

Effect of Laser Irradiation of TiO₂ Particles and Their Property of Decomposition of Methylene Blue

Yu Gito, Yoshitaka Kitamoto, and Hiroyuki Wada*

School of Materials and Chemical Technology, Tokyo Institute of Technology, Japan

**Corresponding author's e-mail: wada.h.ac@m.titech.ac.jp*

The decomposition of an organic compound by irradiation with visible light and ultrasound was successfully improved by laser irradiation to TiO₂ particles. Micron-size TiO₂ powders as raw material in water were irradiated with a laser beam (Nd:YAG, SHG) to obtain nanoparticles. Nanoparticles were examined by scanning electron microscopy (SEM), dynamic light scattering (DLS), X-ray diffraction (XRD), and spectrophotometry. The primary particle size was reduced at high laser fluence. The secondary particle size was reduced to approximately 107 nm from micron size by laser irradiation. The irradiation of laser to anatase TiO₂ did not change the crystal structure. Although laser irradiation to TiO₂ reduced the photocatalytic properties for UV light, it realized photocatalytic properties for visible light. Laser irradiation to TiO₂ reduced the bandgap. Laser irradiation to TiO₂ enhanced ultrasound-induced decomposition of an organic compound.

DOI: 10.2961/jlmn.2023.03.2004

Keywords: nanoparticle, laser ablation, photocatalyst, sonodynamic therapy, radical

1. Introduction

TiO₂ is widely used in a variety of applications because of its chemical stability, biosafety, and superhydrophilicity.¹⁻⁵⁾ The most widely known application is photocatalysis.¹⁾ This is the decomposition of water into oxygen and hydrogen by irradiating anatase TiO₂ (band gap: 3.2 eV) with ultraviolet light below 388 nm. TiO₂ has three crystal polymorphisms.¹⁻³⁾ One is the rutile type, which is stable at high temperatures from 600 °C to 1885 °C. It is used as white pigment and UV-protective material in cosmetics. Another stable one is anatase type which is stable at low temperatures up to 600 °C. It is used in photocatalysts and dye-sensitized solar cells. The brookite type is stable at intermediate temperatures between 816 °C and 1040 °C. The ability of photocatalysis to decompose organic compounds and other materials is also used to solve environmental problems such as water treatment.⁶⁻⁸⁾ An effect similar to this photocatalytic effect is the enhancement of reactive oxygen species generation by ultrasound using TiO₂, which can decompose organic matter.⁹⁻¹¹⁾ Because of its high biocompatibility, this effect of TiO₂ is investigated for cancer treatment. This method is known as sonodynamic therapy (SDT),⁹⁻¹¹⁾ in which TiO₂ nanoparticles administered to cancer cells are irradiated with an ultrasound wave to generate reactive oxygen species, which kill the cancer cells. In addition, it is also used as a sunscreen, taking advantage of its optical property of absorbing ultraviolet light. Recently, TiO₂ is also used as an electrode material for dye-sensitized solar cells and so on.^{12,13)}

Laser processes utilize the interaction of light and matter by irradiating various materials with lasers. There are thermal processes resulting from the optical absorption of matter and optical processes resulting from photochemical reactions. Applications include those related to the removal of materials, such as laser cutting,¹⁴⁾ laser etching,¹⁵⁾ and laser ablation;¹⁶⁾ those related to the addition of materials,

such as laser deposition;¹⁷⁾ and those related to the modification of materials, such as laser doping¹⁸⁾ and laser peening.¹⁹⁾ The treatment methods include treatment in a vacuum or a gas as well as in a liquid, such as laser ablation in liquid^{20,21)} or laser melting in liquid,²²⁾ where the laser is irradiated uniformly on granular material. Laser ablation in liquid is an attractive method for fabricating nanoparticles. The method has been used to fabricate noble metal nanoparticles,^{20,21,23-30)} nanoparticles of organic materials,³¹⁻³³⁾ ceramics,^{26,34-37)} and semiconductors.^{26,38)} This method is a simple procedure that yields high-purity nanoparticle solutions which are suitable for biomedical applications. For ceramic nanoparticles, the advantages of the method are high crystallinity and the formation of multi-element nanoparticles, which are difficult to obtain by solution methods. TiO₂ nanoparticles were also prepared by this method and their photocatalytic effect was demonstrated.³⁹⁻⁴⁷⁾ C Liang et al. prepared TiO₂ nanoparticles and investigated.³⁹⁾ H. Ito et al. investigated differences in the crystal structure of the products as a function of substrate temperature.⁴⁰⁾ The photocatalytic activity has been investigated, but the causes of the enhancement effect are not well understood, except for the decrease in particle size and the increase in the number of particles.⁴¹⁻⁴⁴⁾ S. Emanoel et al. indicated that the reduction by laser ablation in organic solvent increased the optical absorption of visible light.⁴⁵⁾ A. Iwabuchi et al. increased the bandgap of TiO₂ by reduction of particle size.⁴⁶⁾ Q. Guo et al. prepared the nanocomposites of TiO₂ and polymer.⁴⁷⁾

In this study, TiO₂ powders were irradiated with a laser and the prepared nanoparticles were investigated, although many previous studies had used Ti metal as a target. In addition, from the viewpoint of application, the decomposition of organic matter by light irradiation and ultrasonic irradiation of TiO₂ nanoparticles was also investigated. Laser irradiation of TiO₂ nanoparticles improved both the

photocatalytic activity in visible light and the ultrasonic irradiation effect. The photocatalytic effect of visible light irradiation would be related to the reduction in the bandgap. Furthermore, the enhancement of the decomposition of organic matter under ultrasound irradiation, which is also used in sonodynamic therapy, has been investigated.

2. Experimental

25 mL of pure water and 2.5 mg of titanium dioxide powder (anatase type, micron-sized powders) were placed in a container and stirred with a vortex mixer for 1 minute to obtain a suspension. The primary particle size is the size of the particle itself and can be measured by SEM, whereas the secondary particle size is the whole size of the aggregated particles and is usually measured by DLS. The suspension was then stirred with a magnetic stirrer and irradiated with laser light (Spectron Laser system, SL8585G, SHG, wavelength 532 nm, pulse duration 13 ns, repetition frequency 10 Hz) at fluences of 2.8, 1.4, and 0.75 J/cm² for 30 minutes. The schematic of laser ablation in liquid was indicated in the previous paper.⁴⁸⁾

The supernatant of the nanoparticle-dispersed solution was dropped on elastic carbon film on a copper grid and dried to observe them by scanning electron microscope (SEM, Hitachi High-Tech, S-4200, acceleration voltage 2-5 kV, working distance 8 mm). The secondary particle size, which was the size of aggregation, was measured by dynamic light scattering (DLS, HORIBA, nano Partica SZ-100V2, laser wavelength 633 nm, detection angle 173 deg.). The absorbance of the nanoparticle-dispersed solution in a quartz cell was measured by a spectrophotometer. X-ray Diffraction (XRD, Rigaku, Ultima IV) was used to identify the composition of the sample powder. The powder of the laser-irradiated sample was prepared by freeze-drying the supernatant of the nanoparticle-dispersed solution to remove DI water. The diffuse Reflectance Spectrum was measured by spectrophotometer. The band gap was calculated from a Tauc plot based on previous studies.^{49,50)}

The following procedure was used to measure photocatalytic activity: Methylene blue (C₁₆H₁₈N₃SCl·3H₂O, concentration: 0.1 mg/ml, volume: 1 ml) was added to a TiO₂ suspension. Then, light irradiation was performed on it while stirring with a magnetic stirrer and varying the irradiation time. A solar simulator was used as the light source. For visible light irradiation, it and a UV-cut filter (400 nm) were used. After the TiO₂ was removed, the absorbance at 664 nm, the absorption peak of methylene blue, was measured, and the decomposition amount of methylene blue was measured using an absorption spectrum normalized by the initial value.

The following procedure was used for the degradation of an organic compound by ultrasound: Methylene blue (concentration: 0.1 mg/ml, volume: 1 ml) was added to a TiO₂ suspension, which was then irradiated with ultrasound under stirring with a magnetic stirrer for varying durations. After the removal of TiO₂, the decomposition amount of methylene blue was measured by normalized absorbance at 664 nm.

3. Results and Discussion

SEM images of raw material and prepared nanoparticles at each laser fluence are shown in Figure 1. The raw

materials were micron-sized powders formed by nanoparticles with a primary particle size of several hundred nm that were strongly agglomerated by sintering. Although these particles of the raw material had a small primary particle size, it was difficult to apply the characteristics of nanoparticles because the specific surface area was reduced by agglomeration. Therefore, the effect of increasing catalytic activity was not achieved. Optical loss due to Rayleigh scattered light, which is proportional to the sixth power of the particle size, was not reduced. Because particle sizes of several tens to several hundred nanometers are considered optimal for biological applications,⁵¹⁻⁵³⁾ it was difficult to get aggregated raw material into blood vessels. The primary particle size did not change much at 0.75 J/cm² and 1.4 J/cm² but decreased at 2.8 J/cm² than that of the raw material. Fine nanoparticles with a primary particle size of several ten nm were generated by laser ablation at 2.8 J/cm².

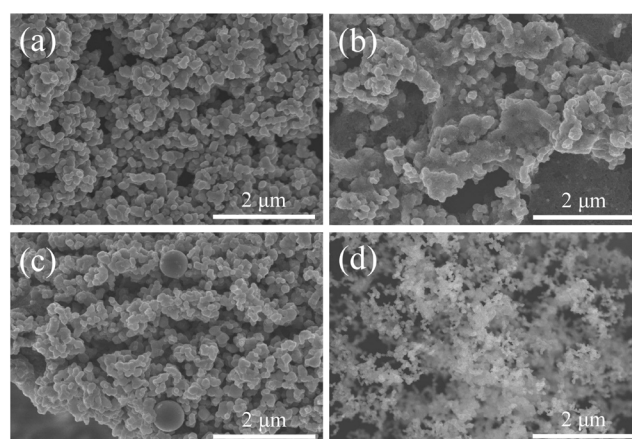


Fig. 1 SEM images of (a) raw material and nanoparticles at each fluence ((b) 0.75 J/cm², (c) 1.4 J/cm² and (d) 2.8 J/cm²).

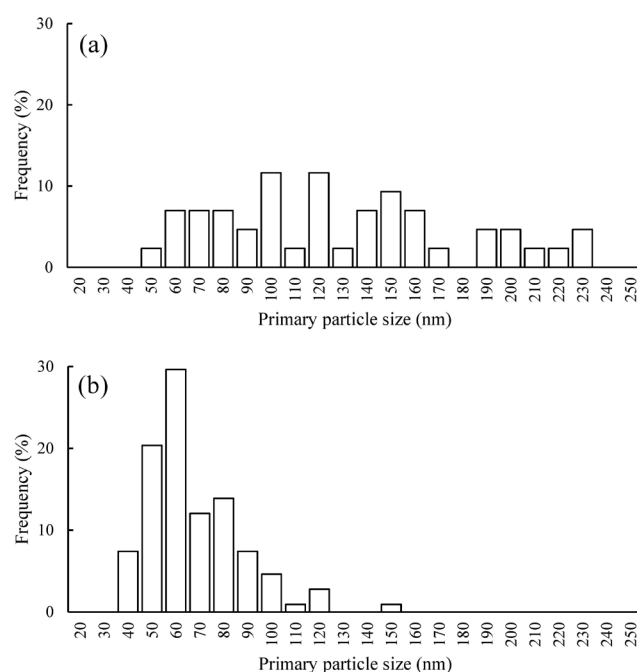


Fig. 2 Histogram of the primary particle size of (a) raw material and (b) nanoparticles at the fluence of 2.8 J/cm².

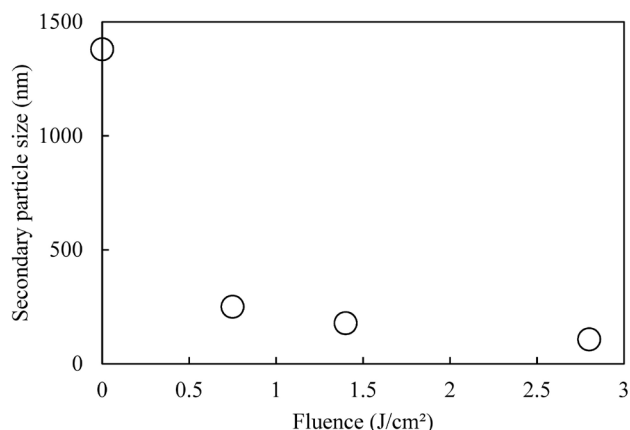


Fig. 3 The secondary particle size of nanoparticles as a function of irradiation-laser fluence.

Figure 2 shows the histogram of the primary grain size of the raw material and nanoparticles at 2.8 J/cm². The reduction of primary particle size by laser irradiation was confirmed. The raw material had a wide particle size distribution with an average value of 134 nm. In contrast, the nanoparticles produced at a fluence of 2.8 J/cm² had a relatively narrow particle size distribution with an average value of 62 nm. In this experiment, nanoparticles of TiO₂ were successfully formed by laser ablation in liquid at 2.8 J/cm², although raw material existed slightly. The shape of the primary particles, both raw material and nanoparticles, were polygonal, while a few spherical nanoparticles of several hundred nanometers were observed at 1.4 J/cm². These would be produced by the liquid melting method.²²⁾ The mechanism of this formation would be that aggregates of nanoparticles were melted by laser light and solidified into a spherical shape by solvent cooling and surface tension. Therefore, the size of some aggregates in this experiment was estimated to be several hundred nm.

Figure 3 shows the secondary particle size of the suspension of raw materials and produced nanoparticles versus laser fluence. The secondary particle size of the micron-sized raw material was reduced to a few hundred nanometers by laser irradiation. Furthermore, with increasing laser fluence, it decreased to about 107 nm at 2.8 J/cm². In this case, when considered together with the primary particle size, several nanoparticles would be agglomerated.

From the above, the morphological change during laser irradiation was estimated. The raw material was an agglomerate with a primary particle size of about 134 nm and a secondary particle size of microns. When irradiated with a laser beam, the secondary particle size decreased while the primary particle size did not change up to 1.4 J/cm². The secondary particle size was approximately 250 nm at 0.75 J/cm² and 178 nm at 1.4 J/cm², decreasing with increasing laser fluence. The primary particle size decreased to about 107 nm by laser ablation in liquid at 2.8 J/cm², indicating that finer nanoparticles were generated. In the case of low fluence such as 0.7 or 1.4 J/cm², aggregated nanoparticles which were the raw material were dispersed without changing the primary particle size by just only fragmentation. However, in the case of high fluence such as 2.8 J/cm², fine nanoparticles with a primary particle size of several ten nm were generated by laser ablation. Parallely

spherical nanoparticles were formed by laser melting in liquid at 1.4 J/cm². These are consistent with the fact that the macroscopic appearance of the dispersed solution changed, as shown in Fig. 4. In the case of the raw material, due to precipitation by its large particle size, the cloudiness caused by Mie scattering was quickly turned to transparent. In the case of fluence of 0.75 J/cm² and 1.4 J/cm², due to fragmentation of the raw material, precipitation occurred slowly and it gradually became transparent. In the case of fluence of 2.8 J/cm², where ablation and nanosizing occurred, it was originally less cloudy due to smaller particle size and did not change significantly after standing.

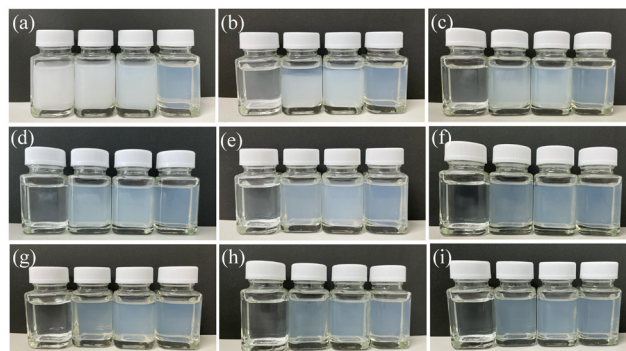


Fig. 4 Macroscopic appearance of the dispersed solution. Left: raw material, center left: 0.75 J/cm², center right: 1.4 J/cm², right: 2.8 J/cm². Standing time: (a) 0 day, (b) 1 day, (c) 2 days, (d) 3 days, (e) 4 days, (f) 7 days, (g) 8 days, (h) 9 days and (i) 10 days.

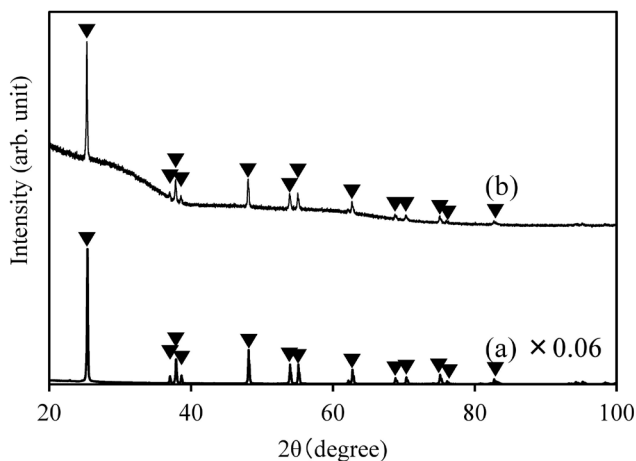


Fig. 5 XRD spectra of (a) raw material and (b) nanoparticles (Laser fluence: 2.8 J/cm²).

Figure 5 shows the XRD patterns of the raw materials and nanoparticles. The raw material in this experiment was anatase type, and nanoparticles in anatase type were obtained without phase change by laser irradiation. Figure 6 shows the photocatalytic activity of raw materials and nanoparticles. Because the vertical axis is normalized absorbance at the initial value, the decrease in this value indicates the decomposition of methylene blue as photocatalytic activity. Despite the increase in specific surface area due to nanosizing, the decrease in normalized absorbance of nanoparticles versus irradiation time indicated the reduction of photocatalytic activity by laser

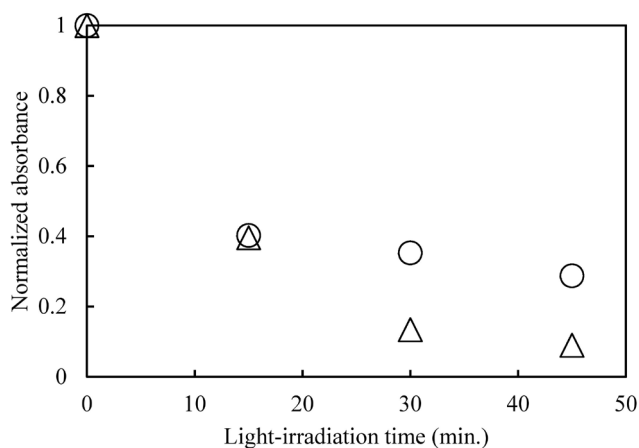


Fig. 6 Time course of normalized absorbance of methylene blue solution decomposed by raw material (open triangle) and nanoparticles (open circle) under irradiation with UV and visible light.

irradiation compared with that of the raw material. One possible reason would be the formation of oxygen-vacancy^{54,55)} levels due to laser irradiation. Since the oxygen-vacancy level was formed at an energy level approximately 1 eV below the conductor.⁵⁶⁾ This would promote exciton recombination and reduce photocatalytic activity.^{56,57)} Laser irradiation of TiO₂ nanoparticles improved photocatalytic activity in visible light, as shown in the decomposition of the organic compound under visible light.

Figure 7 shows the photocatalytic activity of raw materials and nanoparticles when UV light was cut off and only visible light was irradiated. Since the raw material originally shows little photocatalytic activity for visible light, the values for the raw material hardly changed even after light irradiation. This was very different from the results in Figure 6. In contrast, the value of the nanoparticles decreased significantly, which seemed to indicate that laser irradiation imparted photocatalytic activity in visible light. This result supports the formation of oxygen-vacancy levels described in Fig. 6. If oxygen-vacancy levels would be formed about 1 eV below the conductor, electrons would be excited by visible light with a wavelength of approximately 500 nm to 600 nm. Although nanosizing anatase TiO₂ reduced its photocatalytic activity under UV light, its photocatalytic activity under visible light opened the possibility of various applications, such as solving environmental problems, sterilization, and disinfection. Another major advantage of this method was that the generation of visible light photocatalysts by laser irradiation would also promote the photocatalytic effect by increasing the specific surface area since the nanoparticles were also prepared simultaneously.

Figure 8 shows a Tauc plot of the raw material and nanoparticles. The band gaps of the raw material and nanoparticles were 3.2 eV and 2.7 eV, respectively. Although the band gap of raw material was close to the values of anatase TiO₂, that of the nanoparticles was considerably smaller than that of bulk TiO₂. The band gap becomes larger when the nanoparticle size is smaller than the Bohr radius due to quantum confinement effects.⁵⁸⁻⁶¹⁾ The reason for the smaller value in this experiment would be the formation of oxygen-vacancy levels as described in Fig. 6. This laser irradiation-induced decrease in the band gap would extend

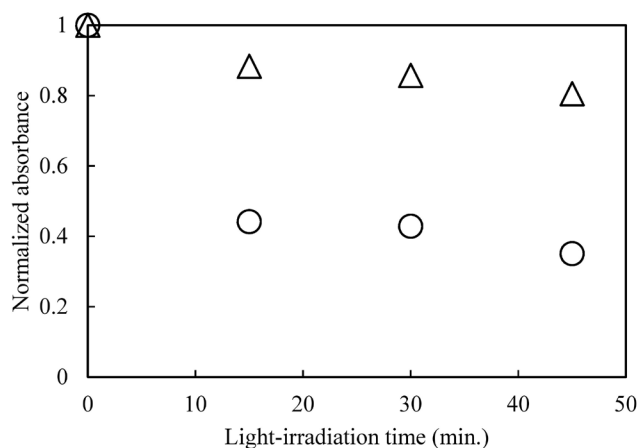


Fig. 7 Time course of normalized absorbance of methylene blue solution decomposed by raw material (open triangle) and nanoparticles (open circle) under the irradiation with only visible light.

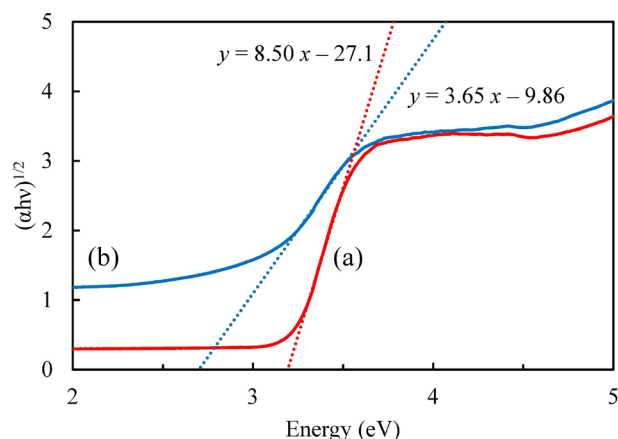


Fig. 8 Tauc plots of (a) raw material and (b) nanoparticles at the fluence of 2.8 J/cm².

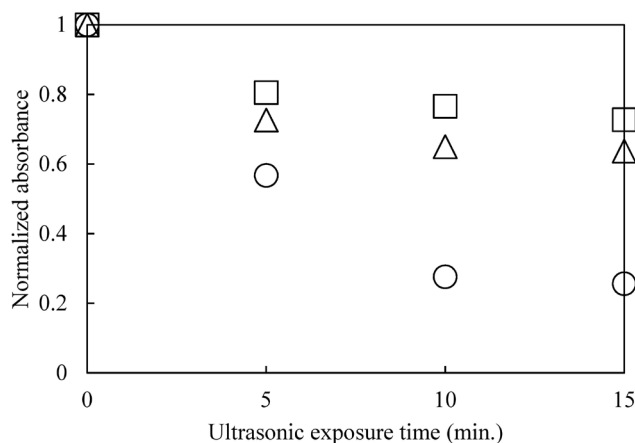


Fig. 9 Time course of normalized absorbance of methylene blue solution decomposed by raw material (open triangle), nanoparticles (open circle) and nothing (open rectangle) under the irradiation with ultrasound.

the wavelength of the absorption edge from 388 nm to 459 nm, which supported the occurrence of photocatalytic activity in visible light.

Figure 9 shows the time course of the decomposition of methylene blue by ultrasonic irradiation for the raw materials, nanoparticles, and no addition case. Ultrasound has the effect of decomposing organic compounds, which is enhanced by the existence of TiO₂.⁹⁻¹¹) It would be due to the enhanced formation of cavitation and reactive oxygen species (ROS) generation on the TiO₂ surface.^{9-11,62}) In this experiment, it was also confirmed that the decomposition of methylene blue was accelerated in the existence of TiO₂ compared to the absence of any TiO₂. Furthermore, the decomposition was significantly accelerated when the TiO₂ nanoparticles prepared by laser irradiation were used. There would be two reasons for the phenomenon. One would be the increase in cavitation due to oxygen vacancy; it had been reported that oxygen vacancy on the TiO₂ surface would be the core of ultrasonic cavitation.⁶³) This

would have further increased cavitation in this study, resulting in a significant increase in the decomposition of the organic compound. The effect is very useful for sonodynamic therapy and a variety of applications. The other reason would be the increase in specific surface area due to the nanosizing and the increase in cavitation generated. Laser irradiation of TiO₂ nanoparticles improved ultrasonic irradiation effect, as shown by the decomposition of the organic compound under ultrasound to TiO₂ nanoparticles.

4. Conclusions

Photocatalysts responsive to visible light were prepared by SHG laser irradiation of TiO₂ powder suspensions, and it also enhanced the decomposition of organic compound by ultrasonic irradiation. The band gap of TiO₂ was decreased by this laser irradiation, suggesting the formation of oxygen vacancies. Although the raw material was micron-sized aggregates, the primary particle size of the prepared nanoparticles was about 62 nm and the secondary particle size was about 107 nm, indicating fragmentation progressed. At the same time, spherical nanoparticles were also produced, probably due to the laser melting method in liquid. The raw material quickly precipitated due to the

large particle size, and the suspension became transparent. On the other hand, the nanoparticles did not change significantly after standing. Laser irradiation produced anatase-type nanoparticles without phase change from the anatase-type raw material. The decomposition of an organic compound by irradiation with visible light and ultrasound to TiO₂ nanoparticles would be significantly proceeded by laser-irradiation. The phenomena are useful for sonodynamic therapy and other applications.

Acknowledgments

The authors wish to thank K. Nakamura at Tokyo Tech. This study was supported by JSPS KAKENHI Grant, the Collaborative Research Project of Materials & Structures Laboratory, and Open Facility Center (Tokyo Tech.).

References

- [1] A. Fujishima and K. Honda: *Nature*, 238, (1972) 37.
- [2] A. Fujishima, T. N. Rao, and D. A. Tryk: *J. Photochem. Photobio. C*, 1, (2000) 1.
- [3] A.L. Linsebigler, G. Lu, and J.T. Yates Jr.: *Chem. Rev.*, 95, (1995) 735.
- [4] B. Chon, S. Choi, Y. Seo, H.S. Lee, C.H. Kim, H.-J. Son, and S.O. Kang: *ACS Sustainable Chem. Eng.*, 10, (2022) 6033.
- [5] J.B. Priebe, J. Radnik, A.J.J. Lennox, M.-M. Pohl, M. Karnahl, D. Hollmann, K. Grabow, U. Bentrup, H. Junge, M. Beller, and A. Brückner: *ACS Catal.*, 5, (2015) 2137.
- [6] K.I. Hadjiivanov and D.K. Klissurski: *Chem. Soc. Rev.*, 25, (1996) 61.
- [7] A. Heller: *Acc. Chem. Res.*, 28, (1995) 503.
- [8] A. Linsebigler, G. Lu, and J.T. Yates: *Chem. Rev.*, 95, (1995) 735.
- [9] D.G. You, V.G. Deepagan, W. Um, S. Jeon, S. Son, H. Chang, H.I. Yoon, Y.W. Cho, M. Swierczewska, S. Lee, M.G. Pomper, I.C. Kwon, and K. Kim: *Sci. Rep.* 6, (2016) 23200.
- [10] C. Dai, S. Zhang, Z. Liu, R. Wu, and Y. Chen: *ACS Nano*, 11, (2017) 9467.
- [11] Q. Feng, W. Zhang, X. Yang, Y. Li, Y. Hao, H. Zhang, L. Hou, and Z. Zhang: *Adv. Healthcare Mater.*, 7, (2018) 1700957.
- [12] B. O'Regan and M. Graetzel: *Nature*, 353, (1991) 737.
- [13] A. Kojima, K. Teshima, Y. Shirai, Yasuo, and T. Miyasaka: *J. Am. Chem. Soc.*, 131, (2009) 6050.
- [14] I. Miyamoto and H. Maruo: *Welding World*, 29, (1991) 283.
- [15] J.G. Lunney, R.R. O'Neill, and K. Schulmeister: *Appl. Phys. Lett.*, 59, (1991) 647.
- [16] R.E. Russo, X. Mao, H. Liu, J. Gonzalez, and S.S. Mao: *Talanta*, 57, (2002) 425.
- [17] D.B. Chrisey, A. Pique, R.A. McGill, J.S. Horwitz, B.R. Ringeisen, D.M. Bubb, and P.K. Wu: *Chem. Rev.*, 103, (2003) 553.
- [18] T. Aoki, Y. Shimizu, A. Miyake, A. Nakamura, Y. Nakanishi, and Y. Hatanaka: *Phys. Status Solidi B*, 229, (2002) 911.
- [19] K.K. Liu and M.R. Hill: *Tribology International*, 42, (2009) 1250.
- [20] J. Neddersen, G. Chumanov, and T. Cotton: *Appl. Spectroscopy*, 47, (1993) 1959.
- [21] A. Fojtik and A. Henglein: *Ber. Bunsen-Ges. Phys. Chem.*, 97, (1993) 252.
- [22] Y. Ishikawa, Q. Feng, and N. Koshizaki: *Appl. Phys. A*, 99, (2010) 797.
- [23] Fumitaka Mafune, Jun-ya Kohno, Yoshihiro Takeda, Tamotsu Kondow, and Hisahiro Sawabe: *J. Phys. Chem. B*, 104, (2000) 9111.
- [24] Takeshi Tsuji, Kenzo Iryo, Norihisa Watanabe, and Masaharu Tsuji: *Appl. Surf. Sci.*, 202, (2002) 80.
- [25] Giuseppe Compagnini, Alessandro A. Scalisi, and Orazio Puglisi: *Phys. Chem. Chem. Phys.*, 4, (2002) 2787.
- [26] S.I. Dolgaev, A.V. Simakin, V.V. Voronov, G.A. Shafeev, and F. Bozon-Verduraz: *Appl. Surf. Sci.*, 186, (2002) 546.
- [27] A.V. Kabashin and M. Meunier: *J. Appl. Phys.*, 94, (2003) 7941.
- [28] Jean-Philippe Sylvestre, Suzie Poulin, Andrei V. Kabashin, Edward Sacher, Michel Meunier, and John H.T. Luong: *J. Phys. Chem. B*, 108, (2004) 16864.
- [29] S. Barcikowski, A. Hahn, A.V. Kabashin, and B.N. Chichkov: *Appl. Phys. A*, 87, (2007) 47.

- [30] Vincenzo Amendola and Moreno Meneghetti: *Phys. Chem. Chem. Phys.*, 11, (2009) 3805.
- [31] Yoshiaki Tamaki, Tsuyoshi Asahi, and Hiroshi Masuhara: *J. Phys. Chem. A*, 106, (2002) 2135.
- [32] K. Omura, R. Yanagihara, and H. Wada: *Jpn. J. Appl. Phys.*, 58, (2019) 128002.
- [33] T. Akimori, K. Nakamura, T. Asahi, and H. Wada: *J. Laser Appl.*, 32, (2020) 022070.
- [34] H. Usui, Y. Shimizu, T. Sasaki, and N. Koshizaki: *J. Phys. Chem. B*, 109, (2005) 120.
- [35] Csaba Laszlo Sajti, Ramin Sattari, Boris N. Chichkov, and Stephan Barcikowski: *J. Phys. Chem. C*, 114, (2010) 2421.
- [36] N. Mintcheva, P. Srinivasan, J.B.B. Rayappan, A.A. Kuchmizhak, S. Gurbatov, and S.A. Kulinich: *Appl. Surf. Sci.*, 507, (2020) 145169.
- [37] M. Amin, J. Tomko, J.J. Naddeo, R. Jimenez, D.M. Bubb, M. Steiner, J. Fitz-Gerald, and S.M. O'Malley: *Appl. Surf. Sci.*, 348, (2015) 30.
- [38] P. Chewchinda, O. Odawara, and H. Wada: *Appl. Phys. A*, 117, (2014) 131.
- [39] Changhao Liang, Yoshiki Shimizu, Takeshi Sasaki, and Naoto Koshizaki: *J. Mater. Res.*, 19, (2004) 1551.
- [40] H. Ito, N. Takada, and K. Sasaki: *Appl. Phys. A*, 79, (2004) 1327.
- [41] M. Zimbone, M.A. Buccheri, G. Cacciato, R. Sanz, G. Rappazzo, S. Boninelli, R. Reitano, L. Romano, V. Privitera, and M.G. Grimaldi: *Appl. Catal. B*, 165, (2015) 487.
- [42] Peisheng Liu, Weiping Cai, Ming Fang, Zhigang Li, Haibo Zeng, Jinlian Hu, Xiangdong Luo, and Weiping Jing: *Nanotechnol.*, 20, (2009) 285707.
- [43] Zeyu Huang, Guoying Feng, Kainan Zhou, Jinghua Han, Zhongbing Shi, Changtao He, Na Xie, and Qiuhui Zhang: *Opt. Express*, 30, (2022) 20482.
- [44] Yu Kwon Kim, Gyuseong Lee, Yuna Kim, and Hyuk Kang: *Korean J. Chem. Eng.*, 34, (2017) 1822.
- [45] S.E. Silva, L.T.B. Mendonça, P.L. Guzzo, A.R. Rodrigues, C.S. Silva, L.L. Lourenço, S. Alves Jr., and W. M. Azevedo: *Mater. Lett.*, 298, (2021) 130021.
- [46] Akira Iwabuchi, Cheow-keong Choo, and Katsumi Tanaka: *J. Phys. Chem. B*, 108, (2004) 10863.
- [47] Qingchuan Guo, Reza Ghadiri, Shizhou Xiao, Cemal Esen, Olaf Medenbach, and Andreas Ostendorf: *Proc. SPIE*, 8243, (2012) 824304.
- [48] F. Yoshimura, K. Nakamura, F. Wakai, M. Hara, M. Yoshimoto, O. Odawara, and H. Wada: *Appl. Surf. Sci.*, 257, (2011) 2170.
- [49] A. Escobedo-Morales, I.I. Ruiz-Lopez, M.L. Ruiz-Peralta, L. Tepech-Carrillo, M. Sanchez-Cantú, and J.E. Moreno-Orea: *Heliyon*, 5, (2019) e01505.
- [50] P.R. Jubu, F.K. Yam, V.M. Igba, and K.P. Beh: *J. Solid State Chem.*, 290, (2020) 121576.
- [51] A. Schadlich, H. Caysa, T. Mueller, F. Tenamberggen, C. Rose, A. Gopferich, J. Kuntsche, and K. Mader: *ACS Nano*, 5, (2011) 8710.
- [52] M. Ohlson, J. Sorensson, and B. Haraldsson: *Am. J. Physiol. Renal Physiol.*, 280, (2001) F396.
- [53] Y. Matsumura and H. Maeda: *Cancer Res.*, 46, (1986) 6387.
- [54] X. Bi, G. Du, A. Kalam, D. Sun, Y. Yu, Q. Su, B. Xu, and A.G. Al-Sehemi: *Chem. Eng. Sci.*, 234, (2021) 116440.
- [55] Z. Tian, S. Du, X. Cheng, J. Zhang, F. Li, Z. Chen, Y. Lv, Y. Zhu, and G. Liu: *Cryst. Growth Des.*, 22, (2022) 6852.
- [56] I. Nakamura, N. Negishi, S. Kutsuna, T. Ihara, S. Sugihara, and K. Takeuchi: *J. Mol. Catal. A*, 161, (2000) 205.
- [57] T. Ihara, M. Miyoshi, M. Ando, S. Sugihara, and Y. Iriyama: *J. Mater. Sci.*, 36, (2001) 4201.
- [58] A.L. Efros and A.L. Efros: *Sov. Phys. Semicond.*, 16, (1982) 772.
- [59] L.E. Brus: *J. Chem. Phys.*, 80, (1984) 4403.
- [60] M.G. Bawendi, M.L. Steigerwald, and L.E. Brus: *Annu. Rev. Phys. Chem.* 41, (1990) 477.
- [61] A. P. Alivisatos: *Science*, 271, (1996) 933.
- [62] Yang Liu, Ying Wang, Wenyao Zhen, Yinghui Wang, Songtao Zhang, Ying Zhao, Shuyan Song, Zhijian Wu, and Hongjie Zhang: *Biomater.*, 251, (2020) 120075.
- [63] A. Nakajima, H. Sasaki, Y. Kameshima, K. Okada, and H. Harada: *Ultrason. Sonochem.*, 14, (2007) 197.

(Received: June 15, 2023, Accepted: September 30, 2023)