Pseudoboehmite Nanorod–Polymethylsilsequioxane Monoliths Formed by Colloidal Gelation

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The addition of a trifunctional silicon alkoxide methyltrimethoxysilane (MTMS) to aluminum oxide hydroxide pseudoboehmite nanorod (PBNR) aqueous dispersions resulted in adhesion between the PBNR colloids to form macroporous monoliths. The use of greater amounts of MTMS led to coarsening of the skeleton and strengthening of the skeletal structure, and the monoliths got water resistance. When a dispersion of zirconium oxide nanoparticles and MTMS was used as a starting material, a macroporous monolith was also obtained by the same simple process. The colloidal gelation occurs because the silanol moiety is more likely to react with the colloid surface of ceramic materials than with other silanols derived from MTMS and their oligomer. Due to the development of material chemistry, colloidal dispersions having various shapes and compositions are becoming available as products. Based on this mechanism, it is expected to be feasible to fabricate various porous monoliths with characteristic morphologies and properties depending on the colloid.
Abstract

The addition of a trifunctional silicon alkoxide methyltrimethoxysilane (MTMS) to aluminum oxide hydroxide pseudoboehmite nanorod (PBNR) aqueous dispersions resulted in adhesion between the PBNR colloids to form macroporous monoliths. The use of greater amounts of MTMS led to coarsening of the skeleton and strengthening of the skeletal structure, and the monoliths got water resistance. When a dispersion of zirconium oxide nanoparticles and MTMS was used as a starting material, a macroporous monolith was also obtained by the same simple process. The colloidal gelation occurs because the silanol moiety is more likely to react with the colloid surface of ceramic materials than with other silanols derived from MTMS and their oligomer. Due to the development of material chemistry, colloidal dispersions having various shapes and compositions are becoming available as products. Based on this
mechanism, it is expected to be feasible to fabricate various porous monoliths with characteristic morphologies and properties depending on the colloid.

Keywords
colloidal gelation, nanorods, pseudoboehmite, polymethylsilsesquioxane, macroporous monoliths

Highlights
- Macroporous monoliths were produced by adding methyltrimethoxysilane to a pseudoboehmite nanorod dispersion.
- Gelation occurred due to the high reactivity between silanol and colloidal surface.
- Production of monoliths with various pore structures can be expected using the colloidal gelation.
1. Introduction

The ongoing development of materials chemistry has allowed various types of micro- and nanoparticle-based colloidal dispersions to be prepared. Colloidal dispersions of ceramics and metallic particles with various shapes and sizes, such as spherical particles, rods, fibers, and plates, are now commercially available. To maintain the dispersed state, additives such as surfactants and polymers are often used.[1] Particles can also be dispersed by charge repulsion under aqueous conditions without coating the dispersoid by appropriately adjusting the pH.[2] Such colloids are known to aggregate at pH changes approaching the isoelectric point and, in some cases, monolithic materials (gels) can be obtained by successful control over this process. Although this phenomenon that colloids form gels is well known and studied,[3-5] these monoliths have attracted limited attention for fabricating porous monoliths because they generally have poor mechanical strength and easily collapse under ambient drying conditions. The preparation method using the colloidal dispersion as a starting material has not clearly demonstrated advantages to other production methods.

In 2008, Schmidt et al. reported that macroporous monoliths could be fabricated by adhering dispersed ceramics or polymer particles using melamine–formaldehyde resin as the “glue”.[6] We have also succeeded in producing polymethylsilsesquioxane (PMSQ) gels with boehmite nanofiber[2] cores by coating and adhering the nanofibers with the trifunctional silicon alkoxide methyltrimethoxysilane (MTMS).[7] In these materials, although the proportion of the colloid (nanofibers) in the skeletal framework was not large, it seems that the formation mechanism was similar to that described in the report by Schmidt et al. The boehmite nanofiber–PMSQ gels had a characteristic fiber-like skeleton derived from the
nanofibers and exhibited relatively high strength. Furthermore, they displayed good thermal insulation properties under low vacuum.

It is known that the properties of porous monoliths can be controlled by their microstructure morphology.[8-10] For example, we have reported that thermal conductivity can be controlled by changing the pore structure of PMSQ macroporous monoliths.[11] When macroporous monolith is prepared by reacting monomers via a sol-gel process, the microstructure obtained by solid-liquid phase separation becomes somewhat similar regardless of composition, which can be predicted by calculation.[12] However, if a colloid having an anisotropic shape is used as a starting material, a complicated structure can be formed.[13] The ability to fabricate monoliths from various forms of colloidal dispersion would broaden the range and composition of available microstructures and permit the development of new materials with novel applications. In this study, the fabrication of macroporous monoliths using pseudoboehmite nanorods (PBNRs) as the colloids and PMSQ derived from the precursor MTMS as the glue was investigated.

2. Experimental
2.1. Materials
Methyltrimethoxysilane and acetic acid were purchased from Tokyo Chemical Industry Co., Ltd. (Japan) and Wako Pure Chemical Industries, Ltd. (Japan), respectively. Pseudoboehmite nanorod acetic acid dispersion A2 (particle diameter 10 nm, particle length 50 nm, pH ~ 3.5, 12.9% dry mass at 80 °C) was kindly provided by Kawaken Fine Chemicals Co., Ltd. (Japan). Zirconium (IV) oxide nanoparticle dispersion (ZrO₂ particle size <100 nm, pH ~ 4, 10 %) was obtained from Sigma-Aldrich Co. LLC (USA).
Results of particle analysis are shown in an electronic supplementary material. All reagents were used as received.

2.2 Preparation of monoliths

To prepare the PBNR–PMSQ monoliths, \( x \) mL of MTMS was first added to 10 mL of the PBNR dispersion A2, and the mixture was stirred for 5 min. After degassing, the mixture was poured into a sealed container and left to stand at 80 °C. The gelation time was approximately 1 h. After 6 h, the obtained gel was washed with ethanol, and the solvent was exchanged for hexane. To prepare the aerogel samples, supercritical CO\(_2\) drying was performed at 40 °C and 10 MPa. The schematic image is shown in Fig. 1.

To prepare the xerogel samples, evaporative drying was performed at RT over 2 d at a controlled evaporation rate. The obtained samples are hereinafter referred to as PP\(x\), where \( x \) denotes the volume (mL) of MTMS added to the PBNR dispersion. To prepare the ZrO\(_2\)–PMSQ aerogel monolith, the procedure described above was repeated using 2 mL of MTMS and 10 mL of the ZrO\(_2\) dispersion.

![Diagram of PBNR-PMSQ monolith preparation](image)

Fig. 1  The schematic image of obtaining a PBNR-PMSQ monolith.

2.3 Characterization

The bulk density was calculated based on the measured weight and volume. The error was within approximately 5%. The microstructure was examined using scanning
electron microscopy (SEM; S-5200, Hitachi High-Technologies Corp., Japan) and transmission electron microscopy (TEM; H-7650, Hitachi High-Technologies Corp., Japan). Uniaxial compression tests were performed using a universal/tensile tester (EZ-SX, Shimadzu Corp., Japan) and a 100 N pressure gauge. Samples were cut to dimensions of approximately $10 \times 10 \times 5$ mm$^3$, and the head speed was $1$ mm min$^{-1}$. The Young’s modulus was calculated for values of compressive stress in the range of 0.2–0.4 MPa. The visible light transmittance was measured using a spectrophotometer (HSU-100H, Asahi Spectra Co., Ltd., Japan) equipped with a halogen light source (HL-20, Asahi Spectra Co., Ltd., Japan) and an integrating sphere (HSU-O-DTR, Asahi Spectra Co., Ltd., Japan). The direct-hemispherical transmittance was recorded, and the obtained transmittance data at 550 nm were normalized to a thickness of 10 mm using the Lambert–Beer equation. Thermogravimetric–differential thermal analysis (TG-DTA) was conducted using a Thermo plus EVO 2 instrument (TG-DTA 8122, Rigaku Corp., Japan). The thermal conductivity was measured at 25 °C using a heat flow meter (HFM 436 Lambda, Netzsch GmbH, Germany) for PP5 xerogel samples with a thickness of approximately 10 mm. Although an attempt was made to perform contact angle measurements by dropping 5 μL droplets of water onto samples of PP5, a large error was observed owing to the surface conditions and reproducible results could not be obtained. The particle size distribution of the pseudoboehmite nanorod and the ZrO$_2$ particle was evaluated using dynamic light scattering (DLS; Zetasizer Nano-ZS, Malvern Instruments Ltd., UK).
3. Results and Discussion

3.1 Properties of PBNR–PMSQ macroporous monoliths

The addition of various amounts of MTMS to samples of the PBNR dispersion and holding at 80 °C for 6 h resulted in the formation of translucent wet monolithic gels. The gel opacity increased with increasing amount of MTMS, which was more apparent after supercritical CO₂ drying. Cracking of the samples sometimes occurred during the subsequent solvent exchange to hexane, although the degree of damage decreased with increasing amount of MTMS. The skeletal structure was found to become stronger upon increasing the amount of PMSQ, which served as a binder between the PBNRs. After supercritical CO₂ drying, the gels shrunk by several to ten-odd percents in length.

Table 1 and Fig. 2 show the physical properties and SEM images, respectively, of the aerogels obtained using various amounts of MTMS. The bulk density of the monoliths increased with increasing amount of MTMS, and the skeletal structure became coarser. The skeleton diameter in PP1 was less than 10 nm, whereas it had almost doubled to 15–20 nm in PP5. TEM observations revealed that the PBNRs underwent a structural change during the reaction (Fig. 3). However, from the SEM image, it is considered that the PBNR partly changed to needle-like crystals. (Since the contrast difference between the original PBNR and PMSQ is small, only needle-like crystals are clearly shown in the TEM images.) As the skeletal structure became coarser, the visible light transmittance of the monolith also decreased greatly. Samples PP1, PP2, and PP3 were translucent bulk bodies that were slightly transparent at thicknesses of several millimeters. In contrast, the coarse skeletal structures of PP4 and PP5 increased the Mie scattering of visible light, resulting in white monoliths that were virtually opaque to visible light (Table 1 and Fig. 4). Although boehmite is hydrophilic, PMSQ is
hydrophobic, and the water resistance of the obtained samples, therefore, increased with increasing amount of MTMS. For instance, whereas PP1 instantly absorbed water resulting in the collapse of the monolith, PP5 underwent no noticeable changes even after floating in water for 1 month.

Table 1  Physical properties of PBNR-PMSQ aerogels.

| Sample | Young's modulus [MPa] | Bulk density [g cm\(^{-3}\)] | Light transmittance \((\lambda = 550 \text{ nm})\) [%] | Light transmittance \((\lambda = 800 \text{ nm})\) [%] |
|--------|-----------------------|-------------------------------|---------------------------------|---------------------------------|
| PP1    | 1.99                  | 0.200                         | 15.7                            | 61.5                            |
| PP2    | 7.60                  | 0.223                         | 3.1                             | 38.2                            |
| PP3    | 9.06                  | 0.250                         | 1.5                             | 31.1                            |
| PP4    | 9.93                  | 0.269                         | 0.2                             | 11.6                            |
| PP5    | 9.07                  | 0.273                         | 0                               | 2.9                             |
Fig. 2  SEM images of PBNR-PMSQ aerogels (a) PP1, (b) PP2, (c) PP3, (d) PP4, and (e) PP5.

Fig. 3  TEM images of the PBNR-PMSQ aerogel PP5 and PBNR (inset).
Fig. 4  Light transmittance of PBNR-PMSQ aerogels. The obtained transmittance data were normalized to a thickness of 10 mm using the Lambert–Beer equation.

Uniaxial compression tests revealed that PP4 exhibited the highest Young’s modulus of the obtained aerogel samples. A higher proportion of PMSQ relative to the PBNRs resulted in thicker the neck between the PBNRs and a stronger microstructure. However, increasing the proportion of PMSQ, which is more flexible than pseudoboehmite crystal, beyond a certain amount caused the Young’s modulus to decrease again. Of the obtained samples, PP5 exhibited the highest yield strength since cracks were least likely to occur, and this sample returned to its original shape after applying 50 % uniaxial compression (Fig. 5a). Although shrinkage occurred upon drying, evaporative drying of PP5 permitted panels of ten centimeters square to be obtained. This xerogel also exhibited water resistance like the corresponding xerogel (Fig 5b). Since it is known that some porous monoliths based on PMSQ are good thermal insulators, the thermal conductivity of this composite material was also measured with the expectation of similar physical properties. However, the thermal conductivity of the PP5 xerogel was 53.9 mW m$^{-1}$ K$^{-1}$, which is equivalent to fiberglass.
wool and perlite and higher than our previous PMSQ macroporous materials.[14,15,11,7] In the samples prepared in this study, a high bulk density was required to obtain a certain strength, and the pore diameter was also large. It is considered that the thermal conductivity of the solid phase or gas phase increased. On the other hand, the heat resistance was similar to that of other PMSQ materials. Upon heating the PP5 aerogel, gradual water loss occurred followed by loss of the methyl group, and the PMSQ was converted to silica at temperatures exceeding 450 °C (Fig. 6).[16]

**Fig. 5** (a) Stress-strain curves of PBNR-PMSQ aerogel PP5 obtained by uniaxial compression. The sample returned to its original shape after the compression cycle. (b) PBNR-PMSQ xerogel PP5 exhibited water resistance.

**Fig.6** Thermogravimetric–differential thermal analysis (TG-DTA) curves of
PBNR-PMSQ aerogel PP5 in the air.

3.2 Formation mechanism of PBNR–PMSQ structure

When preparing PMSQ monoliths using MTMS as the precursor, cage-type and cyclic siloxane oligomers are easily formed in the presence of an acid catalyst, and the product precipitates as a resin.[17] To obtain a homogeneous monolithic gel, it is generally necessary to perform a two-step acid–base reaction while suppressing phase separation via the use of a surfactant or the appropriate solvent composition.[18-21] However, the PBNR–PMSQ system described in this report was obtained without increasing the pH to basic conditions during the reaction, and the entire sol uniformly converted to a gel during the one-step reaction under acidic conditions.

This gelation is because the silanol moieties of hydrolyzed MTMS react with the hydroxyl groups on the PBNR surface under acidic conditions to form Si–O–Al bonds, thereby increasing the acidity of the Si atom and making it more reactive toward the next silanol of another MTMS-derived unit.[22] As the reaction progressed faster on the surface of pseudoboehmite dispersed in an aqueous sol, PMSQ grew on the surface of pseudoboehmite without precipitating as a resin, thereby forming the microstructure. Comparison of the hydrophobicities of PP1 and PP5 indicated that the skeletal structure was hydrophilic at the initial stage of gelation, and subsequent aging increased the hydrophobicity owing to the inclusion of greater amounts of PMSQ. Macroporous monoliths can be obtained using the same process for several other types of pseudoboehmite particle dispersions (10A, Kawaken Fine Chemicals Co., Ltd., Japan; and AS-200 and AS-520-A, Nissan Chemical Corp., Ltd., Japan). Although attempting to use a higher concentration PBNR dispersion solution by evaporating the solvent of A2, it was difficult to prepare a homogeneous sol. It is known that the physical
properties of nanorod dispersions change with concentration,[3] and materials with different properties may be prepared as higher dispersion concentrations could be prepared. Various methods for preparing aluminum oxide hydroxide nanocrystals which can be dispersed in aqueous conditions have been reported.[23-25] It is expected that PMSQ-composite porous monoliths with various structures and properties can be prepared using the synthesis method reported in this paper.

By using metal oxide and hydroxide colloids with an element of lower electronegativity than silicon, it was expected to be possible to prepare various porous monoliths using PMSQ as a glue. Monoliths were indeed formed upon adding MTMS to a ZrO$_2$ nanoparticle dispersion (Fig. 7). However, considerable syneresis occurred during aging, and many cracks appeared. It appears that the morphology of colloidal particles exerts an influence on syneresis. The use of spherical particles seems to lead to a higher probability of cracks and shrinkage and a lower yield than the use of rod- and fiber-like colloids. Further understanding of these phenomena will require investigation of the detailed mechanism and conditions of monolith formation using colloids with a wider variety of shapes.

![Fig. 7](image)

Fig. 7 (a) Photograph and (b) SEM image of ZrO$_2$-PMSQ aerogel.
When tetramethoxysilane (i.e., a tetrafunctional silicon alkoxide) was used instead of MTMS, it underwent reaction with itself to form a network of silica. Consequently, the colloidal particles remained dispersed in the silica gel without assembling a network. In contrast, the use of vinyltrimethoxysilane successfully afforded a crack-free monolith. Therefore, it appears that the function of serving as a glue for pseudoboehmite colloids is a peculiar feature of trifunctional silicon alkoxides.

4. Conclusion
The addition of the trifunctional silicon alkoxide MTMS to PBNR dispersions resulted in adhesion between the colloidal particles to form macroporous monoliths. The use of greater amounts of MTMS led to coarsening of the skeleton and strengthening of the skeletal structure. Since the hydrophilic pseudoboehmite was coated with hydrophobic PMSQ, the water resistance of the obtained materials was greatly improved. Colloidal gelation occurs when MTMS is used as a precursor because the silanol moiety is more likely to react with the pseudoboehmite surface than with other silanols. Based on this mechanism, it is expected to be feasible to fabricate various porous monoliths with characteristic morphologies and properties using dispersion colloids.

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The author declares no competing financial interest.
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Electronic Supplementary Material for

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Fig. S1  Particle size distribution of the pseudoboehmite nanorod dispersion A2.

Fig. S2  TEM image of pseudoboehmite nanorods.
Fig. S3  Particle size distribution of the ZrO$_2$ nanoparticle dispersion.

Fig. S4  TEM image of ZrO$_2$ nanoparticles. Several particles of several tens of nanometers aggregate and are dispersed in the liquid.
