JCS-Japan

January
vol.128

Journal of the Ceramic Society of Japan
2020

FULL PAPER

Polymer-assisted spray drying method for BaTiO₃ particles having single-layer coverage with Fe₃O₄ particles

Teruaki FUCHIGAMI^{1,†}, Xie DI¹ and Ken-ichi KAKIMOTO^{1,2}

¹Department of Life Science and Applied Chemistry, Nagoya Institute of Technology, Nagoya 466-8555, Japan

²Frontier Research Institute for Materials Science, Nagoya Institute of Technology, Nagoya 466-8555, Japan

An integrated approach using anionic polymer sources and conventional spray drying technology was proposed to synthesize inorganic particles covered with single layer of fine particles. Negatively charged poly(acrylic acid) adsorbed on the two particles even though the particles had negative charge and assisted to disperse them individually in suspension. The dispersed 0.25 μm Fe₃O₄ was uniformly accumulated with single layer on 2.0 μm BaTiO₃ particles by their condensation in shrinking sprayed droplets. The poly(acrylic acid) molecules which adsorbed on both particles had a function to bind the two particles, and the Fe₃O₄ fine particles were fixed on BaTiO₃ particles persistently and discretely. The poly(acrylic acid)-assisted spray drying method is applicable for any combination of various functional particles.

©2020 The Ceramic Society of Japan. All rights reserved.

Key-words : Barium titanate, Composite particles, Iron oxide, Spray drying, Supported structure

[Received August 19, 2019; Accepted October 28, 2019]

1. Introduction

Inorganic particles covered with fine particles are promising materials as raw powders for functional ceramics and fillers for organic-inorganic composite materials^{1)–10)} because the fine particles fixed on a surface of large particles dispersed uniformly in the matrix with maintaining the integrated structure, resulting in a unique property that cannot be shown by simply mixing multiple types of powders. In our previous report, (Na,K)NbO₃-SrTiO₃ (NKN-ST)-supported (Na,K)NbO₃-Ba₂NaNb₅O₁₅ (NKN-BNN) particles were fabricated by an electrostatic adsorption of positively charged NKN-ST and negatively charged NKN-BNN particles, and a NKN-ST/NKN-BNN composite ceramic was synthesized using the NKN-ST-supported NKN-BNN particles.²⁾ Dielectric properties of the composite ceramic more reflected the properties of the two particles by using the NKN-ST-supported NKN-BNN particles than using simply mixed the two powders. Using poly(methyl methacrylate) (PMMA)/alumina oxide composite materials synthesized by Fujii et al., an uniform mesh-shaped structure was produced by hot pressing of the composite particles.³⁾ Two different phases are formed in the PMMA/alumina structure, and their different characteristics are functioned simultaneously.

Based on the above advantages, composite particles have been produced via various mechanical and chemical approaches.^{3),4),11)–15)} Among these techniques, an electro-

static adsorption method can produce composite particles with uniform layer structure by alternatively adsorbing substances having positive or negative charges. However, filtration or centrifugation processes are necessary to remove excess polymers inducing aggregation of the particles. Although layer-coated particles can also be obtained by inducing heterogeneous nucleation on the surface of large particles, the chemical synthesis methods often result in relatively low yields or the generation of large quantities of chemical waste. In contrast to these methods, spray drying method is great demand in a powder processing^{16)–21)} because of its low cost, simple apparatus and easy scale-up for mass production. However, fabrication of composite particles with a uniform and single layered shell via typical spray drying method remains a great challenge as it is difficult to inhibit the self-accumulation of particles in sprayed droplets. Therefore, we proposed novel polymer-assisted spray drying method to synthesis fine particle-supported large particles using a conventional equipment. **Figure 1** shows a schematic for the formation of composite particles by the polymer-assisted spray drying method. In contrast to the electrostatic adsorption method, two particles are modified with the same polymers to give a similar charge on the surface of particles. Subsequently, particles dispersed by electrostatic repulsion in particle-polymer suspension are applied to spray drying. The sprayed droplet evaporates from the surface, and the two particles contact by isotropic contraction of the droplets. Finally, the adsorbed polymer functions as a binder and composite particles would be obtained. As synthesis technologies for inorganic fine particles such as milling

[†] Corresponding author: T. Fuchigami; E-mail: fuchigami.teruaki@nitech.ac.jp

Fig. 1. Schematic for fabrication of fine particle-supported inorganic particles by polymer-assisted spray drying method.

process of solid sintering powders and supercritical fluid flow process have been developed,^{22)–26)} combination of various functional particles can be expected through our spray drying method.

In this study, an effect of charge of polymers in the formation of integrated structure was investigated. Three kinds of polymers with different charge, poly(acrylic acid) (PAA), poly(ethylene imine) (PEI) and poly(diallyldimethylammonium chloride) (PDDA), were used to verify the effect of polymer charge. The microstructure of composite particles was observed by field emission scanning electron microscopy (FE-SEM), and elemental mapping were conducted for analysis of the integrated structures. Investigating the quantity of accumulated fine particles on large particles and internal structure of the composite particles is difficult by FE-SEM observation; therefore, we chose a combination of magnetic Fe₃O₄ particles and non-magnetic BaTiO₃ particles for the composite structure, and a magnetization measurement was conducted for the Fe₃O₄/BaTiO₃ composite particles to estimate the accumulation quantity. The combination of magnetic Fe₃O₄ particles and ferroelectric BaTiO₃ particles is also useful for multiferroic ceramics.^{27)–29)} Furthermore, Huo et al. revealed composite particles with the combination of high-dielectric-constant BaTiO₃ particles and large-conductive Fe₃O₄ particles were much better conductive and high dielectric filler than Ag–BaTiO₃ composite particles for percolative composites.³⁰⁾ Finally, PAA, which has negative charge in the suspension, functioned to disperse the two particles individually, and uniform accumulation of Fe₃O₄ fine particles on BaTiO₃ was achieved by PAA-assisted spray drying method. The elemental analysis for phenol resin composite including Fe₃O₄ supported BaTiO₃ particles indicated the persistent and discrete adsorption of Fe₃O₄ fine particles on the BaTiO₃.

2. Experimental methods

2.1 Synthesis of Fe₃O₄-supported BaTiO₃ composite particles

Polymer-solution was prepared by mixing polymers, PAA (Mw. 25,000, FUJIFILM Wako Pure chemical Co., Japan), PEI (Mw. 1,300, Sigma-Aldrich Co. LLC) or PDDA (low molecular weight, Sigma-Aldrich Co. LLC) with distilled water using conventional stirrer and ultrasonic stirrer for 1 h. Particle-suspension including 1.0 g

BaTiO₃ particles (average particle diameter 2.0 μm, Oxalic Method Barium Titanate, Nippon Chemical Industrial Co., LTD, Japan) or 0.4–3.4 g Fe₃O₄ fine particles (average particle diameter 0.25 μm, MG-7300, MITSUI MINING & SMELTING CO., LTD, Japan) and distilled water added drop by drop into the polymer-solution with ultrasonic stirring to obtain BaTiO₃/polymer suspension and Fe₃O₄/polymer suspension. The mass ratio of 1:0.4 was calculated by followings as an ideal mass ratio in which 2.0 μm of BaTiO₃ particles are covered with 0.25 μm of Fe₃O₄ particles in one layer. A number of BaTiO₃ particles with a diameter of 2 μm (N_{BT}) was given by Eq. (1).

$$N_{BT} = \frac{V_{BTtotal}}{V_{BT}} \quad (1)$$

where V_{BT} is volume of single BaTiO₃ particle with a diameter of 2 μm and $V_{BTtotal}$ is volume of 1 g of BaTiO₃ bulk with density of 6.02 g cm⁻³. Surface area of BaTiO₃ particles ($S_{BTtotal}$) was calculated from the N_{BT} and surface area of single BaTiO₃ by Eq. (2).

$$S_{BTtotal} = N_{BT} \times S_{BT} \quad (2)$$

When 0.25 μm of Fe₃O₄ particle with cross-sectional area (C_F) cover $S_{BTtotal}$, a number of Fe₃O₄ particles (N_F) needed to cover BaTiO₃ particles in one layer is able to be estimated by Eq. (3).

$$N_F = \frac{S_{BTtotal}}{C_F} \quad (3)$$

Mass of Fe₃O₄ particles (M_F) needed to cover 1 g of BaTiO₃ particles was calculated from the N_F , volume of single Fe₃O₄ particle (V_F) and density of bulk Fe₃O₄ (5.17 g cm⁻³).

$$M_F = \frac{N_F \times V_F}{5.17} \quad (4)$$

Mass of polymers was adjusted to be mass ratios of polymer/BaTiO₃ = 0.5–4. The particle/polymer suspension was left overnight with continuous stirring to adsorb polymer molecules on particles completely. Then, BaTiO₃/polymer/Fe₃O₄ suspension was obtained by adding Fe₃O₄/polymer suspension to BaTiO₃/polymer suspension drop by drop and followed by ultrasonic stirring for 4 h. Spray drying of the BaTiO₃/polymer/Fe₃O₄ suspension carried out at 170°C and 300 ml h⁻¹ of pumping speed.

2.2 Characterization

Zeta potentials of polymers, raw and polymer-treated particles were measured by dynamic light scattering with a Zetasizer Nano ZS (Malvern Instruments Ltd.). The particle-polymer suspension was prepared by same procedure as synthesis of composite particles with the mass ratio of polymer/BaTiO₃ was 0.5. Microstructure of the composite particles was observed by FE-SEM (JEOL, JSM-7800F) at 15 kV. Magnetization curves were measured using a SQUID (Quantum Design, MPMS) and vibration sample measurement system (VSM, Toei Industry Co., Ltd.) at 300 K from -1.0 to 1.0 T. Saturation magnetization of the Fe₃O₄ fine particles ($74.2 \text{ A} \cdot \text{m}^2/\text{kg}$) at R.T. and 1.0 T measured by SQUID was used for estimation of Fe₃O₄ and BaTiO₃ content in composite particles. The composite particles fabricated with the 1.0:3.4 mass ratio of BaTiO₃ to Fe₃O₄ were impregnated in phenol resin by following procedures. 0.6 g of the composite particles and 3.0 g of phenol resin powders put into polypropylene container, then the container was rolled for 50 min . The mixture was filled into hot press molding equipment (SimpliMet-XPS1, Buehler), and molding carried out at 180°C and 29 MPa for 3 min . For comparison, BaTiO₃–Fe₃O₄–phenol resin composite was fabricated from the powders obtained by simply mixing Fe₃O₄ particles, BaTiO₃ particles, and phenol resin powders. The mass ratio of BaTiO₃ to Fe₃O₄ particles in BaTiO₃–Fe₃O₄–phenol resin was adjusted based on the composition ratio estimated by the magnetization measurement. After cutting and double-sided polishing of molded body, a Carbon coating was carried out for an elemental mapping which was performed using an electron probe microanalyzer (EPMA; JEOL, JXA-8530F) at 15 kV .

3. Results and discussion

Zeta potentials for PAA, PDDA and PEI were -20.3 , 31.9 and -4.8 mV , respectively. **Figure 2** shows zeta potentials of the untreated particles and the particles in the polymer solution. Fe₃O₄ fine particles and BaTiO₃ particles showed 2.1 and -43.1 mV , respectively, before

Fig. 2. Zeta-potentials of untreated particles and particles treated with PAA, PDDA and PEI. Square and circle shapes indicated Fe₃O₄ and BaTiO₃ particle, respectively.

mixing with polymer solutions. Fe₃O₄ particles treated with PAA, PDDA and PEI showed -25.0 , 78.7 and 10.0 mV , respectively. Zeta potential of BaTiO₃ changed from -43.1 mV to -70.1 , 75.7 and 0.3 mV by treating with PAA, PDDA and PEI, respectively. The changes indicated PAA molecules adsorbed onto the surface of BaTiO₃ even though the surface was negatively charged. In contrast to PDDA, PEI was not strongly charged in suspension.

The amount of polymer in solution was optimized by fabrication of the composite particles with different mass ratio of PAA/BaTiO₃ (Fig. S1). When the mass ratio of PAA/BaTiO₃ was more than 1, coarse polymer-particles formed with embedding two kinds of inorganic particles and also the BaTiO₃ particles covered with a thick polymer film were observed. Therefore, the mass ratio was adjusted to be 0.5 to prepare the composite particles. **Figure 3** shows SEM images of Fe₃O₄ supported BaTiO₃ composite particles fabricated by spray drying of mixture of Fe₃O₄ and BaTiO₃ particle-suspension with or without various polymers. Each particle was randomly aggregated in the absence of polymer [Fig. 3(a)]. In the presence of anionic polymer, PAA, Fe₃O₄ fine particles uniformly accumulated on the surface of BaTiO₃ large particles [Fig. 3(b)]. Additionally, the Fe₃O₄/PAA/BaTiO₃ composite particles were not aggregated, suggesting there is no bridging adsorption by PAA molecules among the composite particles. In contrast, although Fe₃O₄ particles accumulated on BaTiO₃ particles, numerous aggregates were formed in the presence of PDDA [Fig. 3(c)]. In the presence of PEI, BaTiO₃ particles were relatively dispersed individually compared with PDDA-treated samples. [Fig. 3(d)]. These differences would depend on the zeta-potentials. Strong electrostatic attraction must be among highly positively charged PDDA and highly negatively charged BaTiO₃ particles, and the BaTiO₃ particles were packed tightly into a center of droplet.³¹⁾ Thus, aggregates with several BaTiO₃ covered with small Fe₃O₄ particles were formed by water evaporation. PEI molecule itself and PEI-treated particles were not strongly charged, therefore the PEI and PEI-treated particles were randomly distributed in a droplet and most of Fe₃O₄ particles were not accumulated onto BaTiO₃ surface because of no electrostatic attraction.³¹⁾ Zeta potentials of PAA, Fe₃O₄ and BaTiO₃ particles were enough to be dispersed individually in the droplet by an electrostatic repulsion force according to DLVO theory. Therefore, the PAA-treated Fe₃O₄ and BaTiO₃ particles were not packed into the center of droplets, and the two particles collided by shrinking of the droplet and uniform Fe₃O₄/PAA/BaTiO₃ composite particles formed. Thus, it was revealed that uniform supporting is possible by using a polymer, PAA, having the same charge as the particles.

Although the mass ratio of 1:0.4 was ideal mass ratio in which $2.0 \mu\text{m}$ of BaTiO₃ particles were covered with $0.25 \mu\text{m}$ of Fe₃O₄ particles in one layer, a few amounts of uniform supported particles were obtained. To increase the coverage, mass ratios of BaTiO₃ and Fe₃O₄ in PAA solution increased from 1.0:0.4 to 1.0:3.4. **Figure 4** showed SEM images of Fe₃O₄/BaTiO₃ composite particles fabri-

Fig. 3. SEM images of Fe₃O₄/polymer/BaTiO₃ composite particles fabricated by spray drying of suspension of Fe₃O₄ and BaTiO₃ particles (a) without polymer, (b) with PAA, (c) with PDDA, and (d) with PEI.

Fig. 4. SEM images of Fe₃O₄/PAA/BaTiO₃ composite particles fabricated by spray drying of Fe₃O₄/PAA/BaTiO₃ mixed solution with mass ratios of BaTiO₃ and Fe₃O₄ were (a) 1.0:0.4, (b) 1.0:0.9, (c) 1.0:1.7 and (d) 1.0:3.4.

cated by spray drying of mixture of Fe₃O₄, BaTiO₃ and PAA. The amount of supported Fe₃O₄ fine particles did not increase when the mass ratios were 1.0:0.9 and 1.0:1.7 [Figs. 4(b) and 4(c)]. Most of BaTiO₃ particles seemed to be covered when the mass ratio was 1.0:3.4 [Fig. 4(d)]; however, it was difficult to identify the quantity of each particle and whether aggregates of Fe₃O₄ or composite particles by FE-SEM observation. Therefore, the content ratio of Fe₃O₄ and BaTiO₃ in the spray dried samples was estimated by magnetization measurements.

Figure 5 shows MH curves of Fe₃O₄ and Fe₃O₄/PAA/BaTiO₃ composite particles fabricated with mass ratios of BaTiO₃ to Fe₃O₄ of 1.0:0.4, 1.0:1.7 and 1.0:3.4. The Fe₃O₄/PAA/BaTiO₃ composite particles showed ferro-magnetic feature. Saturation mass magnetization of Fe₃O₄

powder and Fe₃O₄/PAA/BaTiO₃ composite particles with the mass ratios of 1.0:0.4, 1.0:1.7 and 1.0:3.4 at 1.0 T were 74.2 and 20.6, 55.6, 63.0 A·m²/kg, respectively. There was no significant deference in coercive field strength between Fe₃O₄ powder and Fe₃O₄/PAA/BaTiO₃ composite particles, indicating Fe₃O₄ particles were not oxidized during spray drying at 170°C. Therefore, the decrease in saturation magnetization was due to the inclusion of nonmagnetic BaTiO₃ particles. From this point of view, it is possible to estimate the content of Fe₃O₄ in the composite particles from the saturation mass magnetization of Fe₃O₄ powder and the saturation magnetization of supported particles. The content ratios of Fe₃O₄ particles in spray dried samples were estimated by dividing magnetization of the composite particles by saturated mass

magnetization of Fe_3O_4 particles ($74.2 \text{ A}\cdot\text{m}^2/\text{kg}$) and the content ratio of BaTiO_3 was calculated from the content ratio of Fe_3O_4 . These ratios were summarized in **Table 1** with ideal content ratios calculated from the mass ratios of BaTiO_3 and Fe_3O_4 , 1.0:0.4, 1.0:1.7 and 1.0:3.4 in the starting suspension. There was a difference of 8–14% in the composition ratio of Fe_3O_4 between ideal and spray dried samples. The Fe_3O_4 content rate in the particle-suspension prepared with mass ratio of 1.0:3.4 was 75%, whereas the actual content rate after spray drying was

Fig. 5. MH curves of Fe_3O_4 particles and $\text{Fe}_3\text{O}_4/\text{PAA}/\text{BaTiO}_3$ composite particles fabricated with content ratio of BaTiO_3 to Fe_3O_4 , 1.0:0.4, 1.0:1.7, 1.0:3.4.

Table 1. Content ratios of Fe_3O_4 particles and BaTiO_3 particles in spray dried samples estimated by dividing magnetization of the composite particles by saturated mass magnetization of Fe_3O_4 particles ($74.2 \text{ A}\cdot\text{m}^2/\text{kg}$) and ideal content ratios calculated from the mass ratios of BaTiO_3 and Fe_3O_4 , 1.0:0.4, 1.0:1.7 and 1.0:3.4 in the starting suspension

Mass ratio of BaTiO_3 to Fe_3O_4 in starting suspension	Ideal content ratio $\text{BaTiO}_3/\text{Fe}_3\text{O}_4$ (%)	Estimated content ratio $\text{BaTiO}_3/\text{Fe}_3\text{O}_4$ (%)
1.0:0.4	71/29	79/21
1.0:1.7	37/63	23/77
1.0:3.4	25/75	15/85

85%, suggesting that the composite particles shown in Fig. 4(d) contain aggregates composed only of Fe_3O_4 fine particles. We have considered that the composite structure would be formed by isotropic contraction of the sprayed droplets,^{32)–34)} therefore it is necessary to make the mass ratio of BaTiO_3 and Fe_3O_4 particles 1:0.4 in the individual droplets to obtain uniform integrated structure. The formation of aggregates of Fe_3O_4 particles indicated the absence of BaTiO_3 particles in the droplets. It is considerable that the difference of mobility between Fe_3O_4 and BaTiO_3 particles caused the non-stoichiometric ratio in the droplets. BaTiO_3 particles with larger particle diameter must receive greater Stokes resistance during transfer of suspension by the tube pumping. Sedimentation rate, which is proportional to the square of the particle size, also effected the mobility. Therefore, it would be possible to obtain a more uniform integrated structure by using sub-micro to nano-sized particles for both types of particles.

Figure 6 shows cross sectional SEM image and energy dispersive X-ray spectrometry mapping of BaTiO_3 – Fe_3O_4 -phenol resin composite (BaTiO_3 – Fe_3O_4 -resin) and $\text{BaTiO}_3/\text{PAA}/\text{Fe}_3\text{O}_4$ composite particle-phenol resin composite ($\text{Fe}_3\text{O}_4/\text{PAA}/\text{BaTiO}_3$ -resin). The BaTiO_3 – Fe_3O_4 -resin was prepared from the particles mixed based on the composition ratio estimated by the magnetization measurement. There was no difference between the distributions of BaTiO_3 . On the other hand, Fe_3O_4 fine particles were localized around the surface of BaTiO_3 particles in resin matrix fabricated with $\text{Fe}_3\text{O}_4/\text{PAA}/\text{BaTiO}_3$ composite particle [Fig. 6(a)]. In contrast to $\text{Fe}_3\text{O}_4/\text{PAA}/\text{BaTiO}_3$ -resin, Fe_3O_4 fine particles were not localized and were aggregated in the resin matrix fabricated with the mixture of BaTiO_3 , Fe_3O_4 and phenol resin powders [Fig. 6(b)]. The elemental analysis for $\text{Fe}_3\text{O}_4/\text{PAA}/\text{BaTiO}_3$ -resin composite indicated the persistent and discrete adsorption of Fe_3O_4 fine particles on the surface of BaTiO_3 particles.

4. Conclusions

Polymer-assisted spray drying method was developed for fabrication of fine particle supported inorganic particles

Fig. 6. Cross sectional backscattered electron image and elemental analysis results of (a) $\text{Fe}_3\text{O}_4/\text{PAA}/\text{BaTiO}_3$ -resin and (b) BaTiO_3 – Fe_3O_4 -resin. The mass ratio of BaTiO_3 to Fe_3O_4 particles in BaTiO_3 – Fe_3O_4 -phenol resin was adjusted based on the composition ratio estimated by the magnetization measurement.

with a uniform and single layer. We found that negatively charged PAA molecules functioned to disperse both 0.25 μm Fe₃O₄ particles and 2.0 μm BaTiO₃ particles individually. Then, self-accumulation was accelerated by condensation of two particles in shrinking sprayed droplets and Fe₃O₄ particles were accumulated on BaTiO₃ particles with a single layer. PAA functioned as binder in the dried composite particles, and the Fe₃O₄ fine particles were fixed persistently and discretely. Increasing the amount of Fe₃O₄ particles in the starting suspension increased the coverage of BaTiO₃ particles but also produced the aggregates composed of Fe₃O₄ particles. The formation of aggregates must have been inhibited by making the mobility of Fe₃O₄ and BaTiO₃ particles equal. We can conclude it is possible to obtain Fe₃O₄ supported BaTiO₃ composite particles by PAA-assisted spray drying method with a conventional equipment, and the combination of various functional particles is expected because there is no chemical reaction in the polymer-assisted spray drying process.

References

- 1) S. Luo, S. Yu, R. Sun and C.-P. Wong, *ACS Appl. Mater. Interfaces*, **6**, 176–182 (2014).
- 2) T. Fuchigami, K. Yoshida and K.-I. Kakimoto, *Jpn. J. Appl. Phys.*, **56**, 10PC08 (2017).
- 3) A. Fujii, S. Hirota, Y. Murakami, H. Muto, T. Kawashima, K. Tajiri, H. Shiota, T. Tsurimoto and M. Nagao, *Electr. Eng. Jpn.*, **199**, 3–10 (2017).
- 4) Y. Murakami, A. Fujii, T. Kawashima and M. Nagao, in 2015 IEEE Conf. Electr. Insul. Dielectr. Phenom., 680, IEEE (2015).
- 5) F. Caruso, H. Lichtenfeld, M. Giersig and H. Möhwald, *J. Am. Chem. Soc.*, **120**, 8523–8524 (1998).
- 6) E. R. Kleinfeld and G. S. Ferguson, *Science*, **265**, 370–373 (1994).
- 7) A. Martin and K. Kakimoto, *Jpn. J. Appl. Phys.*, **54**, 10NB06 (2015).
- 8) A. Martin and K. Kakimoto, *Jpn. J. Appl. Phys.*, **53**, 09PB09 (2014).
- 9) N. Matsubara, T. Fuchigami and K.-I. Kakimoto, *J. Ceram. Soc. Jpn.*, **125**, 449–453 (2017).
- 10) D. Popovici and J. Akedo, *Jpn. J. Appl. Phys.*, **49**, 09MA13 (2010).
- 11) T. Fuchigami, R. Kawamura, Y. Kitamoto, M. Nakagawa and Y. Namiki, *Langmuir*, **27**, 2923–2928 (2011).
- 12) T. Fuchigami, R. Kawamura, Y. Kitamoto, M. Nakagawa and Y. Namiki, *Biomaterials*, **33**, 1682–1687 (2012).
- 13) M. Nakamura, K. Katagiri and K. Koumoto, *J. Colloid Interf. Sci.*, **341**, 64–68 (2010).
- 14) T. Fuchigami, K. Yoshida and K. Kakimoto, *Jpn. J. Appl. Phys.*, **56**, 10PC08 (2017).
- 15) N. Ichinose and M. Kimura, *Jpn. J. Appl. Phys.*, **30**, 2220–2223 (1991).
- 16) G.-W. Zhou, J. Wang, P. Gao, X. Yang, Y.-S. He, X.-Z. Liao, J. Yang and Z.-F. Ma, *Ind. Eng. Chem. Res.*, **52**, 1197–1204 (2013).
- 17) A. Stunda-Zujeva, Z. Irbe and L. Berzina-Cimdina, *Ceram. Int.*, **43**, 11543–11551 (2017).
- 18) B. Vertruyen, N. Eshraghi, C. Piffet, J. Bodart, A. Mahmoud and F. Boschini, *Materials*, **11**, 1076 (2018).
- 19) F. Iskandar, A. B. D. Nandiyanto, K. M. Yun, C. J. Hogan, Jr., K. Okuyama and P. Biswas, *Adv. Mater.*, **19**, 1408–1412 (2007).
- 20) D. S. Jung, T. H. Hwang, S. Bin Park and J. W. Choi, *Nano Lett.*, **13**, 2092–2097 (2013).
- 21) N. Hagura, A. Bayu, D. Nandiyanto, F. Iskandar and K. Okuyama, *Chem. Lett.*, **38**, 1076–1077 (2009).
- 22) T. Fuchigami and K. Kakimoto, *Jpn. J. Appl. Phys.*, **55**, 10TB06 (2016).
- 23) T. Fuchigami and K. Kakimoto, *J. Mater. Res.*, **32**, 3326–3332 (2017).
- 24) M. Taguchi, N. Yamamoto, D. Hojo, S. Takami, T. Adschiri, T. Funazukuri and T. Naka, *RSC Adv.*, **4**, 49605–49613 (2014).
- 25) J. Lu, K. Minami, S. Takami, M. Shibata, Y. Kaneko and T. Adschiri, *ACS Appl. Mater. Interfaces*, **4**, 351–354 (2012).
- 26) H. Hayashi and K. Torii, *J. Mater. Chem.*, **12**, 3671–3676 (2002).
- 27) R. Liu, Y. Zhao, R. Huang, Y. Zhao and H. Zhou, *J. Mater. Chem.*, **20**, 10665–10670 (2010).
- 28) Y. Xue, R. Xu, Z. Wang, R. Gao, C. Li, G. Chen, X. Deng, W. Cai and C. Fu, *J. Electron. Mater.*, **48**, 4806–4817 (2019).
- 29) S. Filipović, V. P. Pavlović, M. Mitrić, S. Lević, N. Mitrović, A. Maričić, B. Vlahović and V. B. Pavlović, *J. Adv. Ceram.*, **1**, 133–147 (2019).
- 30) X. Huo, W. Li, J. Zhu, L. Li, Y. Li, L. Luo and Y. Zhu, *J. Phys. Chem.*, **119**, 25786–25791 (2015).
- 31) R. Balgis, T. Ogi, W. Wang, G. M. Anilkumar, S. Sago and K. Okuyama, *Langmuir*, **30**, 11257–11262 (2014).
- 32) A. Suhendi, A. Bayu, D. Nandiyanto, M. M. Munir, T. Ogi, L. Gradon and K. Okuyama, *Langmuir*, **29**, 13152–13161 (2013).
- 33) S. Zellmer, G. Garnweitner, T. Breinlinger, T. Kraft and C. Schilde, *ACS Nano*, **9**, 10749–10757 (2015).
- 34) R. Vehring, W. R. Foss and D. Lechuga-Ballesteros, *J. Aerosol Sci.*, **38**, 728–746 (2007).