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Dependence of size distribution of nanoparticles on hole size uniformity in membrane emulsification

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Abstract

Metal oxide nanoparticles were fabricated by membrane emulsification using alumina through-hole membranes with different hole size uniformity. Hole size of alumina through-hole membrane used for membrane emulsification and the size of obtained nanoparticles were evaluated by SEM observation, and the relationship between the uniformity of hole size and the size distribution of the obtained nanoparticles was investigated. As a result, nanoparticles with higher size uniformity were obtained when the RSD (relative standard deviation) of hole size was 3.8%. This indicates that the hole size uniformity of the emulsification membrane is important for the fabrication of droplets and nanoparticles of uniform size by membrane emulsification.

1. Introduction

Nanoparticles are typical functional materials with various potential applicabilities, including catalysts, batteries, and sensors, because of their unique properties, such as their large specific surface areas and high reactivity [1–8]. Since the properties of nanoparticles depend on their size and shape, it is important to prepare them with uniform sizes and shapes. The chemical reduction of metal ions in a liquid phase is one of the most common methods of preparing nanoparticles [9–11]. However, the control of the uniformity of sizes and shapes is difficult in this method. Even when nanoparticles with uniform sizes and shapes can be obtained by optimizing the preparation conditions, applicable materials are limited. In contrast, template synthesis is effective for preparing nanoparticles with controlled sizes and shapes in a wide variety of materials [12–14]. However, this method is not suitable for the mass production of nanoparticles because the template must be dissolved after the synthesis of the nanoparticles.

Membrane emulsification has been reported to be a high-throughput method for preparing various types of monodispersed emulsion droplet [15]. In this method, droplets are fabricated by extruding a dispersed phase through a porous membrane into a continuous phase. If a solution that can be solidified by a subsequent process is used for the dispersed phase, monodispersed solidified nanoparticles can be obtained by this process [16]. The size of the droplets obtained is determined by the hole size of the emulsification membrane. However, the dependence of the size distribution of the prepared nanoparticles on the uniformity of the hole size of the emulsification membrane has not been examined quantitively, especially on the scale of nanometers. We have reported the formation of monodispersed nanoparticles by membrane emulsification using an alumina through-hole membrane as an emulsification membrane [17–19]. Anodic porous alumina, which is a typical nanohole array material obtained by anodizing an Al substrate in an acidic electrolyte, is suitable as a membrane for membrane emulsification because it has self-organized nanohole array structures with uniform-sized holes [20]. The regularity of hole arrangement and the uniformity of the hole size of anodic porous alumina depend on the anodization conditions. Under optimized anodization conditions, anodic porous alumina with highly ordered hole arrangement and highly uniform-sized holes can be obtained. In addition, on the basis of Al pretexturing, which can control the position of hole generation during anodization, anodic porous alumina with ideally ordered hole arrangements having extremely uniform-sized holes can be fabricated [21]. Owing to these characteristic points, this material is suitable for the examination of the dependence of particle size uniformity

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on the hole size uniformity of the emulsification membrane. In the present work, we studied the dependence of the size distribution of the metal oxide nanoparticles formed by membrane emulsification on the hole size uniformity of the emulsification membrane by using alumina through-hole membrane.

2. Experimental

2.1. Materials

All chemicals were purchased from Nacalai Tesque, Inc., Japan, or Kanto Co., Inc., Japan. Al plates (99.99% purity) used for anodization were provided by UACJ Co., Japan. The aqueous sol solution containing primary nanoparticles of TiO$_2$/ZnO$_2$/SiO$_2$ used for membrane emulsification was provided by Catalysts and Chemicals Ind., Co., Ltd., Japan.

2.2. Preparation of anodic porous alumina membrane used as emulsification membrane

Figure 1(a) shows a schematic diagram of the preparation process of anodic porous alumina with an ordered hole arrangement used for membrane emulsification. Self-ordered anodic porous alumina was fabricated by the previously reported two-step anodization process [22]. Prior to the anodization, an Al plate was polished electrochemically under a constant current of 0.1 A cm$^{-2}$ in a mixed electrolyte of 20 vol% perchloric acid and 80 vol% ethanol at 0 °C for 4 min. The mirror-finished Al plate was anodized in 1 M oxalic acid under a constant voltage of 40 V at 22 °C for 10–720 min. In this study, 1 M oxalic acid was used as an electrolyte for the first anodization instead of 0.3 M oxalic acid used in previous studies because it provides a higher film growth rate and an ordered hole arrangement in a shorter time. The oxide layer formed by the first anodization was then selectively dissolved by etching in an etchant containing 6 wt% phosphoric acid and 1.8 wt% chromic acid at 70 °C for 120 min. This resulted in an Al sheet with a pattern of depression of the surface corresponding to the arrangement of holes on the back surface of the anodic porous alumina formed by the first anodization. The Al sheet with the depression pattern was anodized again in 0.3 M oxalic acid under a constant voltage of 40 V at 17 °C for 150 min to obtain self-ordered anodic porous alumina with uniform-sized holes. Aside from this, ideally ordered anodic porous alumina with extremely uniform-sized holes was fabricated by Al pretexturing using a Ni mold with a convex pattern of 100 nm period and subsequent anodization in 0.3 M oxalic acid at 40 V for 150 min. After the anodization, the residual Al was dissolved selectively in saturated iodine methanol at 50 °C for 30 min, and the alumina layer, which is the barrier layer, at the bottom part of the holes was removed by dry etching using Ar ion milling to obtain an alumina through-hole membrane from the anodized samples. The obtained alumina through-hole membrane was immersed in 5 wt% phosphoric acid at 30 °C for 30 min to adjust the hole size to 60 nm. Prior to membrane emulsification, the alumina membranes were hydrophobically treated with octadecyltrichlorosilane to prevent the wetting of the membrane surface by the dispersed phase during membrane emulsification.

2.3. Preparation of monodispersed nanoparticles by membrane emulsification using alumina through-hole membrane

Figure 1(b) shows a schematic of the procedure for preparing monodispersed nanoparticles by membrane emulsification using an alumina through-hole membrane. In this study, a commercially available aqueous sol solution containing 10 wt% primary nanoparticles of TiO$_2$/ZnO$_2$/SiO$_2$ (Catalysts and Chemicals Ind., Co., Ltd., Japan) was used as a dispersed phase, and kerosene containing the surfactants 2 wt% Span 80 and 1 wt% CR-310, was used as a continuous phase. N$_2$ gas was used to extrude the dispersed phase through the alumina holes into the oil phase to form emulsion droplets. Emulsion droplets were prepared by membrane emulsification at 400 kPa. The resulting emulsion solution was kept at 70 °C for 1 h to form agglomerated nanoparticles by drying droplets in the continuous phase. The agglomerated nanoparticles dispersed in the kerosene were trapped on a filter, and the kerosene on the surface of the nanoparticles was washed away using hexane. The samples obtained in this study were observed by scanning electron microscopy (SEM; JSM-7500F, JEOL). Image analysis software (Mac-View, Mountech Co., Japan) was adopted to evaluate the hole size of anodic porous alumina and the nanoparticle size obtained by membrane emulsification.

3. Results and discussion

3.1. Control of the hole size uniformity of alumina through-hole membrane

Figure 2 shows surface SEM images of alumina membranes fabricated by the two-step anodization process. In the first step (i.e., the first anodization), the samples were anodized for (a) 0, (b) 10, (c) 30, (d) 180, and (e) 720 min. Figure 2(a) shows the hole arrangement in the sample without the first anodization. On the other hand, in the samples anodized for more than 10 min in the first anodization shown in figures 2(b)–(e), the holes were
arranged regularly, and the regularity of the hole arrangement improved as the anodization time increased. In addition, as the anodization time in the first anodization increased, the uniformity of the hole diameter also improved. The values of RSD (relative standard deviation), which indicates the variation in hole size, were (a) 10.4, (b) 8.5, (c) 6.2, (d) 5.3, and (e) 4.2%, respectively. These values were obtained by measuring the diameter of 1000 holes from SEM images. It was observed that the RSD decreased with increasing first anodization time. The results of cross-sectional SEM observations of the samples confirmed that the thickness of the obtained alumina through-hole membrane was 15 μm in all samples. This means that the growth rate of the film is independent of the hole arrangement regularity.

Figure 3 shows the relationship between the first anodization time and the RSD of the hole size of alumina through-hole membrane obtained in the second anodization. The graph shows that the RSD of the hole size...
drops rapidly up to around 30 min after the start of anodization, indicating a rapid increase in hole size uniformity in the early stage of anodization. However, after anodization for 30 min, the change in the RSD of the hole size becomes slower. This indicates that once a certain degree of hole arrangement regularity is reached, the hole size uniformity is not markedly affected thereafter.

Figure 4 shows a surface SEM image of ideally ordered alumina through-hole membrane prepared with Al pretexturing. SEM image in figure 4 shows that extremely uniform-sized holes were formed with ideally ordered arrangement all over the sample. The RSD of the hole size was 3.8%, which was the lowest among the anodic porous alumina samples prepared in this study. This finding means that improving the regularity of hole arrangement improves hole size uniformity.
3.2. Dependence of size distribution of nanoparticles on hole size uniformity of alumina through-hole membrane

Figure 5 shows SEM images of metal oxide nanoparticles obtained by membrane emulsification using alumina through-hole membranes with varying the uniformity of hole size. An alumina through-hole membrane with RSDs of the hole size of (a) 10.4, (b) 5.3, and (c) 3.8% was used for membrane emulsification. The average diameters of the nanoparticles were (a) 113, (b) 89, and (c) 88 nm. The alumina through-hole membrane with RSD of the hole size of 10.4% had a wide hole size distribution and some large holes, resulting in a wide particle size distribution and a large average particle size. On the other hand, when other porous alumina membranes were used as the emulsification membrane, nanoparticles of about the same size were formed. The RSDs of the particle diameter were (a) 15.4, (b) 10.2, and (c) 9.2%. These results indicate that the size uniformity of the nanoparticles obtained by membrane emulsification improves with the pore size uniformity of the membrane used for emulsification. Our previous studies have shown that the size of nanoparticles obtained by membrane emulsification can be controlled by varying the hole diameter of anodic porous alumina used as an emulsification membrane [16–19]. In addition, a linear relationship between hole size and nanoparticle size has also been confirmed. The results of this study show that even small variations in hole size can affect the size of the nanoparticles obtained by membrane emulsification.

Table 1 shows the RSD of hole diameters, average diameters and RSD of obtained nanoparticles. Figure 6 shows the relationship between the RSD of the hole diameter of alumina through-hole membrane and the RSD of the nanoparticle diameter. Figure 6 shows that the more uniform the hole size of the alumina through-hole
Figure 5. SEM images of nanoparticles obtained by membrane emulsification using anodic porous alumina with different hole size uniformity. The RSDs of the hole size were (a) 10.4, (b) 5.3, and (c) 3.8%. The average diameters of the nanoparticles were (a) 113, (b) 89, and (c) 88 nm.

Table 1. The RSD of hole diameters, average diameters and relative standard deviation of obtained nanoparticles.

| Membrane Type                      | RSD of Hole Diameter (%) | Average Diameter (nm) | RSD of Nanoparticle Diameter (%) |
|------------------------------------|--------------------------|------------------------|----------------------------------|
| Anodic porous alumina membrane     | 10.4                     | 5.3                    | 3.8                              |
| Metal oxide nanoparticle           | 113                      | 89                     | 88                               |
|                                    | 15.4                     | 10.2                   | 9.2                              |
membrane, the more uniform the size of the resulting nanoparticles. A linear relationship was also observed between the two. The results obtained here are for nanoparticles prepared with the combination of dispersed and continuous phases used in this study, and it is expected that the RSD of the obtained nanoparticle diameter will change when the dispersed and continuous phases are changed. However, our previous studies have shown that the diameter of fine particles obtained by membrane emulsification can be controlled by adjusting the hole size of alumina through-hole membrane used for emulsification, regardless of the type of phase, dispersed and continuous. From these results, it can be concluded that the higher the hole size uniformity of the emulsification membrane, the more uniform the diameter of the resulting fine particles. The reason why the obtained nanoparticle size uniformity does not perfectly match the hole size uniformity of alumina through-hole membrane has not been clarified in detail, but it is considered to be due to a slight variation in the critical size for the droplet to detach from the membrane surface. We expect that further improvement of the size uniformity will be possible by introducing an uneven structure on the surface of the membrane to facilitate the detachment of droplets.

4. Conclusions

Metal oxide nanoparticles were prepared by membrane emulsification using alumina through-hole membranes with different hole size uniformity. The size distribution of the resulting nanoparticles was measured and found to correlate well with the hole size uniformity of the emulsification membrane. From this finding, it is concluded that the use of emulsification membranes with highly uniform-sized holes is essential for the preparation of uniform-sized nanoparticles by membrane emulsification. The membrane emulsification using anodic porous alumina with highly uniform-sized holes is suitable for the high-efficiency preparation of uniform-sized nanoparticles. The obtained monodispersed nanoparticles can be used for various functional devices, such as drug carriers, batteries, and sensors.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Wang C, Cheng L, Lin Y, Wang X, Ma X, Deng Z, Li Y and Liu Z 2013 Adv. Funct. Mater. 23 3077
[2] Sun T, Zhang Y S, Pang B, Hyun D C, Yang M and Xia Y 2014 Angew. Chem. Int. Ed. 53 12320
[3] Howes P D, Chandrawati R and Stevens M M 2014 Science 346 53
[4] Zanganeh S et al 2016 Nat. Technol. 26 986
[5] Wissing S A and Müller R H 2003 Int. J. Pharm. 254 65
[6] Zhan L, Yang T, Lei C M, Wu W B and Huang C Z 2018 Sens. Actu. B: Chem. 255 1291
[7] Wang K, Sun D, Pu H and Wei Q 2021 Talanta 223 121782
[8] Zhang W, Zheng T, Ai B, Gu P, Guan Y, Wang Y, Zhao Z and Zhang G 2022 Appl. Surf. Sci. 593 153388
[9] Pei A, Ruan L, Liao J, Fu H, Zeng L, Liu J, Li M, Chen B H and Zhu L 2021 Catal. Lett. 151 559
[10] Zhang T, Yu Z, Huang F, Tang C and Yang C 2021 AIP Adv. 11 085220
[11] Yu Z, Zhang T, Li K, Huang F and Tang C 2022 Nanomaterials 12 360
[12] Yoo S, Liu L and Park S 2009 J. Colloid Interface Sci. 339 183
[13] Jia Z, Liu J and Shen Y 2007 Electrochem. Commun. 9 2739
[14] Albuntas S, Celik M and Buyukkerin F 2021 MRS Commun. 11 675
[15] Nakajima T, Shimizu M and Kukizki M 1991 Key Eng. Sci. 61 513
[16] Yanagishita T, Fujimura R, Nishio K and Masuda H 2010 Langmuir 26 1516
[17] Yanagishita T, Maejima Y, Nishio K and Masuda H 2014 RSC Adv. 4 1538
[18] Yanagishita T, Inoue T, Kondo T and Masuda H 2018 Chem. Lett. 47 551
[19] Yanagishita T, Asami R and Masuda H 2021 Mater. Res. Express 8 025003
[20] Masuda H and Fukuda K 1995 Science 268 1466
[21] Masuda H, Yamada H, Satoh M, Asob M, Nakao M and Tamamura T 1997 Appl. Phys. Lett. 71 2770
[22] Masuda H and Satoh M 1996 Jpn. J. Appl. Phys. 35 126