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# Preparation of hollow alumina microspheres by microwave-induced plasma pyrolysis of atomized precursor solution

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## Abstract

Hollow alumina microspheres have been prepared by microwave-induced (MI) plasma pyrolysis of atomized aerosols of precursor solutions and subsequent calcination at 1300 °C for 2 h. When an aqueous solution of 0.5 mol dm$^{-3}$ $Al(NO_3)_3$ without any additives was used as a precursor, hollow $\alpha$-$Al_2O_3$ microspheres with a thick shell wall were prepared after post-calcination at 1300 °C. The addition of a polypropylene (PO)–polyethylene(EO) blockcopolymer (molecular weight: 2900–6500) to the precursor solution was effective for increasing the yield of hollow microspheres, but resulted in the formation of many cracks and holes in the thinned shell wall. Hollow alumina microspheres with a thin, but strong, shell layer could be prepared by the simultaneous addition of tetraethylorthosilicate.
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*Keywords:* $Al_2O_3$; Hollow microsphere; Ultrasonic spraying; Microwave-induced plasma; Microspheres

## 1. Introduction

Preparation of hollow microspheres has been a subject of extensive investigations because of their wide range of applications: catalyst supports,[1] ion absorbers,[2] drug delivery systems,[3,4] biomaterials,[5] electronic,[6] electromagnetic[7] and optical materials,[8–10] as well as lightweight and/or adiabatic materials offering economical benefits and energy saving.[11–13] Some hollow ceramic microspheres such as silica balloons, shirasu balloons (shirasu: siliceous ejecta, especially being widespread mainly in the southern area of Kyushu, Japan) and alumina balloons have been already commercialized as a lightweight and/or adiabatic material. However, silica-based balloons are difficult to be prepared in uniform and controlled size. Alumina balloons prepared by a spray method of molten alumina are difficult to apply to various fields due to their large size, although they exhibit sufficient mechanical strength. Therefore, development of a tailored fabrication process for hollow microspheres with uniform and controlled size is desired for improving the properties of composite materials.

Hollow ceramic microspheres have been prepared by several methods, such as spray drying,[14] spray pyrolysis,[15,16] sol–gel process with and without a template[17–20] and thermal plasma treatment of metal powder.[21] We have also prepared hollow microspheres of alumina, titania and zirconia with a mechanofusion system by employing polymethyl methacrylate microspheres as a template[22–27] and by ultrasonic spray pyrolysis of $Al(NO_3)_3$ solution with a specially designed mist-supply apparatus.[28] However, the mechanofusion system is only useful for preparing hollow microspheres larger than several microns in diameter. In the latter ultrasonic spray pyrolysis, the morphology and diameter of the resultant hollow ceramic microspheres are usually difficult to be controlled.

We have already demonstrated the potential of microwave-induced (MI) plasma in preparing various functional ceramic materials[29,30] as well as in decomposing many hazardous materials in air under atmospheric pressure[31–33] or in waste water.[34] This MI-plasma generated by utilizing conductive SiC ceramics as a trigger can be operated at

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relatively low power and therefore at low cost, compared with other plasma systems used for fabricating ceramics.[21,35,36]

In the present study, therefore, preparation of hollow $Al_2O_3$ microspheres has been attempted by utilizing MI-plasma pyrolysis of some kinds of precursor aerosols atomized ultrasonically.

## 2. Experimental

Fig. 1 shows an experimental equipment employed for the preparation of hollow alumina microspheres by MI-plasma spray pyrolysis of an aqueous $Al(NO_3)_3$ solution. A few pieces of SiC ceramics prepared by crushing a commercial SiC-based heating element (Siliconit, Siliconit Konetsu Kogyo Co., Ltd.) were set in the plasma reactor (quartz tube, 55 cm in length and 18 mm in internal diameter), as a trigger to generate MI-plasma under atmospheric Ar-based flowing gas (total flowing rate: $2000\,cm^3\,min^{-1}$). Microwave power (400–600 W) was supplied from a 2.45 GHz magnetron (Nissin Co., Ltd., MPS-15D).

A plastic tube equipped with a polyethylene thin film at one end was set perpendicular over an ultrasonic vibrator (Honda Electric Co., Ltd., HM-303N, 2.4 MHz) at a distance of 0.5–1.0 cm in water. The tube was then filled with an aqueous $Al(NO_3)_3$ solution ($0.5\,mol\,dm^{-3}$). In some cases, to the solution was added a polyoxypropylene(PO)–polyoxyethelene(EO) blockcopolymer (PE10500 (molecular weight (MW): 6500, EO content: 50%), PE9400 (MW: 4600, EO content: 40%) or PE6400 (MW: 2900, EO content: 40%) from BASF Japan Co., Ltd.) in $0.1\,mmol\,dm^{-3}$ or tetraethylorthosilicate (TEOS, $Si(OCH_2CH_3)_4$, from Kishida Chemical Co., Ltd.) in $0.523–15.7\,mmol\,dm^{-3}$.

The aerosol of an $Al(NO_3)_3$ solution generated by the ultrasonic vibrator was carried up by Ar flowing ($100\,cm^3\,min^{-1}$) and then was introduced into a plasma reactor by an additional Ar–$O_2$ carrier gas (Ar: $1800\,cm^3\,min^{-1}$, $O_2$: $100\,cm^3\,min^{-1}$). Alumina powders deposited down plasma streamer inside the reactor were post-calcined at 1300 °C for 2 h in air.

The powders with and without the post-calcination were characterized by a transmission electron microscope (TEM, JEOL Ltd., JEM-2010 or JEM-100S), a scanning electron microscope (SEM, Hitachi, Ltd., S-2250N) and X-ray diffraction analysis (XRD, Rigaku Corp., RINT 2000). The emission spectrum of the MI plasma was analyzed with a

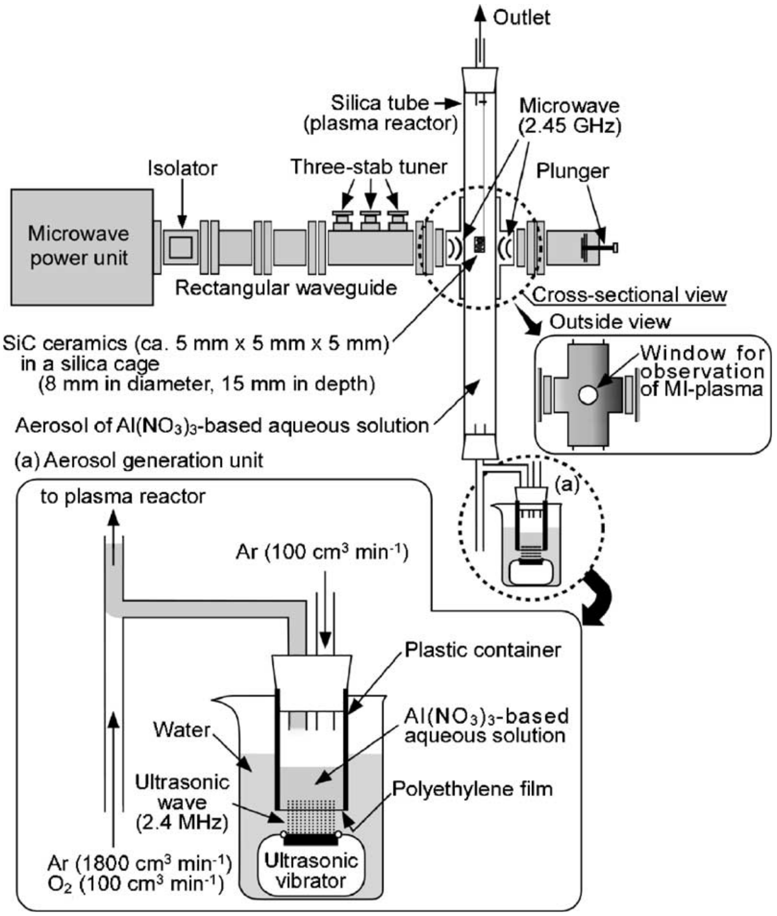


Fig. 1. Schematic drawing of a preparation apparatus of hollow alumina microspheres using ultrasonic spray and MI-plasma.

photonic multi-channel analyzer (C7473, Hamamatsu Photonics K. K.).

## 3. Results and discussion

### 3.1. Emission spectra of MI-plasma

Fig. 2 shows emission spectra of MI-plasma generated from SiC ceramics under various flowing gases at a microwave power of 500 W. Under pure Ar flowing (1800 $cm^3$ $min^{-1}$), many emission peaks ascribable to neutral Ar atom were observed in the wavelength range of 200–950 nm as observed in the case of inductively coupled plasma (ICP) under pure Ar flowing,[37,38] as shown in Fig. 2a, but no peak originating from Ar ions[37–40] appeared under the present conditions. In addition, small peaks assignable to OH radical (281–295 nm and 306–325 nm), H (ca. 434 nm and ca. 486 nm), $N_2^+$ (ca. 388 nm, ca. 389 nm, ca. 391 nm and ca. 428 nm) and NH (ca. 336 nm) appeared, probably due to trace amounts of $H_2O$ and $N_2$ remaining inside the plasma reactor. Besides them, an emission peak of Na atom was observed.

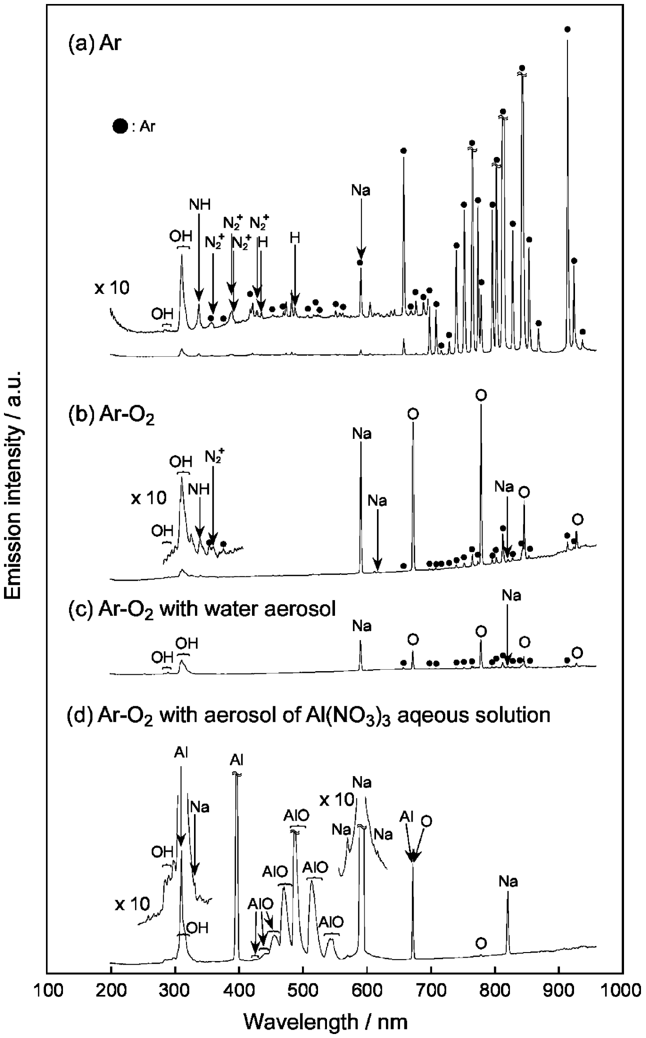


Fig. 2. Emission spectra of MI-plasma generated under various flowing gases. (a) Ar (2000 ml $min^{-1}$), (b) Ar (1900 ml $min^{-1}$)–$O_2$ (100 ml $min^{-1}$), and Ar (1900 ml $min^{-1}$)–$O_2$ (100 ml $min^{-1}$) containing (c) water aerosol and (d) with aerosol of 0.5 mol $dm^{-3}$ $Al(NO_3)_3$ aqueous solution.

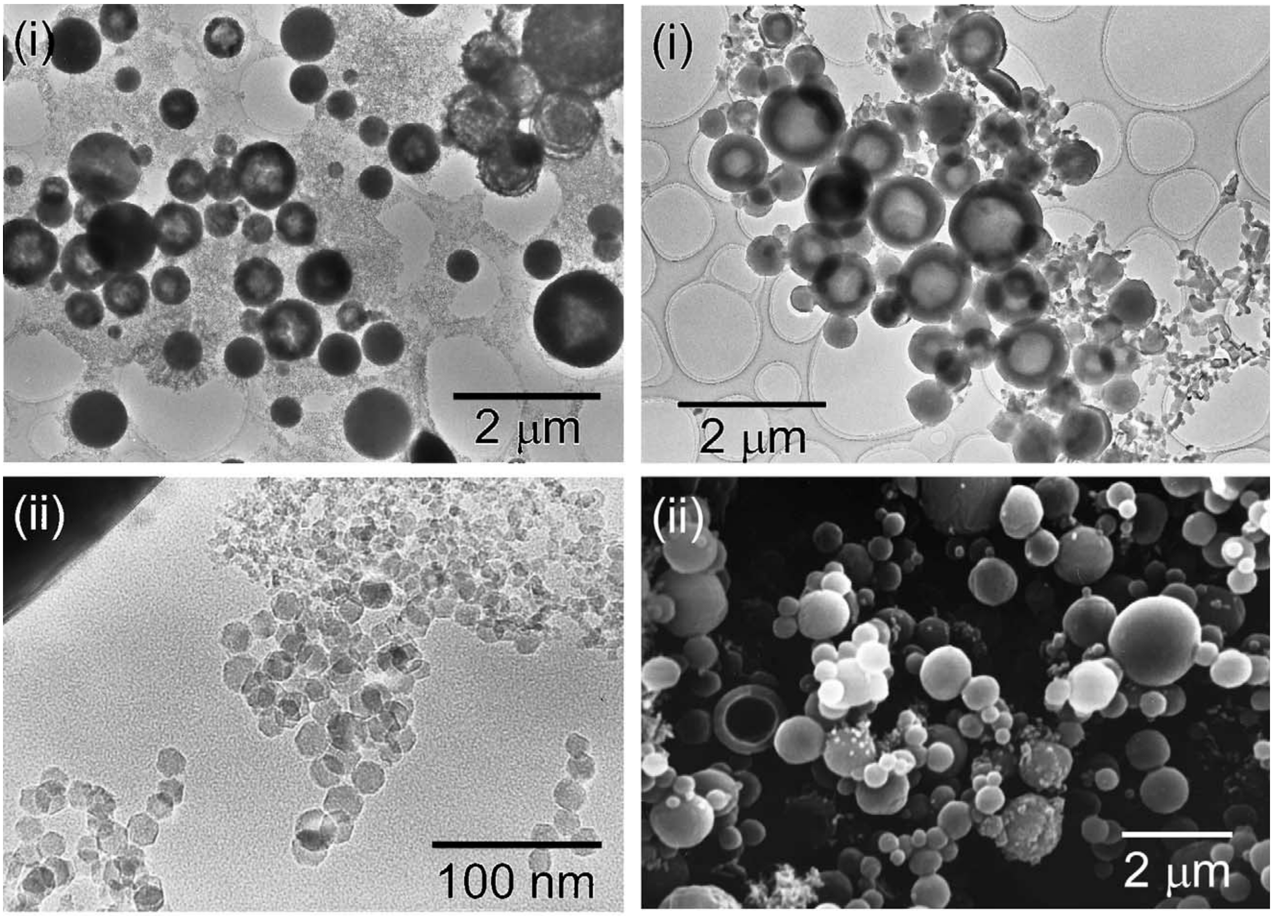
The intensity of emission peaks ascribable to Ar atom drastically reduced and then four prominent O emissions appeared at ca. 778 nm, ca. 673 nm, ca. 845 nm and ca. 927 nm,[40,41] as shown in Fig. 2b, when $O_2$ gas at the flow rate of 100 $cm^3$ $min^{-1}$ was mixed with the Ar flowing.

When the aerosol of distilled water, which was atomized by the ultrasonic wave of 2.4 MHz, was introduced, the relative intensity of emissions from OH radical to those of O atom increased, as shown in Fig. 2c, but the intensities of all spectra became weak, probably due to consumption of the microwave power to heat the aerosol. When the aerosols of aqueous $Al(NO_3)_3$ solutions were mixed, three strong emissions assignable to Al atom (ca. 309 nm, ca. 396 nm and ca. 669 nm) were additionally observed together with large and broad AlO emissions between 420 and 560 nm.[42] In the case of ICP,[38] oxide emissions are generally observed in the preheating zone, where incomplete desolvation and decomposition processes are taking place. The appearance of the AlO emission peaks implies formation of some species with Al-O bonding, e.g., $Al(OH)_3$, AlOOH or $Al_2O_3$, in the plasma streamer.

No change in emission spectrum, in comparison to that shown in Fig. 2d, was induced by the addition of PO–EO blockcopolymer or TEOS, probably due to their low concentrations in the $Al(NO_3)_3$ aqueous solution.

### 3.2. MI-plasma pyrolysis of atomized $Al(NO_3)_3$ aqueous solution

Fig. 3 shows TEM and SEM photographs of alumina microparticles prepared by MI-plasma pyrolysis of atomized $Al(NO_3)_3$ aqueous solution without any additives prior to calcination. The as-prepared microparticles were spherical, independently of their sizes (the diameter: 0.2–2.0 μm), as shown in Fig. 3a(i). The ratio of the yield of hollow microspheres, including incomplete hollow structure, to that of solid microparticles was below 40%. Besides such mirospheres, many hexagonal nanoparticles (15–20 nm in diameter) were observed as in Fig. 3a(ii). Post-calcination at 1300 °C for 2 h in air led to an increase in the yield of hollow microspheres, as seen in Fig. 3b(i), but some solid microparticles, mostly below ca. 0.5 μm in diameter, still remained. In addition, fine particles, which have been likely produced by grain growth of many hexagonal nanoparticles, were observed around hollow microspheres, as shown in Fig. 3b(i). The SEM photograph shown in Fig. 3b(ii) shows that the surface of the hollow microspheres is relatively smooth. Moreover, the hollow structure of the microspheres can be recognized from the fractured section of a microsphere at the left side of Fig. 3b(ii). However, these hollow microspheres are considered to be unsatisfactory as



(a) as-prepared

(b) post-calcined

Fig. 3. TEM and SEM photographs of microparticles (a) as-prepared from 0.5 mol dm$^{-3}$ Al(NO$_3$)$_3$ aqueous solution and (b) post-calcined at 1300 °C for 2 h.

a lightweight material, because their shell walls are rather thick.

Fig. 4a shows an XRD pattern of the as-prepared microspheres via the MI-plasma pyrolysis of the atomized aerosol

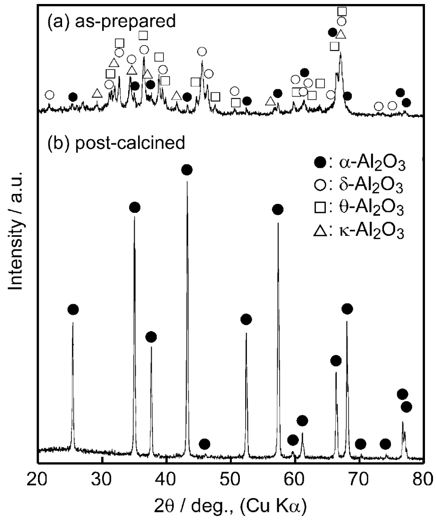


Fig. 4. XRD patterns of microparticles (a) as-prepared from 0.5 mol dm$^{-3}$ Al(NO$_3$)$_3$ aqueous solution and (b) post-calcined at 1300 °C for 2 h.

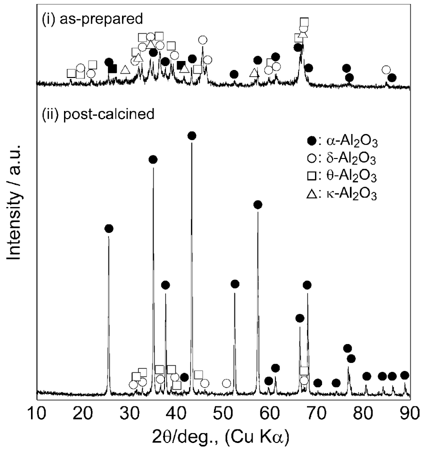
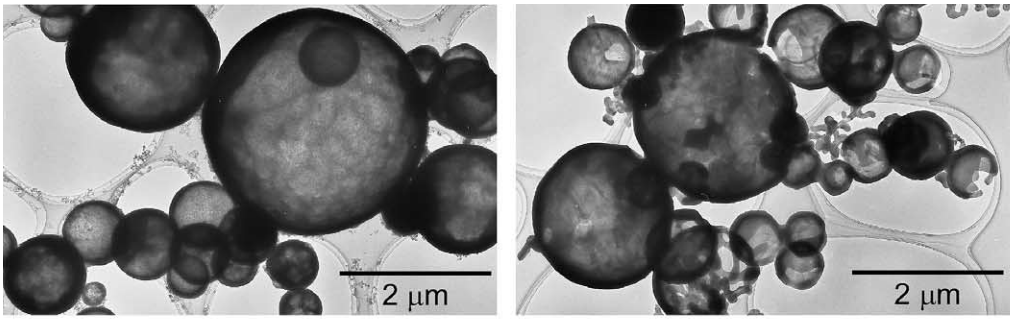
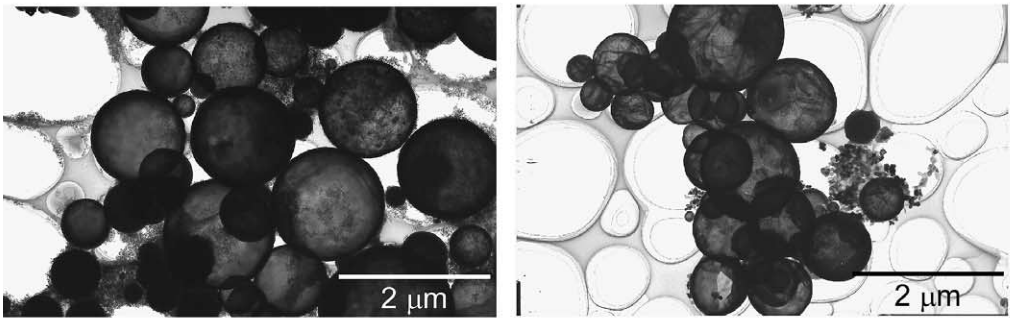


Fig. 5. XRD patterns of Al$_2$O$_3$ microparticles (a) as-prepared from 0.5 mol dm$^{-3}$ Al(NO$_3$)$_3$ aqueous solution mixed with 0.1 mmol dm$^{-3}$ PE6400 and (b) post-calcined at 1300 °C for 2 h.



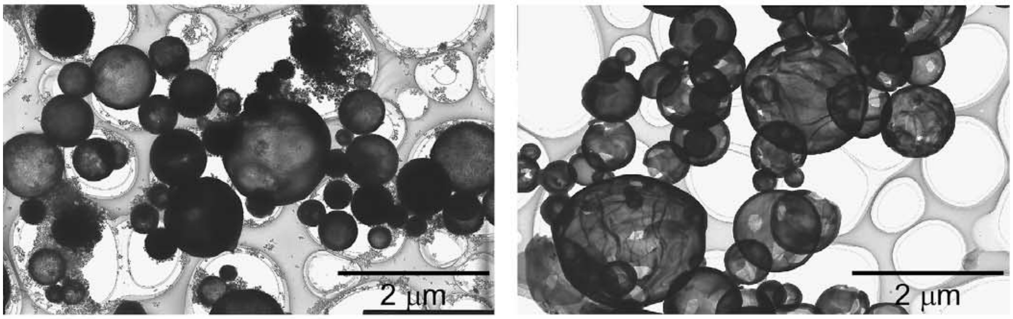
(a) PE10500

(i) as-prepared (ii) post-calcined



(b) PE9400

(i) as-prepared (ii) post-calcined

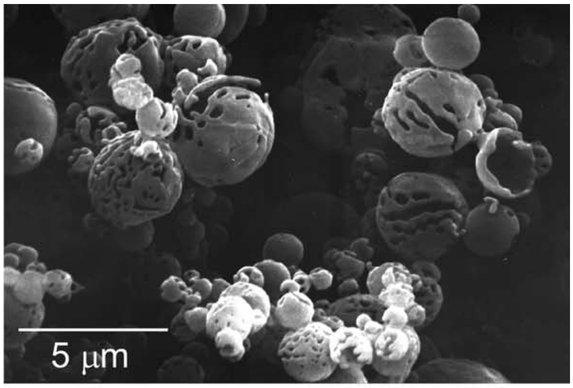


(c) PE6400

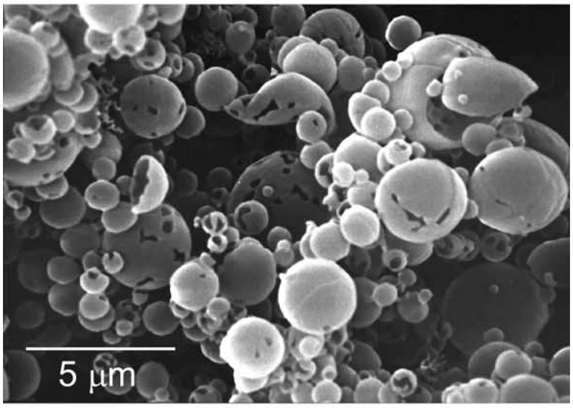
(i) as-prepared (ii) post-calcined

Fig. 6. TEM photographs of $Al_2O_3$ microparticles prepared from 0.5 mol $dm^{-3}$ $Al(NO_3)_3$ aqueous solution mixed with 0.1 mmol $dm^{-3}$ PO–EO blockcopolymers ((a) PE10500, (b) PE9400 and (c) PE6400). (i) As-prepared and (ii) post-calcined at 1300 °C for 2 h.

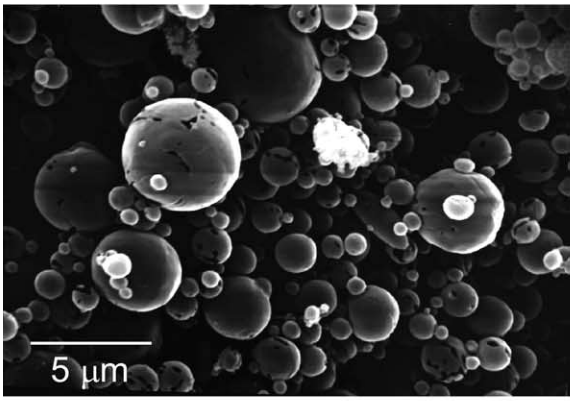
of an aqueous $Al(NO_3)_3$ solution (0.5 mol $dm^{-3}$). Four crystal phases existed, $\alpha$-$Al_2O_3$ (corundum), $\delta$-$Al_2O_3$, $\theta$-$Al_2O_3$ and $\kappa$-$Al_2O_3$. Among the latter three transition phases of alumina, $\delta$-$Al_2O_3$ was the largest amount in the as-prepared powder. In our previous study, where the atomized aerosols of aqueous $Al(NO_3)_3$ solutions were pyrolized in an electric furnace heated at 1300 °C for 1 h,[23] only $\delta$-$Al_2O_3$ was obtained. Therefore, it is considered that rather complex reactions have occurred in the present MI-plasma pyrolysis. By referring to the data shown in Fig. 4a, the nanoparticles observed in Fig. 3a(ii) can be ascribed to $\alpha$-$Al_2O_3$ due to their hexagonal morphology. They may have been prepared from small droplets of the aqueous $Al(NO_3)_3$ solution, while hollow microspheres has arisen from large ones. Small droplets are believed to transform easily to $\alpha$-$Al_2O_3$ by instantaneous and complete evaporation of water, followed by thermal decomposition of $Al(NO_3)_3$. In the case of large droplets, however, evaporation of water and then condensation of $Al(NO_3)_3$ are anticipated to be limited to the surface region of the droplets at the initial stage. Then, transition phases of alumina ($\delta$-$Al_2O_3$, $\theta$-$Al_2O_3$ and $\kappa$-$Al_2O_3$) are considered to be formed as a shell wall via aluminum hydroxide or aluminaum oxyhydroxide as an intermediate[43]. The mass transportation from the core of the droplet to the surface during successive evaporation of water will thicken the shell wall. Hollow microspheres are considered to be formed by such a process. This may be the main reason for the appearance of the hollow structure only for particles larger than 0.5 μm in diameter. Since such a process is rather time-consuming in comparison with the reaction in small droplets, transformation to α-$Al_2O_3$ is considered to be limited. From these considerations, the as-prepared hollow microspheres are likely to be composed of transition phases of alumina. These transition phases could be transformed into thermodynamically stable α-$Al_2O_3$ by post-calcination at 1300 °C for 2 h in air, as shown in Fig. 4b.



(a) PE 10500



(b) PE9400



(c) PE6400

Fig. 7. SEM photographs of $Al_2O_3$ microparticles prepared from 0.5 mol dm$^{-3}$ $Al(NO_3)_3$ aqueous solution mixed with 0.1 mmol dm$^{-3}$ PO–EO blockcopolymers ((a) PE10500, (b) PE9400 and (c) PE6400) after post-calnication at 1300 °C for 2 h.

### 3.3. Effect of additives in $Al(NO_3)_3$ aqueous solution

Three kinds of PO–EO blockcopolymers were added to the aqueous $Al(NO_3)_3$ solution in an attempt to obtain a well-developed hollow structure for the alumina microspheres. XRD patterns of the microparticles obtained with the addition of PE6400 are shown in Fig. 5. Very similar XRD patterns were also observed for the addition of PE10500 and PE9400. The amount of α-$Al_2O_3$ in the as-prepared powder slightly increased with the addition of PE6400. This may have arisen from additional heating due to combustion of the PO–EO blockcopolymers mixed in the droplets. However, a little amount of δ-$Al_2O_3$ and θ-$Al_2O_3$ still remained even after the post-calcination, although the main phase was α-$Al_2O_3$. Therefore, organic residues from the PO–EO blockcopolymers may inhibit the transformation of δ-$Al_2O_3$ and θ-$Al_2O_3$ into α-$Al_2O_3$. TEM photographs of the hollow alumina microparticles obtained by employing the three kinds of PO–EO blockcopolymers are shown in Fig. 6. The addition of the PO–EO blockcopolymers in the precursor solution resulted in enlargement of the diameter of the as-prepared hollow alumina microspheres and thinning of the shell wall, compared with those prepared without the

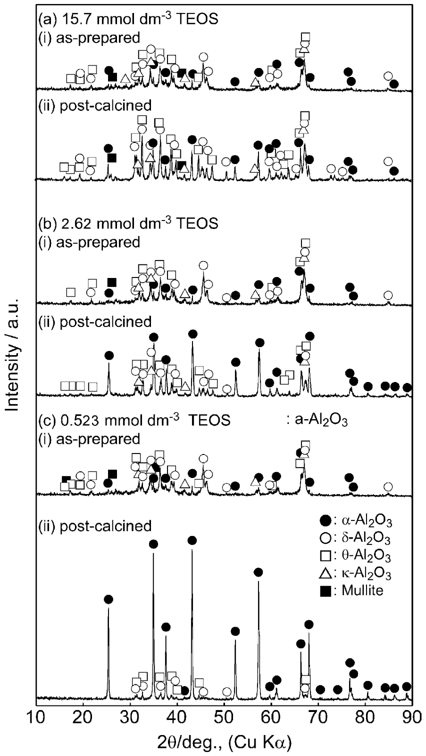
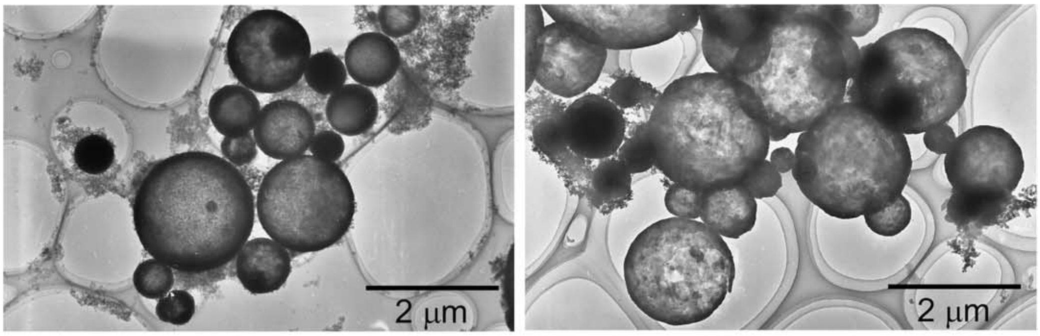
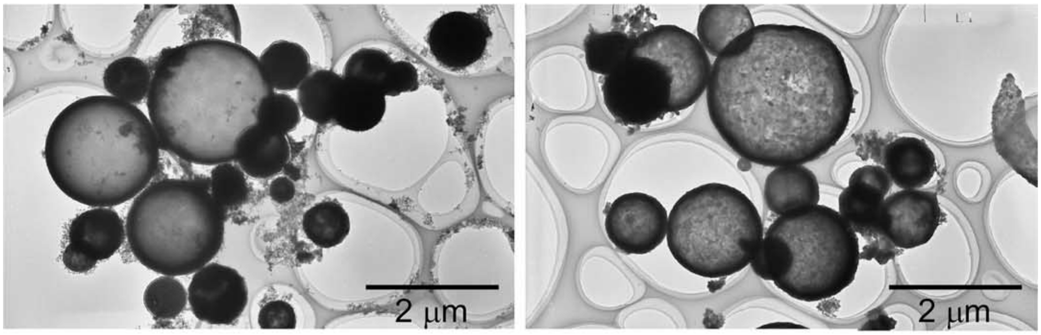


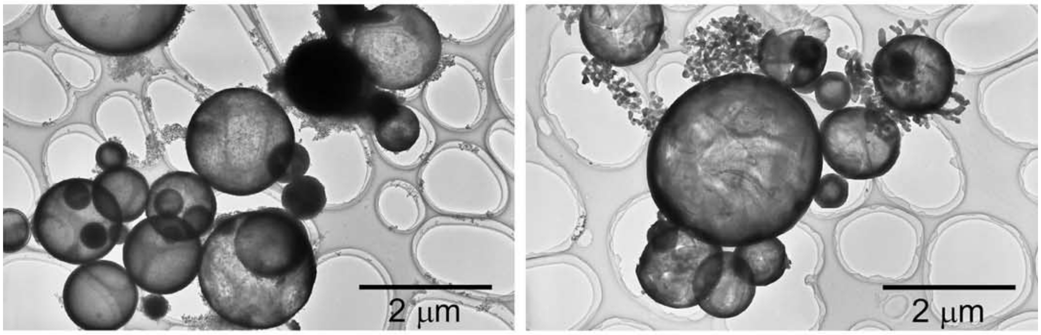
Fig. 8. XRD patterns of $Al_2O_3$ microparticles prepared from 0.5 mol dm$^{-3}$ $Al(NO_3)_3$ aqueous solution mixed with 0.1 mmol dm$^{-3}$ PE6400 and TEOS ((a) 15.7, (b) 2.62 and (c) 0.523 mmol dm$^{-3}$). (i) As-prepared and (ii) post-calcined at 1300 °C for 2 h.



(a) TEOS: 15.7 mmol dm$^{-3}$
(i) as-prepared (ii) post-calcined



(b) TEOS: 2.62 mmol dm$^{-3}$
(i) as-prepared (ii) post-calcined

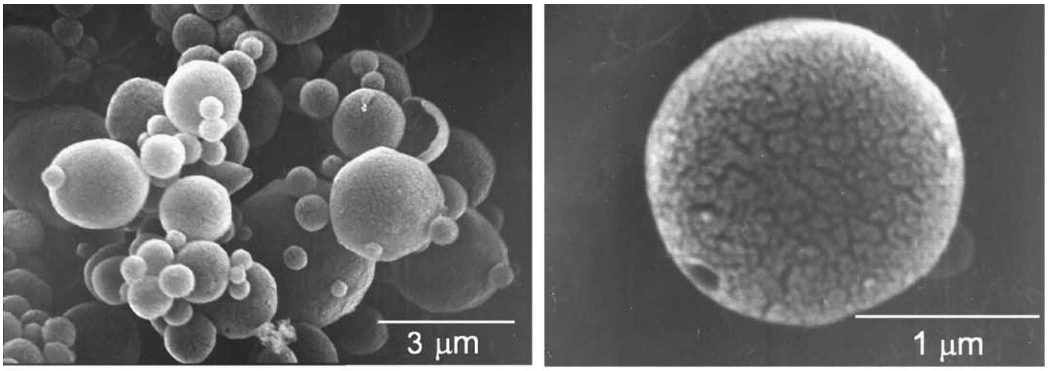


(c) TEOS: 0.523 mmol dm$^{-3}$
(i) as-prepared (ii) post-calcined

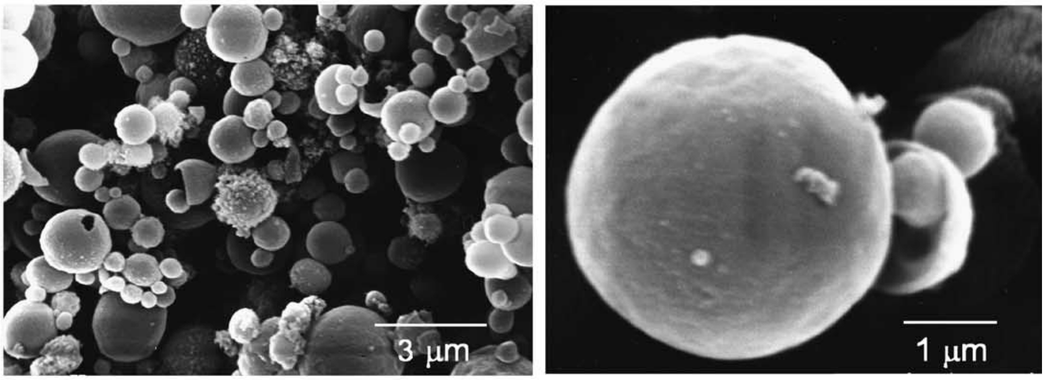
Fig. 9. TEM photographs of $Al_2O_3$ microparticles prepared from 0.5 mol dm$^{-3}$ $Al(NO_3)_3$ aqueous solution mixed with 0.1 mmol dm$^{-3}$ PE6400 and TEOS ((a) 15.7, (b) 2.62 and (c) 0.523 mmol dm$^{-3}$). (i) As-prepared and (ii) post-calcined at 1300 °C for 2 h.

PO–EO blockcopolymers (see Fig. 3). In addition, the diameter of the microspheres tended to increase with increasing the molecular weight (MW) of the PO–EO blockcopolymers. Such changes in morphological size may be induced by gases (e.g., CO, $CO_2$ and $H_2O$) evolved by rapid decomposition or combustion of the PO–EO blockcopolymers during the hollowing process. On the other hand, the addition of the PO–EO blockcopolymers caused formation of many large cracks and holes in the thin alumina shell walls after post-calcination, as shown in TEM (Fig. 6(ii)) and SEM (Fig. 7) photographs. In addition, the cracks and holes became large with increasing the MW of the PO–EO blockcopolymers and then with increasing the diameter of microspheres.

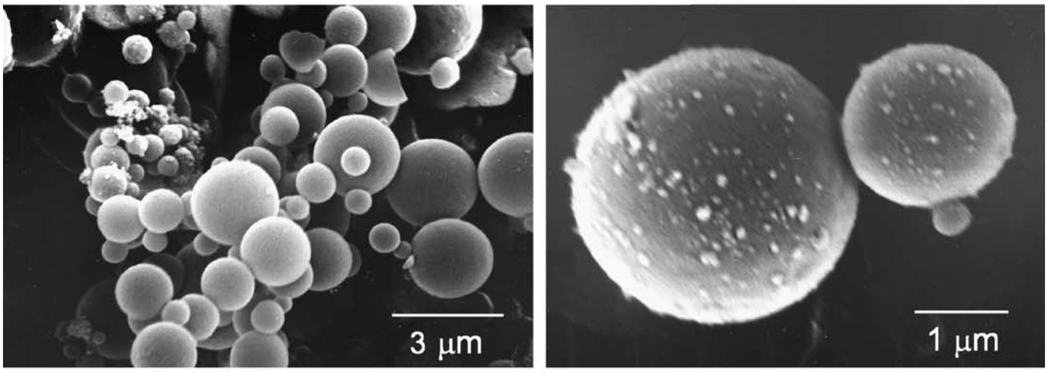
In the next experiments, therefore, co-addition of TEOS was tested for the aqueous $Al(NO_3)_3$-PE6400 solution, in order to diminish the cracks and holes after post-calcination. Fig. 8 shows XRD patterns of the as-prepared and post-calcined powders prepared from the precursor solution containing various amounts of TEOS. When 15.7 mmol dm$^{-3}$ TEOS was added, mullite phase appeared in the XRD pattern of the as-prepared powder, together with α-$Al_2O_3$ and three kinds of transition phases of alumina. In this case, the



(a) TEOS: 15.7 mmol $dm^{-3}$



(b) TEOS: 2.62 mmol $dm^{-3}$



(c) TEOS: 0.523 mmol $dm^{-3}$

Fig. 10. SEM photographs of $Al_2O_3$ microparticles prepared from 0.5 mol $dm^{-3}$ $Al(NO_3)_3$ aqueous solution mixed with 0.1 mmol $dm^{-3}$ PE6400 and TEOS ((a) 15.7, (b) 2.62 and (c) 0.523 mmol $dm^{-3}$) after post-calcination at 1300 °C for 2 h.

three transition phases could not be transformed into $\alpha$-$Al_2O_3$ even after calcination at 1300 °C for 2 h in air, as shown in Fig. 8a(ii). Namely, the diffraction peaks of $\theta$-$Al_2O_3$ increased slightly as a result of the post-calcination, whereas those of $\alpha$-$Al_2O_3$ decreased. A similar tendency in phase transition was observed for the powder prepared from the precursor solution containing 2.62 mmol $dm^{-3}$ TEOS (see Fig. 8b), but the intensity of $\alpha$-$Al_2O_3$ phase was much higher than those of the transition phases after post-calcination. When the amount of TEOS was reduced to 0.523 mmol $dm^{-3}$, the main phase after post-calcination became $\alpha$-$Al_2O_3$, though small peaks from $\delta$-$Al_2O_3$ and $\theta$-$Al_2O_3$ still remained.

Fig. 9 shows TEM photographs of alumina microparticles prepared from aqueous $Al(NO_3)_3$–PE6400 solutions containing different amounts of TEOS. It is obvious that the addition of the smallest amount of TEOS (0.523 mmol $dm^{-3}$, Fig. 9c) is effective for reducing the formation of cracks and holes after post-calcination, as shown in Fig. 9c(ii). From

SEM photographs of these hollow microshperes after post-calcination in Fig. 10, it is apparent that the surface of the microspheres is rather smooth. Si-components dispersed among the alumina nanoparticles are anticipated undoubtedly to enhance the mechanical strength of the shell wall of the hollow microspheres.

## 4. Conclusion

Hollow alumina microspheres have been prepared by MI-plasma pyrolysis of atomized aerosols of precursor solutions and subsequent calcination at 1300 °C for 2 h. When an aqueous solution of 0.5 mol dm$^{-3}$ Al(NO$_3$)$_3$ without any additives was treated in MI-plasma, the yield of hollow microspheres among the resultant particles was less than 40%. In addition, hollow microspheres were composed mainly of δ-Al$_2$O$_3$, θ-Al$_2$O$_3$ and κ-Al$_2$O$_3$ phase. Besides hollow and dense microspheres in micron-size, many hexagonal nanoparticles of α-Al$_2$O$_3$ (15–20 nm in diameter) were also formed. Post-calcination of the as-prepared particles resulted in an increase in the yield of hollow microspheres and also in enhanced transformation into α-Al$_2$O$_3$. Addition of PO–EO blockcopolymers to the precursor solution was effective for increasing the yield of hollow microspheres, but resulted in an increase in diameter of the microspheres and the formation of disadvantageous cracks and holes in the thinned shell wall. Hollow microspheres with a thin but strong shell could be prepared by co-addition of TEOS to the precursor solution containing blockcopolymers.

## Acknowledgement

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## References

1. Sakanishi, K., Hasuo, H., Mochida, I. and Okuma, O., Preparation of highly dispersed NiMo catalysts supported on hollow spherical carbon black particles. *Energy Fuels*, 1995, **9**, 995–998.
2. Bae, E., Chah, S. and Yi, H., Preparation and characterization of ceramic hollow microspheres for heavy metal ion removal in wastewater. *J. Colloid Interface Sci.*, 2000, **230**, 367–376.
3. Josech, N. J., Lakshmi, S. and Jayakrishnan, A., A floating-type oral dosage form for piroxicam based on hollow polycarbonate microspheres: in vitro and in vivo evaluation in rabbits. *J. Control. Release*, 2002, **79**, 71–79.
4. Sato, Y., Kawashima, Y., Takeuchi, H. and Yamamoto, H., Physicochemical properties to determine the buoyancy of hollow microspheres (microballoons) prepared by the emulsion solvent diffusion method. *Eur. J. Pharm. Biopharm.*, 2003, **55**, 297–304.
5. Qiu, Q.-Q., Ducheyne, P. and Ayyaswamy, P. S., Fabrication, characterization and evaluation of bioceramic hollow microspheres used as microcarriers for 3-D bone tissue formation in rotating bioreactors. *Biomaterials*, 1999, **20**, 989–1001.
6. Kellerman, D. W., Review of low dielectric constant thick film electronic ceramics using hollow microspheres. In *MRS Symposium Proceedings, Vol 372*, ed. D. L. Wilcox, M. Berg, T. Bernat, D. Kellerman and J. K. Cochran, 1995, pp. 239–245.
7. Kim, S.-S., Kim, S.-T., Ahn, J.-M. and Kim, K.-H., Magnetic and microwave absorbing properties of Co–Fe thin films plated on hollow ceramic microspheres of low density. *J. Magn. Magn. Mater.*, 2004, **271**, 39–45.
8. Yin, J., Qian, X., Yin, J., Shi, M. and Zhou, G., Preparation of ZnS/PS microspheres and ZnS hollow shells. *Mater. Lett.*, 2003, **57**, 3859–3863.
9. Kang, Y. C., Roh, H. S. and Park, S. B., Sodium carbonate flux effects on the luminescence characteristics of (Y$_{0.5}$Gd$_{0.5}$)$_2$O$_3$: Eu phosphor particles prepared by spray pyrolysis. *J. Am. Ceram. Soc.*, 2001, **84**, 447–449.
10. Nyman, M., Caruso, J. and Hampden-smith, M. J., Comparison of solid-state and spray-pyrolysis synthesis of yttrium aluminate powders. *J. Am. Ceram. Soc.*, 1997, **80**, 1231–1238.
11. Kiser, M., He, M. Y. and Zok, F. W., The mechanical response of ceramic microballoon reinforced aluminum matrix composites under compressive loading. *Acta Mater.*, 1999, **47**, 2685–2694.
12. D'Almeida, J. R. M., An analysis of the effect of the diameters of glass microspheres on the mechanical behavior of glass-microsphere/epoxy-matrix composites. *Compos. Sci. Tech.*, 1999, **59**, 2087–2091.
13. Sodeyama, K., Sakka, Y., Kamino, Y., Hamaishi, K., Kokusho, T. and Seki, H., Preparation and properties of lightweight pottery using shirasuballon (in Japanese). *J. Ceram. Soc. Jpn.*, 1998, **106**, 333–338.
14. Zhang, B. and Freddy, B., Hollow ceramic microsphere. In *Proceedings of the Fabr. Adv. Mater. VIII*, ed. K. A. Khor, T. S. Srivatsan, M. Wang, W. Zhou and F. Boey, 2000, pp. 489–492.
15. Madler, L. and Pratsinis, S. E., Bismuth oxide nanoparticles by flame spray pyrolysis. *J. Am. Ceram. Soc.*, 2002, **85**, 1713–1718.
16. Jada, S. S., Preparation of hollow zircon (ZrSiO$_4$) microspheres by the spray-pyrolysis method. *J. Mater. Sci. Lett.*, 1990, **9**, 565–568.
17. Park, J.-H., Oh, C., Shin, S.-I., Moon, S.-K. and Oh, S.-G., Preparation of hollow silica microspheres in W/O emulsions with polymers. *J. Colloid Interface Sci.*, 2003, **266**, 107–114.
18. Ren, T.-Z., Yuan, Z.-Y. and Su, B.-L., Surfactant-assisted preparation of hollow microspheres of mesoporous TiO$_2$. *Chem. Phys. Lett.*, 2003, **374**, 170–175.
19. Yin, J., Qian, Z., Yin, J., Shi, M., Zhang, J. and Zhou, G., Preparation of polystyrene/zirconia core-shell microspheres and zirconia hollow shells. *Inorg. Chem. Commun.*, 2003, **6**, 942–945.
20. Ni, Y., Wang, I. F., Liu, H., Liang, Y., Yin, G., Hong, J. *et al.*, Fabrication and characterization of hollow cuprous sulfide (Cu$_{2-x}$S) microspheres by a simple template-free route. *Inorg. Chem. Commun.*, 2003, **6**, 1406–1408.
21. Karoly, Z. and Szepvolgyi, J., Hollow alumina microspheres prepared by rf thermal plasma. *Powder Technol.*, 2003, **132**, 211–215.
22. Kato, T., Ushijima, H., Katsumata, M., Hyodo, T., Shimizu, Y. and Egashira, M., Fabrication of hollow alumina microspheres via core/shell structure of polymehylmethacrylate/alumina prepared by mechanofusion. *J. Mater. Sci.*, 2002, **37**, 2317–2321.
23. Kato, T., Ushijima, H., Katsumata, M., Hyodo, T., Shimizu, Y. and Egashira, M., Preparation of core/shell microspheres of polymethylmethacrylate/alumina by mechanofusion as a precursor of hollow alumina microspheres. *Mol. Cryst. Liq. Cryst.*, 2002, **376**, 101–106.
24. Egashira, M., Kato, T., Hyodo, T. and Shimizu, Y., Preparation of hollow alumina microspheres by mechanofusion and ultrasonic spray pyrolysis. *Key Eng. Mater.*, 2003, **247**, 427–432.
25. Fukunaga, M., Kato, T., Hyodo, T., Shimizu, Y. and Egashia, M., Fabrication of hollow titania microspheres by mechanofusion (in Japanese). In *Proceedings of the Ceram. Soc. Jpn. 2003 Meeting*, 2003, p. 171.

26. Kato, T., Ushijima, H., Katsumata, M., Hyodo, T., Shimizu, Y. and Egashira, M., Effect of core materials on the formation of hollow alumina microspheres by mechanofusion process. *J. Am. Ceram. Soc.*, 2004, **87**, 60–68.
27. Fukunaga, M., Kato, T., Hyodo, T., Shimizu, Y. and Egashia, M., Fabrication of hollow titania microspheres by mechanofusion (in Japanese). In *Proceedings of the Ceram. Soc. Jpn. 2004 Meeting*, 2004, p. 72.
28. Kato, T., Tashiro, M., Sugimura, K., Hyodo, T., Shimizu, Y. and Egashira, M., Preparation of hollow alumina microspheres by ultrasonic spray pyrolysis. *J. Ceram. Soc. Jpn.*, 2002, **110**, 146–148.
29. Minehira, K., Takao, Y., Shimizu, Y. and Egashira, M., Direct nitridation of aluminum by microwave-induced-plasma under atmospheric pressure. *Key Eng. Mater.*, 1999, **159–160**, 59–64.
30. Ogawa, K., Hyodo, T., Takao, Y., Shimizu, Y. and Egashira, M., Synthesis of tin utilizing microwave-induced-plasma generated from SiC ceramics. In *Proceedings of the Forty-ninth Annual Meeting of ISE*, 13–18 September 1998, p. 53.
31. Shimizu, Y., Akai, Y., Hyodo, T., Takao, Y. and Egashira, M., Decomposition of trichlorotrifluoroehtane by microwave-induced Ar plasma generated from SiC ceramics under atmospheric pressure. *J. Electrochem. Soc.*, 1999, **146**, 3052–3057.
32. Shimizu, Y., Ogawa, K., Akai, Y., Hyodo, T., Takao, Y. and Egashira, M., Decomposition of toxic halogenated hydrocarbons by microwave-induced Ar plasma generated from SiC ceramics under atmospheric pressure. *Electrochemistry*, 2001, **69**, 508–515.
33. Shimizu, Y., Inada, H., Hyodo, T. and Egashira, M., Decompsition of chlorinated aromatics by microwave-induced Ar plasma generated using SiC ceramic trigger under atmospheric pressure. *Electrochemistry*, 2003, **71**, 860–865.
34. Shimizu, Y., Nakamoto, Y., Hyodo, T. and Egashira, M., Decomposition of organic compounds by microwave-induced plasma in liquid phase. *Electrochemistry*, 2004, **72**, 92–97.
35. Lu, Z. P., Or, T. W., Stachowics, L., Kong, P. and Pfender, E., Synthesis of zirconium carbide in a triple torch plasma reactor using liquid organometallic zirconium precursors. In *MRS Symposium Proceeding, Vol 190*, ed. D. Apelian and J. Szekely, 1990, pp. 77–82.
36. Fincke, J. R. and Swank, W. D., Behavior of alumina particles in atmospheric pressure plasma jets. In *MRS Symposium Proceeding, Vol 190*, ed. D. Apelian and J. S. Szekely, 1990, pp. 207–212.
37. Kano, K. and Akatsuka, H., Spectroscopic measurement of electron temperature and density in argon plasmas based on collisional-radiative model. In *Advances in plasma physics research*, *Vol 3*, ed. F. Gerard. Nova Science Pub., Inc., 2002, pp. 55–85.
38. Zander, A. T., Spectral interferences and line selection in plasma emission spectrometry. In *Inductively coupled plasmas in analytical atomic spectrometry*, ed. A. Montaser and D. W. Golightly. VCH Pub., 1994, pp. 299–339.
39. Montaser, A., Ohls, K. D. and Golightly, D. W., Inductively coupled plasmas in gases other than argon. In *Inductively coupled plasmas in analytical atomic spectrometry*, ed. A. Montaser and D. W. Golightly. VCH Pub., 1994, pp. 877–948.
40. Griem, H. R., *Plasma spectroscopy*. McGraw-Hill Book Co., 1964.
41. Hrachova, V., Diamy, A.-M., Kylian, O., Kanka, A. and Legrand, J.-C., Behavior of glow and microwave discharges of oxygen. In *Advances in plasma physics research*, *Vol 3*, ed. F. Gerard. Nova Science Pub., Inc., 2002, 33–54.
42. Alkemade, C. T. and Herrmann, R., *Fundamentals of analytical flame spectroscopy*. Adam Hilger Ltd., 1979.
43. Misra, C., Industrial alumina chemicals, *ACS Monograph* Series, No. 184, Am. Chem. Soc. Pub., 1986.