Ultralow-Bulk-Density Transparent Boehmite Nanofiber Cryogel Monoliths and Their Optical Properties for a Volumetric 3D Display

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ABSTRACT Ultralow-bulk-density transparent porous monoliths have unique optical properties such as low refractive index, and usually can be obtained via supercritical drying to prevent deformation and collapse of microstructure. We succeeded in fabricating a transparent cryogel with a bulk density of 3.5 mg cm^{-3} via vacuum freeze-drying of a monolithic wet gel

composed of boehmite nanofibers. In the case of adding a functional material into the starting sol, a composite material can be obtained. The composite cryogel with a fluorescent molecule was applied to a volumetric three-dimensional (3D) display.

TEXT

Since aerogels were first reported, researchers have investigated about their various unique properties.[1-2] Especially, silica aerogels are transparent, low bulk density structural materials with low thermal conductivity, and various potential applications have been studied. However, aerogels are fragile and difficult to handle. Their main applications have been in, for example, space exploration and experimental equipment involving accelerators,[3-5] which are too specialized to appear in everyday life. Because the manufacture of a high-porosity aerogel requires a supercritical drying process under high pressure, the specification of the pressure-resistant container constrains the volume and size of the processed samples.

Recent research has led to the development of a method for obtaining aerogel-like materials with high visible-light transmittance without the need for supercritical drying. Several aerogel-like xerogels with silica and silsesquioxane compositions can be obtained, in which the microstructure is almost maintained in the wet gel.[6-8] Deformation and breakage due to capillary shrinkage during drying are avoided by taking advantage of the flexible skeleton structure of the xerogel. However, the range of bulk densities of those xerogels obtained by the evaporation drying method is limited, and it is difficult to obtain materials with low bulk densities below 100 mg cm^{-3}. The optimum bulk density of aerogels used as a heat insulating material is about 150 mg cm^{-3},[9] whereas much lower bulk density is desirable when used as a transparent optical material.[10] It is therefore essentially impossible to obtain an optical material with ultralow bulk density using a drying process other than supercritical drying.

Recent studies on nanofibers have resulted in a number of one-dimensional (1D) aerogels and their composites.[11-16] By using nanofibers, bulk density can be suppressed lower than conventional aerogels having a continuous structure of fine particles, and several ultralow-bulk-density ones have been reported. We also succeeded in fabricating aerogels with bulk densities of 5 mg cm^{-3} or less with a visible light transmittance exceeding 90 % for a 10-mm-thick sample.[17] Those aerogels are composed of boehmite nanofibers (BNFs, AlOOH composition)[18] and have high visible light transmittance and a low refractive index (~1.001, estimated with reference to the previous research[19]). Due to those optical properties, an object placed on these aerogels appears as if it were floating. For transparent monoliths, applications as a nanoglue[20] by dispersing functional materials such as chromic materials and nanoparticles inside is proposed for a device in which a response is visually observed. However, replacement of the internal liquid of a wet gel with a supercritical fluid during drying displaces the material dispersed in the monoliths. Thus, it is difficult to obtain functional composite BNF aerogels.

In 2017, Hayase devised a method for preparing transparent boehmite nanofiber gel beads several millimeters in diameter via vacuum freeze-drying.[21] Though it is convenient for the purpose of obtaining dried object keeping the original outer shape,[22] it is usually difficult to obtain transparent porous monoliths by freeze-drying due to crystallization of the internal liquid and subsequent morphological changes.[23-24] To maintain the structure of the solid phase in the wet gel during freezing, a highly diluted BNF dispersion was directly dropping into liquid nitrogen and freezing it instantaneously. As a result, it has become possible to obtain small monoliths via vacuum freeze-drying by minimizing the disorder of the structure. Furthermore, by dispersing the functional material in the BNF dispersion before freezing, phosphorescence and photochromism functions can be imparted to the product. However, this method has problems

such as the impossibility of scale-up and limited application possibilities. Here, we report another method for the preparation of larger BNF transparent monoliths via vacuum freeze-drying. By fabricating a wet BNF gel with the strength to keep outer shape when placed in boiling liquid nitrogen, it became possible to obtain cylindrical or plate-shaped cryogels. In addition, we demonstrate the application of the obtained cryogel as an optical material.

The scheme of cryogel preparation is shown in Figure 1a. The wet BNF gels for obtaining cryogels were fabricated by optimizing the BNF aerogel preparation method previously reported.[17] First, hexamethylenetetramine (HMT) was added to a dilute acetic acid aqueous dispersion containing 0.45 % (dry mass) nanofibers, and the mixture was heated to prepare a BNF wet gel approximately 15 mm in diameter and 5 mm high (Figure 1b). The gel was immersed in methanol for 24 h to remove acetic acid and HMT and then the solvent was exchanged with tert-butyl alcohol (TBA). Small broken pieces and TBA attached to the surface of the obtained bulk gel were carefully wiped off with paper and the gel was immersed directly in liquid nitrogen. The wet gel was instantly frozen, but some samples collapsed due to supercooling. The frozen BNF gel was transferred to a vacuum chamber and BNF cryogel was obtained following removal of TBA by sublimation. During this process, we could observe that TBA gradually sublimed and the gel became transparent (Figure 1c, Movie S1)

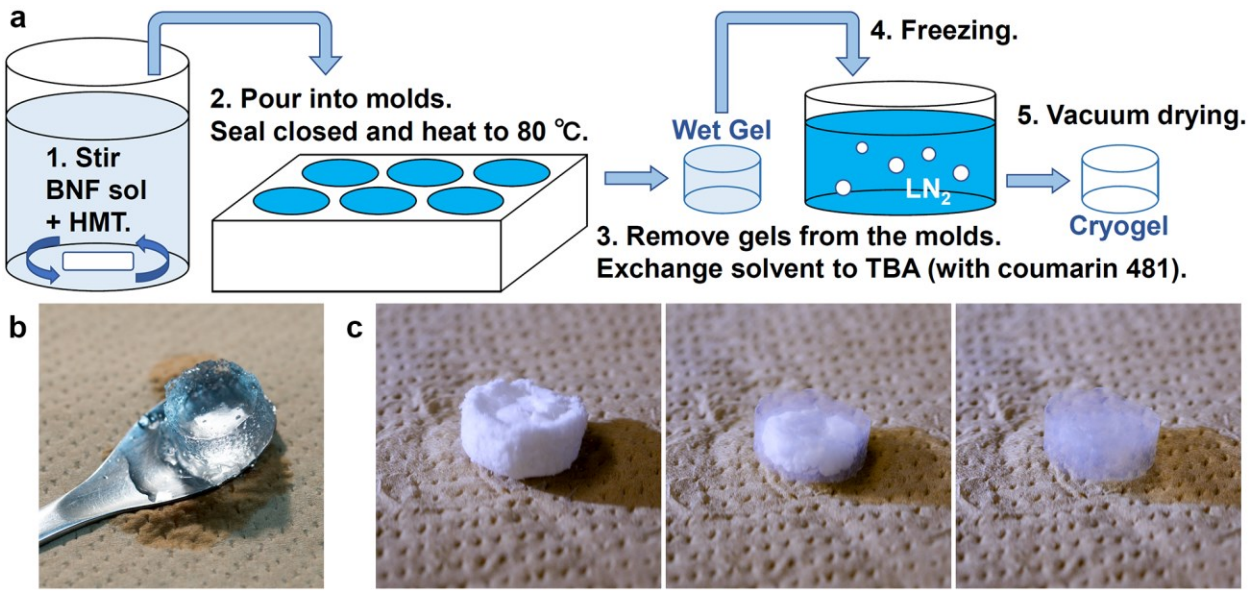

Figure 1. (a) Schematic image of cryogel preparation. (b) Photograph of the BNF wet gel before frozen by liquid nitrogen. (c) Photographs of the BNF frozen gel during vacuum drying (from left to right, see also Movie S1).

The bulk density of the obtained cryogel was about 3.5 mg cm^{-3} (Figure 2a), which is smaller than the 4.5 mg cm^{-3} for aerogel obtained by preparing a wet gel under similar conditions and using supercritical drying.[17] Supercritical drying results in shrinkage during an exchange of the internal liquid whereas freeze-drying causes little change in the bulk volume. The visible light transmittance of a 5-mm-thick sample of the cryogel was about 70 % but varied depending on the degree of roughness of the surface at the time of freezing. The appearance, together with a transmittance graph, of the BNF cryogel is shown in Figure 2b. The visible light transmittance of aerogels prepared by freeze-drying is inferior to that of aerogels prepared by supercritical drying; nonetheless, transparent BNF monoliths can be obtained using vacuum freeze-drying. We performed image processing (direct–global separation) to evaluate the obtained gel.[25-26] Histograms and images showing the total light transmittance and the intensity distribution of direct light at an angle within about 5° of the direction of radiation (Figure S1) are shown in

Figure 3 and Figure S2, respectively. These results confirmed that light scattering was stronger in the cryogel than in the aerogel. We expected that this was likely due to the crystallization of TBA producing micrometer-scale localized aggregated structures, resulting in Mie scattering. However, structural observation by a field emission scanning electron microscopy (FESEM) showed almost no significant aggregation compared to the case of the aerogel (Figure S3). The BNF cryogels look transparent unless observed under a strong light source.

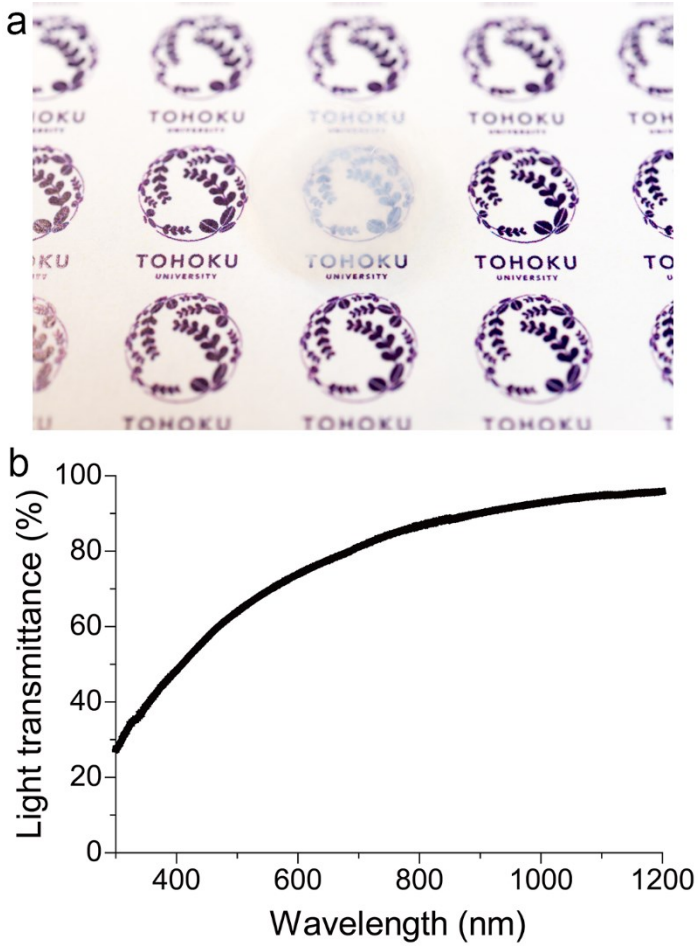

Figure 2. (a) Photograph of the 5-mm-thick BNF cryogel. (b) The light transmittance of the BNF cryogel (normalized into those of 5 mm-thick samples using the Lambert–Beer equation).

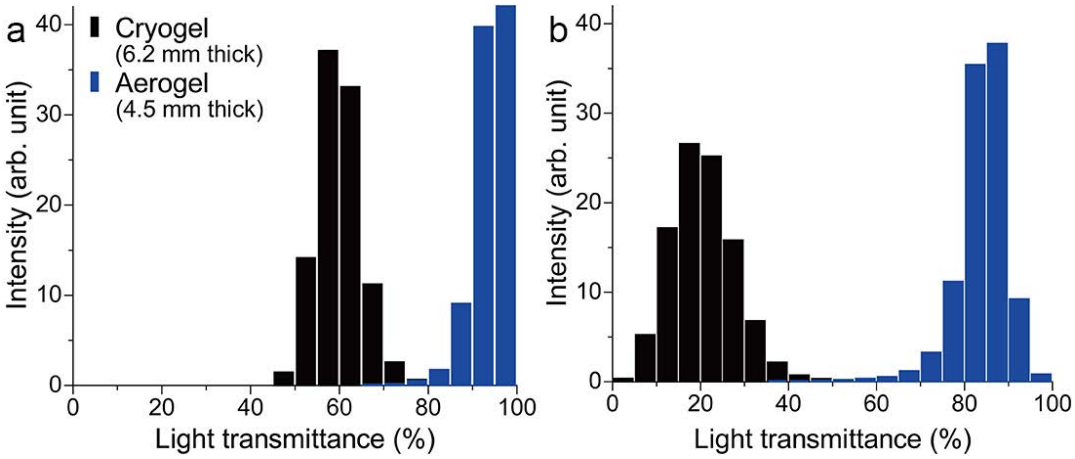

Figure 3. Histograms of (a) total light transmittance and (b) direct light obtained by image processing (direct–global separation). From the difference between the two types of histograms, it can be seen that stronger scattering occurs in the cryogel than in the aerogel.

As previously reported, BNF cryogels can contain various functional substances, such as fluorescent molecules, photochromic materials, and magnetic nanoparticles, and the locations of these functional substances can be fixed within the monolith. In this study, we added the fluorescent molecule 7-(diethylamino)-4-(trifluoromethyl)coumarin (coumarin 481) to the wet gel to prepare a monolithic transparent cryogel (Figure S4a,b) and investigated its application as a light emitter in a three-dimensional (3D) display. Until today, various methods for preparing 3D displays have been reported and all have both advantages and disadvantages.[27] For example, methods using holograms have been studied for many years but the visual field is still limited. Volumetric displays use 3D space; since voxels (volume-pixels) are directly drawn in space using light emission, scattering, and reflection, such displays are attracting attention as a technology capable of projecting 3D images without being influenced by the observation position.[28-33] The volumetric display reported by Saito et al. is the first method to propose aerial display by using nanosecond laser as a light source.[30] However, it requires high irradiation energy in order to generate a plasma to be a voxel, which is not safe if it touches the human body.

In recent years, Ochiai et al. reported a “touchable” aerial display using femtosecond laser.[32] Those displays have the advantage of not requiring a light emitter and can be described in the aerial space freely. On the other hand, the method using a light emitter also has advantages that it is possible to generate voxels with considerably lower irradiation energy than aerial plasma displays. Since the limited light source energy can be efficiently used for voxel generation, the number of drawable voxels possessed by the display can be improved dramatically. Also, unlike aerial displays with only white voxels, this method has a possibility that can be developed into a color expression of images by devising the fluorescent material and the screen configuration.

Using a transparent gel with a low refractive index as a light emitter, it is expected that a volumetric display seamlessly blended with the background environment can be produced. Since the refractive index of the porous monolith is determined by the ratio between the solid phase and the pore, the refractive index of the ultralow density material is close to the value of air. For BNF cryogels, the refractive index is estimated to be 1.001 in the air, which is considerably lower than that of acrylic 1.49 and transparent silica aerogel 1.02 (with density 0.15 g cm^{-3}, for thermal insulation).[19] Using a cylindrical BNF cryogel monolith with 15 mm diameter and 5 mm thick as a display and a femtosecond laser as a light source, we conducted experiments to move the focal point inside the monolith (Figure 4, Movie S2).[34-35] Although the light spot elongated in the optical axis direction according to the specification of the device (spreading of the depth of focus, Figure S5),[36-37] we observed that the point of bright light emission inside the cryogel moved. Despite problems, such as suppressing light scattering inside the gel and improving the optical system, we anticipate that ultralow-bulk-density transparent porous monoliths can be used as materials for 3D displays, because the refractive index and the surface reflection of the cryogels are suppressed lower than other solids such as acrylic resins (Figure S4c) and

hydrogels,[34, 38-39] and the 3D image is projected in the space with less discomfort. Furthermore, BNF cryogels hold possibility in applications such as environmental response sensors and scintillators by utilizing their optical properties.

Since a microstructure can be obtained with less change from the wet gel, aerogels are still superior to cryogels when considering the optical application. In addition, although there are no limitations on the thickness when preparing the transparent aerogels, transparent cryogels having a thickness of 5-7 mm or more cannot be prepared by our present technique. For thick samples, the cooling rate will be insufficient. Under such conditions, crystals of TBA will grow large and the microstructure will be destroyed during freezing, which causes light scattering. However, aerogels have the disadvantage of requiring a high-pressure process for production (supercritical drying), which limit the scale-up due to the necessity of a dedicated autoclave. Besides, the supercritical fluid used for drying washes off the fluorescent molecules inside the wet gels. Our cryogels are obtained via a cheaper and simpler process than the aerogels and can disperse functional materials inside. Despite the restrictions on the thickness of the cryogels, it is possible to scale up the area because the drying process does not require a high-pressure autoclave with limited diameter. Furthermore, since the interface between BNF cryogels is inconspicuous, it would also be possible to prepare a thicker light emitter with stacking. To raise the optical properties and to obtain thicker panels, we are now developing tools that freeze the wet gel by more efficient cooling. Nanofiber cryogels are expected to be improved closer to aerogels in the future.

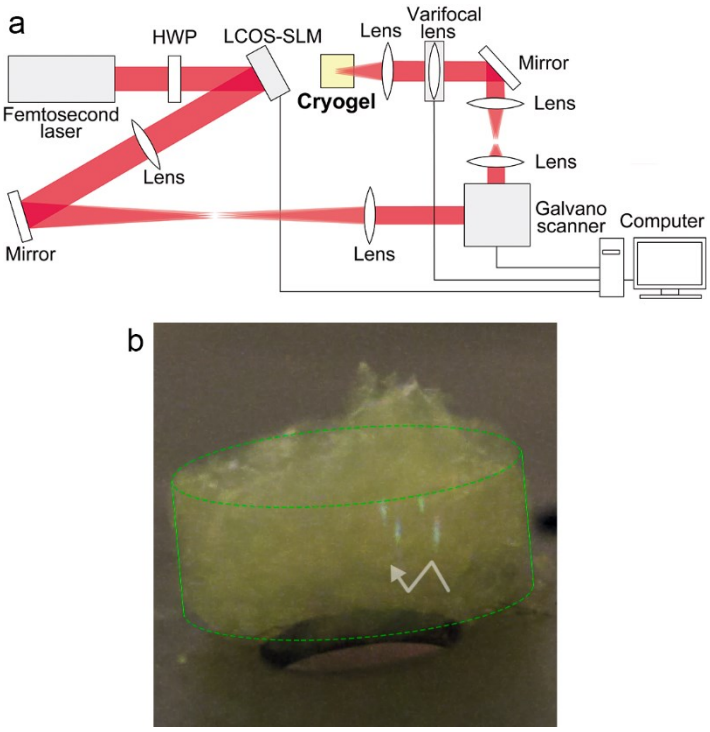

Figure 4. (a) Schematic image of the optical system used for the experiment of the volumetric 3D display. (b) Composite photograph showing how the light spot moves in a cylindrical composite BNF cryogel with coumarin 481 (since the upper part is disturbed, an extension line is added). See also Movie S2.

In summary, ultralow-bulk-density transparent porous monoliths composed of boehmite nanofibers and the transparent composite were obtained via vacuum freeze-drying instead of supercritical drying. The bulk density of the BNF cryogel was 3.5 mg cm^{-3}, and a 5-mm-thick sample had a transmittance of about 70 %. By adding a fluorescent substance to the starting composition, the applicability of the cryogel as a light emitter for 3D displays was demonstrated. In order to put the BNF cryogels into practical use as a light emitter for a larger display, we will continue to improve the freezing process and work on more detailed optical measurements such

as refractive index. Given our current finding of the simpler drying process, we expect that research on nanofiber porous monoliths will be accelerated.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Experimental details, schematic image of direct/global light, photograph and direct/global image of the gels, FESEM image of the cryogel, photograph of spherical aberration, spectrum of the LCD, and image showing the analyzed region of the gels (PDF)

A time-lapse movie of the BNF gel during vacuum drying. One second in this movie is equal to 1 h of the actual time. (MPG)

A movie of using cryogel as a light emitter of a volumetric three-dimensional display. The light spot is moving. (MPG)

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Notes

The authors declare no competing financial interest.

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