaporate the ceramic target by irradiation of a high-energy pulsed laser assisted with injection of high-pressure noble or reactive gas synchronized with the laser pulse. For laser ablation, a high photon energy Nd : YAG laser (fundamental wavelength = 1064 nm) and ArF (193 nm) or KrF (248 nm) excimer lasers have been used.

There have been few studies about TiO_2 fabrication except for thin films.[13–16] In this study, ultrasmall TiO_2 particles of <10 nm have been fabricated by pulsed Nd : YAG laser ablation and conditions of fabrication and parameters controlling particle size are discussed.

Experimental

Laser ablation experiment

Laser ablation was carried out on a TiO_2 rod target prepared by pressing TiO_2 powder and sintering at 1400 °C for 2 h. The apparatus was a combination of a molecular beam generator[17] and an ablation system as shown in Fig. 1. The vacuum system employed in the ablation experiments consisted of a stainless-steel chamber pumped by three pumps; a 900 l s^{-1} 18 in. diffusion pump, a 3000 l s^{-1} 10 in diffusion pump, and a 1500 l s^{-1} turbomolecular pump. The pressure in the chamber was $<1.2 \times 10^{-8}$ Pa.

The TiO_2 target was irradiated by a Q-switched Nd : YAG laser. The wavelength of irradiating light was varied from the fundamental to the second and fourth harmonic of the Nd : YAG laser. In this study, 266 nm (5 ns pulse width, 70 mJ $pulse^{-1}$), 532 nm (5 ns, 260 mJ $pulse^{-1}$) and 1064 nm (6 ns, 455 mJ $pulse^{-1}$) were used. The repetition time was 10 Hz. The target TiO_2 rod was rotated (1 rpm) so that the laser could irradiate the clear surface of the target constantly during the rotation. The target irradiated by the laser was excited and produced a plasma plume on its surface. A high pressure $Ar-O_2$ gas mixture (purity $>99.9\%$ for both gases) was injected into this plume for *ca.* 200 µs to cool it, injection being synchronized with the laser pulse. The synchronization was very sensitive because of a time delay for the injected gas to reach the plume on the surface of the target and the gas was injected 1 ms earlier than the pulse. The injection pressure of the mixture gas was varied up to 5×10^5 Pa and six conditions were tested. The concentration of O_2 was varied from 1 to 5 to 10%.

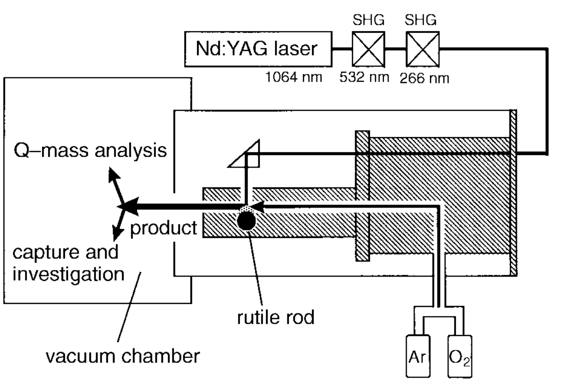

Fig. 1 Schematic diagram of the apparatus

Analysis of the products

The cluster ions of the plume were analyzed by a Q-mass analyzer. Results from the analyzer may be somewhat different from the actual distributions because of ionization ratio effects. However, in this study, the ionization source was a high-energy laser and laser excitation was not influenced by coexistent elements. Therefore, the ionization ratio of each ion was estimated to be equal and the ion intensity analysis is thus believed to be accurate.

Particles were captured on carbon coated grids (Fig. 2) and investigated by transmission electron microscopy (TEM). Particles sizes were determined using the image mode and crystal structures have been identified using selected area electron diffraction (SAED).

Dependence of injection pressure, laser wavelength, and O_2 concentration in the gas mixture were examined to determine the optimum fabrication conditions. Dependence of injection pressure was examined by ion intensity analysis using a Q-mass analyzer. Laser wavelength dependence was related to the ion intensity and the captured particle size and structure. The O_2 concentration dependence was related to the size of particles.

Results and Discussion

Injection pressure dependence

TiO_2 nanocrystals were obtained by injection gas cooling of the plasma plume. Thus pressure is one of the most important parameters for the fabrication and it was directly related to the cooling rate. The injection pressure dependence of TiO_2 and Ti ion intensity is shown in Fig. 3. The TiO_2 ion intensity increased with injection gas pressure, whereas the Ti ion intensity decreased. This result indicates that TiO_2 species are generated by collisions with high-injection pressure gas. For the limitation of vacuum capability, the injection pressure was limited to 5×10^5 Pa, and examination of laser wavelength and O_2 concentration dependence was carried out on products at 5×10^5 Pa.

Laser wavelength dependence

Fig. 4 shows the laser wavelength dependence of ion intensity of TiO_2 and Ti in the plasma plume. There was a large amount of Ti ions and the TiO_2 ion intensity using a wavelength of 266 nm was much lower than of Ti. On the other hand, TiO_2 ion intensity with 532 and 1064 nm wavelength light was four orders of magnitude higher than that at 266 nm and was almost equal to the Ti ion intensity. The influence of laser power of each wavelength was not considered because the behavior of Ti and TiO_2 was obviously different.

The laser wavelength dependence might be related to the difference of the excitation mechanism of the target material. The difference between 266, 532 and 1064 nm light is due to the photon energy (4.66, 2.33 and 1.17 eV respectively). The crystal structure of the target was rutile-type, and its maximum absorption wavelength is at 413 nm, so the target absorbs only 266 nm laser light. The target which absorbs laser light is electronically highly excited and entirely decomposed into Ti and O ions. In this process, the probability of Ti and O ion recombination is very low. Therefore, 266 nm wavelength laser

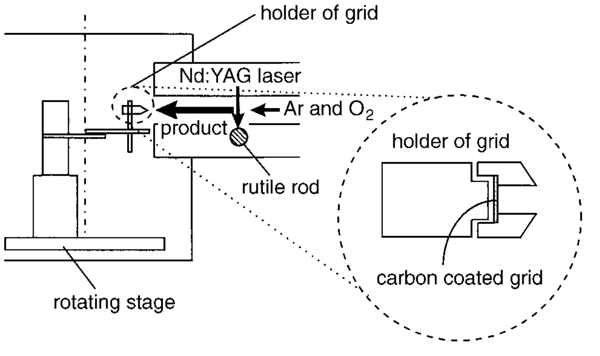

Fig. 2 Schematic diagram of the capture of particles

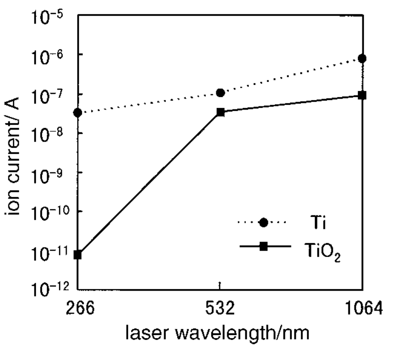

Fig. 4 Laser wavelength dependence on TiO_2 and Ti ion intensity (gas mixture: Ar 90%–O_2 10%, injection pressure: 5×10^5 Pa)

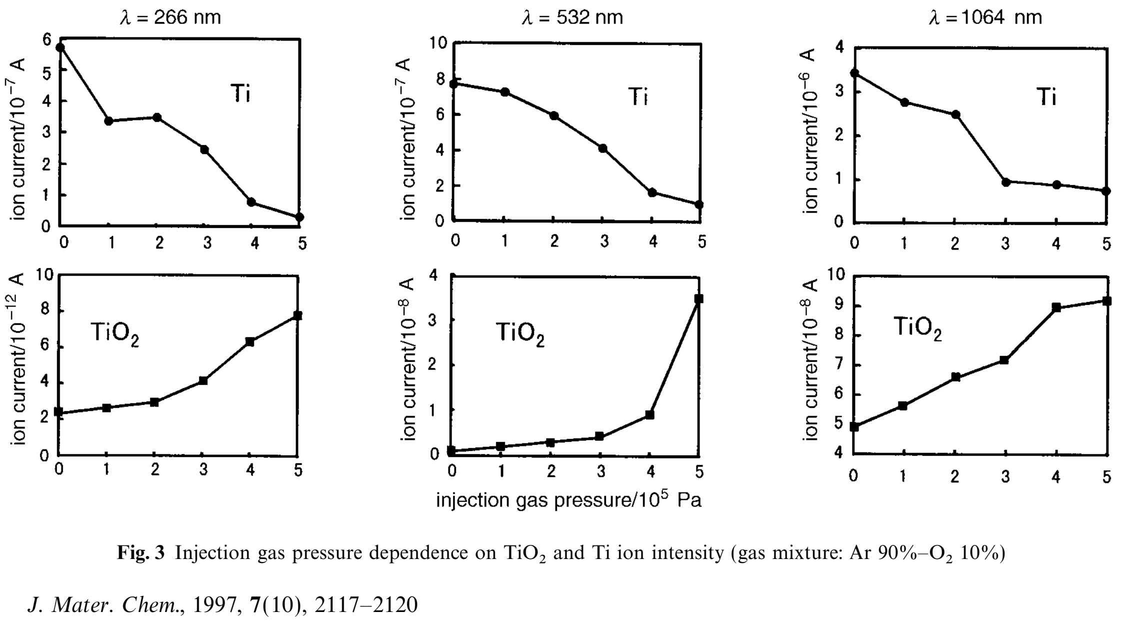

Fig. 3 Injection gas pressure dependence on TiO_2 and Ti ion intensity (gas mixture: Ar 90%–O_2 10%)

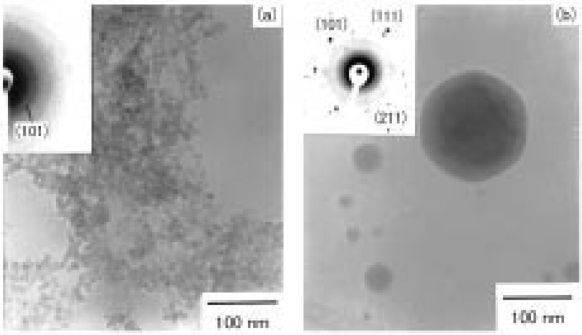

Fig. 5 TEM and SAED images of spherical particles prepared by Ar 90%–O_2 10% gas mixture injection. Wavelength (a) 532 nm, (b) 1064 nm.

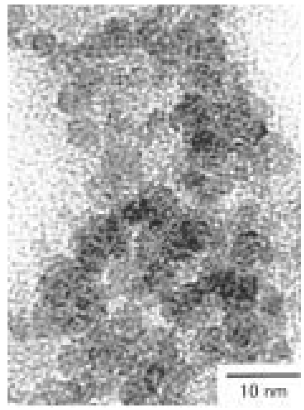

Fig. 6 TEM image of TiO_2 particles prepared by Ar 95%–O_2 5% gas mixture injection using a 532 nm wavelength laser

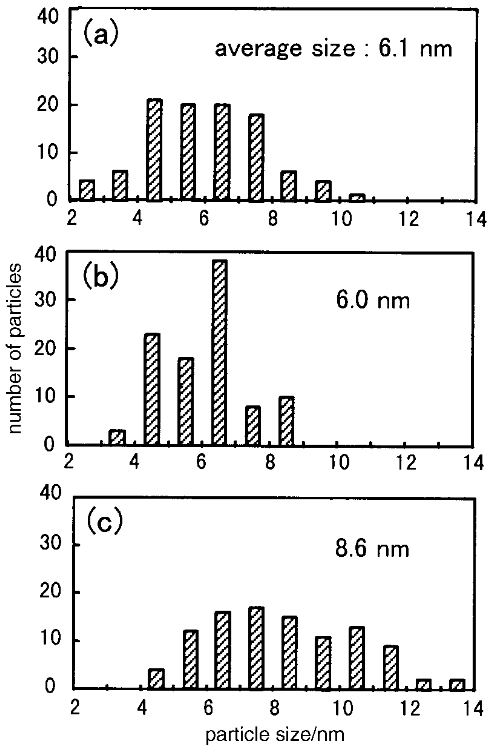

Fig. 7 Size distributions of TiO_2 particles prepared by 532 nm wavelength laser. Gas mixture: (a) Ar 99%–O_2 1%, (b) Ar 95%–O_2 5%, (c) Ar 90%–O_2 10%.

was not appropriate for generating TiO_2 species. 532 and 1064 nm wavelength laser breaks Ti—O bonds by thermal excitation and in this case, many titanium oxide ions exist in the plasma (mainly TiO ions[14,15]). In all cases, ions in the plasma can react by injection of an Ar and O_2 gas mixture. Oxygen atoms of oxygen gas attach to titanium ions or titanium oxide ions to form TiO_2 species [the Ti—O bond (6.92 eV) is stronger than O—O (5.12 eV)[18,19]]. From these results, 532 or 1064 nm wavelength laser was required for formation of fine TiO_2 particles.

The most suitable excitation wavelength (532 or 1064 nm) could not be differentiated by ion intensity analysis. The particles prepared using 532 and 1064 nm light were captured and investigated by TEM and SAED as shown in Fig. 5. At 1064 nm, the average particle size was large with a wide distribution (particles > 100 nm were found). The crystal structure of these particles corresponded to the rutile-type according to SAED. 1064 nm light breaks only a few Ti—O bonds of the target because its photon energy is very low compared with the bond energy of Ti–O; the big particles are simply fragments of the target, and do not arise from the process of recombination of oxygen and Ti ions or titanium oxide ions. By contrast, in the image of the product obtained with 532 nm wavelength, few large particles were observed, and almost all particles were small with comparatively uniform size. SAED reveals a 'powder pattern' whose peaks correspond to an anatase-type structure, which is strongly suggested to be stoichiometric. From these results, 532 nm wavelength laser light is appropriate for formation of homogeneous TiO_2 particles.

O_2 concentration dependence

The oxygen content in the gas mixture affects the reaction in the plasma plume. No reaction could occur in the case of Ar gas injection. Therefore, O_2 content plays an important role in the product particle size and particles were prepared at low O_2 concentration gas injection. The sizes of almost all particles prepared using 5% O_2 were < 10 nm as shown in Fig. 6. The size distributions of the particles prepared by injection of 1, 5 and 10% O_2 concentration in the gas mixture are shown in Fig. 7. The data at 1 and 5% differed little but the distributions were narrower and the average particle size smaller than that at 10% O_2. These results indicate that small and uniform particles are formed by injection of a low O_2 concentration gas mixture. Addition of oxygen to titanium and titanium oxide ions occurs only in the plasma over a very short time and limited area. In the plasma, not only titanium and titanium oxide ions but also a large amount of oxygen ions could be identified by Q-mass analysis. Oxygen ions are lighter than titanium ions, and they primarily fly out from the reaction zone. The collision frequency does not depend on O_2 concentration in this work since the injection pressure was equal in all experiments. The oxygen concentration becomes lower when the collision frequency of oxygen decreases, which leads to a slower reaction rate with titanium and titanium oxide ions, therefore, in the short reaction time, injection of a low O_2 concentration (< 5% in the gas mixture) corresponds to a small amount of additional oxygen atoms leading to the formation of ultrasmall TiO_2 particles of < 10 nm.

Conclusions

We have succeeded in the fabrication of ultrasmall anatase particles of < 10 nm by a pulsed Nd:YAG laser ablation method. 532 nm wavelength laser light and high-pressure gas mixture injection were required for formation of small and uniform TiO_2 particles. The O_2 concentration of the injected gas mixture was an important parameter in controlling particle size. The average particle size was *ca.* 6 nm at $<5\%$ O_2 concentration in the gas mixture.

Laser ablation is one of the most useful techniques to fabricate ultrasmall semiconductor particles of <10 nm. We are now studying the spectroscopic properties of plasma to understand the fabrication mechanism and are also investigating the optical properties of TiO_2 nanoparticles synthesized in this study for application as a highly activated photocatalyst.

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