We succeeded in fabricating the uniform spherical titanium oxide (TiO2) hollow particles improved photocatalytic activity by doping nitrogen under visible light irradiation using new processing. To prepare the uniform spherical nitrogen-doped TiO2 particles with monodispersed size distribution and monodispersed pore distribution, we performed the reaction crystallization within the confined droplet by inkjet nozzle. The absorption edge of the TiO2 particles shifted to the lower wavelength side with an increase in the sintering temperature. TiO2 particles prepared by an inkjet process exhibited spherical porous structures with uniform size distribution, resulting that this process would be controllable to nitrogen-doped TiO2 particles. The results indicated that the chemical states of the nitrogen doping and the light absorption characteristics of the TiO2 particles could be controlled by the sintering temperature.

1. Introduction

Titanium oxide (TiO2) is a substance which can be expected to utilize visible light mainly by ultraviolet (UV) light corresponding to the band gap energy depending on structural modification.1) Attention has been drawn as photocatalytic materials used for paints, water treatment chemicals, and dye-sensitized solar cells.2)–8) The properties of these materials have been greatly affected by the particle size, particle shape, and size distribution of individual particles constituting the materials.9),10) Therefore, controlling particle properties of TiO2 particles is quite of importance. Preparation of hollow particles has been attracted as one method of creating the materials with high functionality.11),12) Hollow particles could provide the material with characteristics such as low specific gravity, high specific surface area, good surface permeability, and high light absorption.13) As examples of preparing hollow particles, there are a template method,14) a centrifugal method,15) spray-drying,16) and a spray pyrolysis method.17) The template method has been widely used, because its method just requires the preparation of hollow particle as a template. However, this method needs the removal process of template using a thermal decomposition or a chemical decomposition. These operations may cause the destruction of particles, or environmental contamination.18) Additionally, the TiO2 particles with uniform size distribution was demanded because products of photocatalytic activity with TiO2 particles were developed as thin film.19) The control of TiO2 with uniform particle size distribution and pore diameter was quite difficult.

We focused on the template free method using a piezo type inkjet nozzle. Since the template free method does not require template removal from products, it is possible to produce high-quality hollow particles with a small environmental burden. Inkjet nozzles have features such as being able to produce minute and uniform droplets, meaning that it may be possible to control the droplet diameter.20) A uniform spherical interface can be obtained by discharging droplets from the inkjet nozzle toward an organic solvent that separates into water and two phases. The morphology of TiO2 particles could be controlled by utilizing the obtained spherical interface as a particle precipitation field.21) The hollow TiO2 particles with uniform spherical morphology were successfully produced by a process using an inkjet nozzle. The basic principle of photocatalysis process is started with the formation of photo-generated charge carriers, and namely $h^+−e^−$ pairs upon the absorption of UV light.22)–27) TiO2 shows photocatalytic activity under UV light irradiation due to its wide band gap (3.2 eV), and UV light consists of a small fraction (5%) of the solar spectrum compared to the visible light (45%).28)–30) These efforts have
been made to reduce this energy barrier for optical response of TiO₂ to move from UV to visible spectrum range.

In the present study, N-doped TiO₂ with uniform spherical morphology was synthesized. Nitrogen has been found to be easily incorporated into TiO₂ due to its proximity to oxygen, low ionization energy and high stability in TiO₂. The implantation of N impurity into TiO₂ crystal lattice was believed to substitute for the lattice oxygen sites and modified the electronic structure due to the introduction of localized states at the top of the valence band. This modification in the electronic structure of TiO₂ resulted in the reduction of bandgap and, therefore, a most probable factor for the enhancement of photocatalytic activity under visible-light. We proposed the novel preparation method of N-doped TiO₂ particles. We tried to prepare homogeneous spherical N-doped TiO₂ hollow particles by applying interfacial reaction crystallization using inkjet nozzles.

2. Experimental section

2.1 Materials

Hydrochloric acid (HCl), acetonitrile (99%), titanium tetraisopropoxide (TTIP) (95%), hexane (97%), and urea (99%) were purchased from Nacalai Tesque Inc. (Kyoto, Japan).

2.2 Methods

2.2.1 Preparation of TiO₂ particles

The TiO₂ particles were prepared using an interfacial sol–gel processing. Distilled water adjusted to pH 2.0 using HCl was added to acetonitrile with volume fraction of 10 vol.%. Six ml of TTIP was added to 60 ml of hexane. Acetonitrile was used for varying the reaction rate with water, where acetonitrile was miscible with water but created liquid-liquid interface with hexane. Hexane and acetonitrile were sufficiently dehydrated by the molecular sieve before examination. TTIP was selected as a starting precursor of the TiO₂ particles for sol–gel process, and hexane was used as an organic solvent for forming liquid-liquid interface with water. A schematic diagram of the sol–gel processing for preparation of TiO₂ particles using inkjet nozzle (IJHB-1000, Microjet Co., Ltd.) and inkjet driver (IJHC-10, Microjet Co., Ltd.) is illustrated in Fig. 1. The aqueous solution was filled in the inkjet nozzle whose nozzle diameter was 80 μm. The droplets discharged from inkjet nozzle were observed with a light microscope (Moticam 1000, Shimadzu Rika Co., Ltd.) at intervals of 0.2 ms by a blue diode. The aqueous solution was dropped into the organic solution using an inkjet nozzle. Hydrolytic condensation polymerization reaction occurred while stirring. Then, it was solid–liquid separated using a vacuum filter, and dried for 24 h at room temperature. TiO₂ particles were prepared by syringe process to compare with inkjet nozzle process. The syringe process was prepared by pipettor under the same operating conditions.

2.2.2 Nitrogen doping of TiO₂ particles

Nitrogen was doped the porous TiO₂ particles by calcination method. Porous TiO₂ particles (20 mg) were added in 0.01 M of urea aqueous solution (20 mL) for doping nitrogen to the inner surface of the porous TiO₂ particles. Then, the urea aqueous solution added TiO₂ particles was placed under a low-pressure environment and returned to normal pressure again, so that the urea aqueous solution permeated into the hollow particles. After that, the solution was dried in the oven at 80°C for 24 h. The obtained particles were calcined at 400°C for 6 h. The calcination was carried out at average temperature raising rate of 5 °C/min.

Nitrogen doped TiO₂ particles calcined at 300, 400, 500 and 600°C for 6 h were prepared by the syringe process. The calcination was carried out at average temperature raising rate of 5 °C/min for 6 h.

2.3 Characterization

The morphology and surface structure of TiO₂ particle was observed by scanning electron microscopy (SEM; VE7800, Keyence Co., Ltd.). All samples were sputtered with a thin layer of gold under vacuum (Hitachi, E-1045)
to prevent disturbance of images. The particle size was evaluated by the image analysis software (WinROOF, Mitani Co., Ltd.), and determined in Martin diameter from selecting SEM photographs randomly.

The inner structure of the TiO₂ particles was examined by cutting particles with an ion milling apparatus (E-3500; Hitachi High-Technologies Corporation) and observing the cross sections by SEM. In addition, the cross sections were analyzed by elemental titanium mapping using an energy dispersive X-ray spectrometer (EDS; EMAX ENERGY EX-420; Horiba Corporation, Japan) that was connected to a field emission-type scanning electron microscope (SU8020; Hitachi High-Technologies Corporation).

The pore characteristics of TiO₂ particles were evaluated by Brunauer–Emmett–Teller (BET) method with nitrogen adsorption analyzer (Micromeritics, Tristar3000). All the samples were degassed at 200°C under vacuum prior to the measurement.

Titania has three kinds of crystal structure such as anatase, rutile, and brookite. The crystal structure of samples was evaluated by X-ray powder diffraction (Rigaku, RINT2000) with Cu Ka (λ = 0.15406 nm) to investigate the influence of the urea on the crystal structure of the TiO₂. The high purity silicon powder was used as a reference for peak position and peak intensity for this measurement. Silicon powder was mixed to the sample at 20%. Phase identification was performed using a continuous scan of 20 − 60° 2θ, using 0.02° steps.

TiO₂ particles absorbance was determined using a UV–vis spectrophotometer (JASCO, V-570). Approximately 100 mg of TiO₂ was set in a solid sample container. The light absorption intensity was measured for light having a wavelength of 200 to 800 nm, and a light absorption spectrum was prepared.

Paramagnetic nitrogen species intensity of TiO₂ hollow particles and not hollow particles were measured by electron spin resonance (ESR; JES-FA100 ESR spectrometer, JEOL Co., Tokyo, Japan). The sample (20–30 mg) was placed in a quartz ESR tube (φ = 5 mm). Mn²⁺ in MgO was used as standards. Microwave power was 5 mW and frequency was 9.448 ± 0.001 GHz. Center field of magnetic field and sweep width were set up 336 and 10 mT. Modulation frequency, modulation width, time constant and sweep time in signal channel were 100 kHz, 0.2 mT, 0.03 s and 1 min.

3. Results and discussion

3.1 Difference in TiO₂ particles morphology between the inkjet process and the syringe process

TiO₂ particles were prepared by two different processes. Figures 2(a) and 2(b) show the SEM images of TiO₂ particles prepared by the syringe process before and after calcination, respectively. The morphology of TiO₂ particles prepared by syringe process was a tabular form before and after calcination, presuming that the spherical particles of TiO₂ would be broken in the formation process of particles because non-uniform droplet has non-uniform shell thickness and leads to stress weak. Figures 2(c) and 2(d) show the SEM images of TiO₂ particles prepared by the inkjet process before and after calcination, respectively. TiO₂ particles prepared by inkjet process exhibited spherical morphology with smooth surface. This was due to the formation of particles along the uniform micro-spherical interface by using inkjet nozzle. Our previous paper reported that the hydrolysis and polycondensation reaction concurrently occurred along the spherical interface between hexane and aqueous solution droplets discharged.

![Fig. 2. SEM images of (a) TiO₂ particles produced by syringe process, (b) TiO₂ particles produced by syringe process after calcination, (c) TiO₂ particles produced by inkjet process and (d) TiO₂ particles produced by inkjet process after calcination.](image-url)
from the inkjet nozzle. Therefore, particle can be con-
structed spherical shape by inkjet process resulted.38) The
shell structure also is strong to thermal stress, and TiO2
particles could remain spherical shape even after calcina-
tion. Cross-sectional SEM images of the TiO2 particles
prepared by inkjet process that were cut by the ion milling
apparatus and element mapping of the inner surfaces are
shown in Fig. 3. From Fig. 3, it is obvious that the TiO2
particles prepared by inkjet process possess hollow struc-
ture. The hollow structure obtained by the inkjet process
could be expected to have light reflection and light diffu-
sion characteristics by the difference in refractive index
between shell and inside unlike the solid structure.39)
These characteristics promoted the light-harvesting func-
tion, resulting in the enhancement of the photocatalyst.

Figure 4 shows the difference in particles size distri-
butions of TiO2 particles prepared by syringe and inkjet
process. Compared with the particle size distribution of
TiO2 particles before the calcination, TiO2 particles pre-
pared by inkjet process obviously had more uniform
distribution than that of syringe process. The geometric
standard deviation of particles by the syringe and the inkjet
process was 1.63 and 1.11, respectively. The median par-
ticle size of particles by the syringe and the inkjet process
was 54.2 and 57.7 μm, respectively. The particle size dis-
tribution of TiO2 exhibited the similar tendency before
and after calcination. The geometric standard deviation
of TiO2 particles calcined at 400°C by syringe and inkjet
process was 1.54 and 1.12, respectively. The median parti-
cle size of TiO2 particles by syringe and inkjet process
was 62.5 and 51.1 μm, respectively. The particle size dis-
tribution of TiO2 particles would affect the photocatalytic
activity. The preparation of homogeneous TiO2 particle
properties was required since the thin film of TiO2 particles
supporting metals has been developed to practicalize TiO2
particles as photocatalyst.40) Figure 5 shows nitrogen
adsorption–desorption isotherms of TiO2 particles calcina-
tion. Both TiO2 particles prepared by syringe and inkjet
process exhibit type IV adsorption isotherms, indicating a
characteristic of mesopores.41) The BET specific surface
area of TiO2 particles prepared by syringe and inkjet pro-
cess was 101.8 ± 5.33 and 97.69 ± 4.83 m²/g, respectively.
There was no significant difference in the BET specific
surface area of TiO2 particles between syringe and inkjet
process. Especially, the nitrogen adsorption–desorption
isotherms in the range (P/P0 = 0.05–0.30) estimated by
BET method showed the same shape between syringe and
inkjet process. Figure 6 shows the pore size distributions
from adsorption of TiO2 particles prepared by syringe and
inkjet process after calcination. Adsorption average pore
width of particles by syringe process and by inkjet process

Fig. 3. SEM images and color mapping using EDS cross
sections of the TiO2 particle prepared by inkjet process.

Fig. 4. Particles size distributions of TiO2 particles prepared by (a) syringe process, (b) syringe process after
calcination, (c) inkjet process and (d) inkjet process after calcination.
was 7.14 and 4.88 nm, respectively. The particles obtained by inkjet process had smaller pore diameters and narrower pore distribution than that of the particles obtained by syringe process. The obtained TiO₂ particles were secondary particles formed by the agglomeration of the primary particles. The secondary particles obtained by syringe process were tabular-like morphology shown in Figs. 2(a) and 2(b), whereas the secondary particles obtained by the inkjet method were porous structures. Several cracks between the primary particles were formed, resulting in the formation of several pores in the particles. The mean size of cracks between the primary particles would exhibit the mesopores range from 2 to 50 nm. We consider the present particles as agglomerated particles with mesopores. The pore size distribution of TiO₂ particles is of the same importance as the particle size distribution to enhance the photocatalytic activity, because the increase in the specific surface area and pore structure could induce the momentary increase of the reactive site to enhancing the decomposition efficiency. The thin film of TiO₂ with monodisperse mesoporous particles exhibited the high photocatalysis activity. The TiO₂ particles prepared by inkjet process showed more spherical shape, monodispersed size distribution, and monodispersed pore distribution than that of the particles obtained by syringe process although there was no significant difference in the BET specific surface area of TiO₂ particles between syringe and inkjet process. The differences in particle properties between syringe and inkjet process led to the significant improvement in the photocatalytic activity. Additionally, we could produce the lightweight photocatalytic materials since the TiO₂ particles obtained by inkjet method were porous structures. The reaction crystallization of TiO₂ particles within the confined space created using inkjet nozzle would lead to preparing the homogeneous particle properties of TiO₂.

3.2 Effect of urea on the crystal structure of TiO₂

The effect of urea on the crystal structure of TiO₂ particles was investigated. Figure 7 shows the change in XRD patterns of TiO₂ particles with/without urea calcined at various temperatures. Regardless of the urea addition, the results of XRD indicated that the existence ratio of anatase crystal form increased with calcination temperature.
Further increase in calcination temperature at 600°C induced the transition of crystal form to rutile structure. All peaks of N-doped TiO$_2$ particles were weaker and broader than that of the un-doped TiO$_2$ particles. The results suggested that the urea addition to TiO$_2$ particles would affect the particle growth during calcination. The urea would be recognized as an impurity for TiO$_2$ particles. The presence of impurities inhibited the particle growth of during TiO$_2$ calcination.

3.3 Effect of calcination temperature on the light absorption of TiO$_2$

Images of N-doped TiO$_2$ particles calcined at each temperature are shown in Fig. 8. N-doped TiO$_2$ particles calcined at any temperature were yellow-colored, and this result was corresponded with the previous results. The particles calcined at 400°C exhibited the brightest yellow among the samples. Figure 9 shows the absorbance of TiO$_2$ samples. The absorbance region of these N-doped TiO$_2$ particles was found to be narrower with an increase in the calcination temperature. The absorbance intensity of particles calcinated at 400°C was the highest value in the range from 400 to 500 nm. Nakano et al. previously reported that the bandgaps of TiO$_2$ decreased with the $x$ values of TiO$_2$ due to oxygen deficient states in the TiO$_2$ band gap. The photo-absorption of S-doped TiO$_2$ in the visible region was strongest when the powder was calcined at 500°C, in the powder calcined at 500, 600 and 700°C. The reflectance of N-doped TiO$_2$ particles was found to be lower with an increase in calcination temperature in the range from 150 to 400°C. This finding concluded that the absorbance of N-doped TiO$_2$ calcinated at 400°C was the highest. From the above, the amount of oxygen defects and nitrogen dopants are maximum at 400°C, when the energy received during calcination exceeds a certain value, nitrogen dopants in TiO$_2$ replaced oxygen in air. As a result, the absorption intensity of visible light becomes highest when calcined at 400°C. Therefore, the calcination temperature 400°C would be suitable for increasing the visible light absorption intensity of TiO$_2$ prepared by this process.

3.4 Evaluation of nitrogen by ESR

ESR signals of TiO$_2$ particles prepared by inkjet process, inkjet process (after 1 month), without urea, and without adding acetonitrile are shown in Fig. 10. The peaks of paramagnetic nitrogen species (N-dopant) with g value of 2.005 were detected respectively in TiO$_2$ particles prepared by inkjet process, inkjet process (after 1 month), and without urea. The peak of TiO$_2$ particles without urea could be derived from nitrogen of acetonitrile contained in discharged solution. This is obvious by comparing the ESR signals of TiO$_2$ particles prepared without urea and without adding acetonitrile. Therefore, nitrogen doping into TiO$_2$ particles prepared by inkjet process was succeeded by this nitrogen doping method. The amount of N-dopant to TiO$_2$ particles by inkjet nozzle increased. This is because
nitrogen doping could be efficiently achieved by confining ammonia for decomposing urea inside the hollow TiO$_2$ particles. The concentration of nitrogen radicals of N-dopant to TiO$_2$ particles by inkjet process was $1.164 \times 10^{15}$ spin numbers/g immediately after preparation and $0.3527 \times 10^{15}$ spin numbers/g after one month, respectively. The nitrogen radicals within TiO$_2$ hollow particles retained for one month although the concentration of nitrogen radicals decreased with time. The radicals in the substances are generally quite unstable. The cause of holding the doped nitrogen in TiO$_2$ hollow particles after one month was assumed that the radicals within the hollow structure remained stable without any undue effect of external environment. The N-doped TiO$_2$ particles prepared by inkjet process would be superior in terms of stability of radicals.

3.5 Evaluation of visible light response

Figure 11 shows the light absorption spectra of TiO$_2$ particles with/without adding urea. The light absorption intensity of TiO$_2$ particles was increased by adding urea in the range from 400 to 500 nm. Considering that the band gap of N-dopant is 3.0 eV (410 nm), the electrons can be excited by absorbing visible light in N-dopant TiO$_2$ particles prepared by the inkjet process. These findings indicated a noticeable shift of absorption edge to the visible light region was observed for the N-dopant TiO$_2$ particles samples in comparison with undoped TiO$_2$ particles.

3.6 Speculated formation mechanism of N-dopant TiO$_2$ particles

The proposed formation mechanism of N-dopant TiO$_2$ particles based on this study is represented in Fig. 12. The porous TiO$_2$ particles were dispersed in the urea solutions. Immediately after dispersing TiO$_2$ particles into the solutions, the hollow TiO$_2$ particles remained floating state for lower density compared to that of urea solutions. The hollow TiO$_2$ particles were immersed into the urea solutions following the decompression. The urea solution could be introduced into the hollow particles of TiO$_2$ through the pores by restoring atmospheric pressure. Ammonia would decompose to nitrogen and hydrogen within this hollow space. The nitrogen generated by this decomposition was replaced with oxygen within TiO$_2$ particles, resulting in the formation of N-dopant TiO$_2$ particles. The substitution ratio of nitrogen to oxygen in the TiO$_2$ would be enhanced due to the limited space of hollow TiO$_2$ particles. The stability of doped nitrogen in TiO$_2$ hollow particles was improved without any undue effect of external environment. The confined crystallization using inkjet process could succeed in preparing the uniform spherical TiO$_2$ particles with hollow structures. This process could be expected to prepare the other materials such as N-doped zinc oxide with hollow microspheres.

4. Conclusion

In this study, N-doped TiO$_2$ hollow particles were prepared by the droplet atomization process using inkjet nozzle. From the results, uniformly spherical TiO$_2$ hollow particles were produced by using inkjet process compared with existing syringe process. By using this process, nitrogen was doped inside and outside the hollow, and the light absorption intensity of 400 to 500 nm was improved.
Furthermore, because it is also excellent in handling properties, this process can be expected to be applied to the field of photocatalyst as a technology for producing TiO$_2$ having high photocatalytic activity under visible light. By preparing the uniform spherical TiO$_2$ hollow particles, the development of high stability of N-dopant TiO$_2$ particles was successful. Additionally, the application of this process could be expected to prepare modified N-doped TiO$_2$ structure for its characteristic properties and photocatalytic performance.

Acknowledgements This work was partially supported by the Japan Society for the Promotion of Science KAKENHI grant (No. 16K06837) (Tokyo, Japan) and by the Salt Science Research Foundations (No. 18A2) (Tokyo, Japan).

References
1) S. A. Bakar and C. Ribeiro, J. Photoch. Photobio. C, 27, 1–29 (2016).
2) Y. Ren, C. Sun, K. Li, L. Wang and M. Song, Ceram. Int., 42, 1339–1344 (2016).
3) M. Xi, L. Wu, J. Li and X. Li, J. Mater. Sci., 50, 7293–7302 (2015).
4) A. A. Habibpanah, S. Pourhashem and H. Sarpoolaky, J. Eur. Ceram. Soc., 31, 2867–2875 (2011).
5) P. A. Pekakis, N. P. Xekoukoutsakis and D. Mantzavinis, Water Res., 40, 1276–1286 (2006).
6) B. S. Huang, H. H. Tseng and M. Y. Wey, J. Ceram. Soc. Jpn., 117, 753–758 (2009).
7) S. Yamagida, J. Ceram. Soc. Jpn., 126, 625–631 (2018).
8) Y. Liu, F. Xin, F. Wang, S. Luo and X. Yin, J. Alloy. Compd., 498, 179–184 (2010).
9) L. Agartan, D. Kapusz, J. Park and A. Ozturk, Ceram. Int., 41, 12788–12797 (2015).
10) M. Hosokawa, K. Nogi, M. Naito and T. Yokoyama, “Nanoparticle Technology Handbook”, second ed, Elsevier (2012).
11) V. Loryuenyong, K. Angammuaysiri, J. Sukcharoenpong and A. Suwannasri, Ceram. Int., 38, 2233–2237 (2012).
12) S. Nagamine, A. Sugioka, H. Iwamoto and Y. Konishi, Powder Technol., 186, 168–175 (2008).
13) J. Lan, J. Cai, L. Si, C. Yang and B. Li, Ceram. Int., 41, 7937–7943 (2015).
14) R. Jiang, H.-Y. Zhu, H.-H. Chen, J. Yao, Y.-Q. Fu, Z.-Y. Zhang and Y.-M. Xu, Appl. Surf. Sci., 319, 189–196 (2014).
15) Y. Watanabe, Y. Hattori and H. Sato, J. Mater. Process. Tech., 221, 197–204 (2015).
16) F. Qi, X. Xu, J. Xu, Y. Wang and J. Yang, J. Am. Ceram. Soc., 97, 3341–3347 (2014).
17) A. B. Haugen, I. K. Umakiri, C. Simon and M. A. Eimarsrud, J. Eur. Ceram. Soc., 31, 291–298 (2011).
18) Z. Chen, F. Wang, H. Zhang, T. Yang, S. Cao, Y. Xu and X. Jiang, Mater. Lett., 151, 16–19 (2015).
19) G. Li, J. Zhu, W. Tian and C. Ma, Mater. Res. Bull., 44, 271–275 (2009).
20) H. Tamura, K. Kadota, Y. Shirakawa, Y. Tozuka, A. Shimosaka and J. Hidaka, Adv. Powder Technol., 25, 847–852 (2014).
21) K. Kadota, H. Tamura, Y. Shirakawa, Y. Tozuka, A. Shimosaka and J. Hidaka, Chem. Eng. Res. Des., 92, 2461–2469 (2014).
22) A. Fujishima, T. N. Rao and D. A. Tryk, J. Photoch. Photobio. C, 1, 1–21 (2000).
23) A. Fujishima, X. Zhang and D. A. Tryk, Surf. Sci. Rep., 63, 515–582 (2008).
24) A. Fujishima, K. Hashimoto and T. Watanabe, “TiO2 Photocatalysis: Fundamentals and Applications”, BKC (1999).
25) H. Sakai, R. Baba, K. Hashimoto, A. Fujishima and A. Heller, J. Phys. Chem., 99, 11896–11900 (1995).
26) Y. K. Lai, J. Y. Huang, H. F. Zhang, V. P. Subramaniam, Y. X. Tang, D. G. Gong, L. Sundar, L. Sun and C. J. Lin, J. Hazard. Mater., 184, 855–863 (2010).
27) K. Ikeda, H. Sakai, R. Baba, K. Hashimoto and A. Fujishima, J. Phys. Chem. B, 101, 2617–2620 (1997).
28) K. Hou, B. Tian, F. Li, Z. Bian, D. Zhao and C. Huang, J. Mater. Chem., 15, 2414–2420 (2005).
29) S. H. Ahn, J. H. Koh, J. A. Seo and J. H. Kim, Chem. Commun., 46, 1935–1937 (2010).
30) W.-G. Yang, F.-R. Wan, Q.-W. Chen, J.-J. Li and D.-S. Xu, J. Mater. Chem., 20, 2870–2876 (2010).
31) T. Lindgren, J. M. Mwabora, E. Avenda, J. Jonsson, A. Hoel, C.-G. Granqvist and S.-E. Lindquist, J. Phys. Chem. B, 107, 5709–5716 (2003).
32) X. Jiang, Y. Wang and C. Pan, J. Am. Ceram. Soc., 94, 4078–4083 (2011).
33) C. Li, Z. Zhao, H. S. Lomboleni, H. Huang and Z. Peng, J. Mater. Res., 32, 737–747 (2017).
34) M.-H. Ryu, K.-N. Jung, K.-H. Shin, K.-S. Han and S. Yoon, J. Phys. Chem. C, 117, 8092–8098 (2013).
35) S. Saktihivel, M. Janczarek and H. Kissh, J. Phys. Chem. B, 108, 19384–19387 (2004).
36) V. A. Lebedev, D. A. Kozlov, I. V. Kolesnik, A. S. Poluboyarinov, A. E. Beckerikli, W. Grünert and A. V. Garshhev, Appl. Catal. B-Environ., 195, 39–47 (2016).
37) T. Tanaka, K. Kadota, Y. Tozuka, A. Shimosaka and Y. Shirakawa, Ceram. Int., 42, 9963–9971 (2016).
38) Y. Tominaga, K. Kadota, A. Shimosaka, M. Yoshida, K. Oshima and Y. Shirakawa, J. Cryst. Growth, 490, 11–18 (2018).
39) M. Chigane, J. Surf. Finish. Soc. Jpn., 63, 100–105 (2012).
40) M. Kitano, F. Funatsu, M. Matsuoka, M. Ueshima and M. Anpo, J. Phys. Chem. B, 110, 25266–25272 (2006).
41) K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscow, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, Pure Appl. Chem., 57, 603–619 (1985).
42) J. N. Watson, L. E. Iton and J. W. White, Chem. Commun., 24, 2767–2768 (1996).
43) J. C. Yu, J. Yu, W. Ho and J. Zhao, J. Photoch. Photobio. A, 148, 331–339 (2002).
44) S. A. Bakar and C. Ribeiro, J. Photoch. Photobio. C, 27, 1–29 (2016).
45) Y. Zhao, X. Qiu and C. Burda, Chem. Mater., 20, 2629–2636 (2008).
46) A. T. Pham, R. Seto, J. Schömké, D. Y. Joh, A. Chilkoti, E. Fried and B. B. Yellen, Soft Matter, 12, 7735–7746 (2016).
47) C. Burda, Y. Lou, X. Chen, A. C. S. Samia, J. Stout and J. L. Gole, Nano Lett., 3, 1049–1051 (2003).
48) T. Nakano, R. Ito, S. Kogoshi and N. Katayama, J. Phys. Chem. Solids, 98, 136–142 (2016).
49) T. Ohno, T. Mitsui and M. Matsumura, Chem. Lett., 32, 364–365 (2003).
50) Z. Zhang, J. Long, X. Xie, H. Lin, Y. Zhou, R. Yuan, W. Dian, Z. Ding, X. Wang and X. Fu, ChemPhysChem, 13, 1542–1550 (2012).
51) Y. Wang, T. Liu, Q. Huang, C. Wu and D. Shan, J. Mater. Res., 31, 2317–2328 (2016).