Preparation of SiO$_2$–PVA nanocomposite and monolithic transparent silica glass by sintering

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We present a procedure for fabricating transparent silica glass that involves the sintering of green bodies prepared from an inorganic–organic nanocomposite. The nanocomposite was prepared from fumed silica and poly(vinyl alcohol) (PVA). We investigated the SiO$_2$–PVA nanocomposite by Fourier transform infrared spectrometry (FT-IR) measurement, transmission electron microscopy and electron energy-loss spectroscopy, and the results revealed homogeneously dispersed SiO$_2$ nanoparticles and PVA. We examined the relationship between the pH and $\zeta$ potential of the SiO$_2$ suspension and the formability of the SiO$_2$–PVA nanocomposite. Formability of the SiO$_2$–PVA nanocomposite was dependent on the pH of the SiO$_2$ suspension, and a monolithic SiO$_2$–PVA nanocomposite without cracks was obtained using a SiO$_2$ suspension at around the isoelectric point (pI). By sintering the SiO$_2$–PVA nanocomposite in air at 1100°C, monolithic transparent silica glass was obtained with no cracks. The glass is highly transparent from the ultraviolet to the visible region.

Key-words: Nanocomposite, Silica, Glass, Sintered, Transparent

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1. Introduction

Silica glass attracts considerable interest because of its excellent properties of low thermal expansion, chemical durability and mechanical strength, and high transmittance in the vacuum–ultraviolet to near-infrared region. As a result, silica glass is used for laboratory glassware, IC photomask substrates, crucibles for melting high-purity silicon, optical fiber, etc. Bulk silica glass has been produced by various methods such as the melting method, VAD method,$^{1,3}$ and sol–gel method.$^{31}$

The powder-sintering method,$^{3,4,6}$ which enables easy shaping of the glass at low temperatures, is an attractive alternative because it consumes relatively little energy and allows good formability of the glass. We previously reported the fabrication of transparent silica glass via the powder-sintering method.$^{3}$ We first prepared a slurry in which micrometer-sized SiO$_2$ particles were dispersed in water. The slurry was then poured into a mold and dried to yield a green body. Finally, bulk silica glass was obtained by sintering the green body at 1400–1600°C under high vacuum (10$^{-3}$ Pa). As the goal in this case was to obtain transparent silica glass, the green body was sintered under high vacuum to avoid devitrification by crystallization.

In the present study, we focused on using nanometer-sized SiO$_2$ particles as a starting material and obtained transparent silica glass by sintering the particles in air. In previous research, highly transparent silica glass rods$^{33}$ and tubes$^{34}$ were made from a colloidal silica suspension consisting of several dozen nanometer-sized fumed silica particles, followed by gelation, drying, and sintering in He atmosphere. Monolithic porous silica green bodies without cracking were obtained by using a high-concentration suspension and fabricating large pores in the green bodies to avoid cracks due to capillary force during gel drying.$^{33}$ In other research, fumed silica and silicon alkoxide were used as starting materials and monolithic transparent silica glass without cracks was obtained.$^{3,34}$

For the present research, we prepared monolithic silica glass by using an inorganic–organic nanocomposite. To prepare a homogeneous green body without cracks, and to obtain monolithic transparent silica glass by sintering in air, an inorganic–organic nanocomposite was prepared using SiO$_2$ nanoparticles and poly(vinyl alcohol) (PVA). SiO$_2$–PVA nanocomposites have been extensively investigated to improve PVA properties such as mechanical strength, thermostability, gas permeability, etc.$^{9–12}$ However, there are no reports on silica glass prepared from a SiO$_2$–PVA nanocomposite; moreover, the process for preparing a monolithic nanocomposite as the glass precursor has not been revealed. In this study, we explored the means for preparing a SiO$_2$–PVA nanocomposite without cracks. Monolithic transparent silica glass was obtained by sintering the nanocomposite in air at 1100°C.

2. Experimental procedure

The SiO$_2$–PVA composite was prepared from SiO$_2$ nanoparticles and PVA. The SiO$_2$ suspension (8 wt%) was prepared by adding fumed silica (mean particle diameter 7 nm, Nippon Aerosil, Tokyo, Japan) to distilled water followed by dispersion through ultrasonication after which the pH was adjusted to 2–8 with 0.1 and 1.0 M HNO$_3$ or NaOH. PVA (8 wt%; average degree of polymerization 1500–1800, degree of hydrolysis 78–82 mol%, Wako Pure Chemical Industries, Tokyo, Japan) water solution was prepared by adding PVA to distilled water followed by mixing at room temperature. The PVA water solution and the suspension were mixed (weight ratio of SiO$_2$:PVA = 80:20) and stirred at room temperature for 12 h to obtain SiO$_2$–PVA slurry. The slurry was cast into a Petri dish and dried at 30°C in air. Gelation took place as the water evaporated from the slurry; hence, the gel gradually shrank. After drying the gel, a SiO$_2$–PVA composite was obtained. We investigated the morphology of the SiO$_2$–PVA composite by...
transmission electron microscopy (TEM; JEM-1300NEF, JEOL, Tokyo, Japan) and electron energy-loss spectroscopy (EELS). The thermal behavior of the SiO$_2$–PVA composite was examined by thermogravimetry and differential thermal analysis (TG–DTA; Thermo Plus TG8120, Rigaku, Tokyo, Japan) at a heating rate of 5°C/min.

Silica glass was obtained by heat-treating the SiO$_2$–PVA composite at 600°C for 3 h and then sintering at 1100°C for 3 h in air at a heating rate of 5°C/min starting from room temperature. The morphology of the heat-treated bodies was observed by field emission scanning electron microscopy (FE-SEM; JSM-6701F, JEOL, Tokyo, Japan). Surface area and pore size of the heat-treated bodies were calculated using the Brunauer–Emmett–Teller (BET) theory and Barrett–Joyner–Halenda (BJH) method, respectively, with nitrogen sorption. Fourier transform infrared (FT-IR) absorption spectra of the SiO$_2$–PVA composite and heat-treated bodies were measured by FT-IR spectrometer (FTIR-8400, Shimadzu, Kyoto, Japan). We measured the transmission spectrum from 200 to 800 nm of the silica glass (produced by sintering the SiO$_2$–PVA composite) with an ultraviolet visible spectrophotometer (UV–Vis; UV-2400PC, Shimadzu, Kyoto, Japan). Vickers hardness ($H_v$) of the glass was determined by using a Vickers hardness testing system (MKH-H1, Mitutoyo, Kanagawa, Japan) with a pyramid diamond indenter and applied load of 100 g. Glass density was measured by the Archimedes method using kerosene as the immersion liquid.

3. Results and discussion

3.1 Preparation of SiO$_2$–PVA nanocomposite

**Figure 1** shows the zeta ($\zeta$) potential of the SiO$_2$ suspension with 8 wt% as a function of pH. The SiO$_2$ suspension has an isoelectric point (pI) of $\sim$3.0, and the $\zeta$ potential of the SiO$_2$ suspension is positive at $<$~3.0 and negative at $>$~3.0. **Table 1** shows the pH and $\zeta$ potential of the SiO$_2$ suspension and describes the appearance of the SiO$_2$–PVA composite prepared from the SiO$_2$ suspension. Monolithic SiO$_2$–PVA composites without cracks were obtained from SiO$_2$ suspension at pH 2.1, 2.6, and 3.3. On the contrary, SiO$_2$–PVA composites obtained from SiO$_2$ suspension at pH 4.2, 5.4, and 7.4 had some cracks or were separated into small pieces. These results indicate that monolithic SiO$_2$–PVA composites were fabricated by using SiO$_2$ suspension at pH 2–4 (around pI). We were able to obtain monolithic SiO$_2$–PVA composites by using the SiO$_2$ suspension having a $\zeta$ potential absolute value of around zero.

As a result, we prepared a monolithic SiO$_2$–PVA composite (SiO$_2$–PVA = 80:20, weight ratio) from a SiO$_2$ suspension at pH 3.2. **Figure 2** shows the FT-IR absorption spectra of (a) PVA, (b) fumed silica, (c) SiO$_2$–PVA composite, (d) transparent silica glass obtained by sintering the SiO$_2$–PVA composite at 1100°C in air, and (e) commercially available silica glass. FT-IR absorption bands and their assignment$^{11(13),21}$ for the samples are listed in **Table 2**. In the FT-IR spectrum of the SiO$_2$–PVA composite, characteristic bands originating from PVA (1095, 1437, 1645, 1724, and 2943 cm$^{-1}$) and fumed silica (470, 804, 975, 1095, and 1645 cm$^{-1}$) are observed. This result indicates that the SiO$_2$–PVA composite consists of fumed silica (SiO$_2$ nanoparticles) and PVA. **Figure 3** shows a TEM image and EELS elemental mapping images of the SiO$_2$–PVA composite. The TEM image indicates that the morphology consists of several dozen nanometer-sized grains. The EELS elemental mapping images for Si, C, and O show no obvious agglomeration of SiO$_2$ nanoparticles or PVA. These results indicate that the morphology of the composite consists of SiO$_2$ nanoparticles and PVA homogeneously dispersed on a nanometer scale.

![Fig. 1](image1.png)

**Fig. 1.** Zeta ($\zeta$) potential of SiO$_2$ suspension with 8 wt% as a function of pH.

![Fig. 2](image2.png)

**Fig. 2.** FT-IR absorption spectra of (a) PVA, (b) fumed silica, (c) SiO$_2$–PVA composite, (d) transparent silica glass obtained by sintering the SiO$_2$–PVA composite at 1100°C in air, and (e) commercially available silica glass.

<table>
<thead>
<tr>
<th>pH</th>
<th>$\zeta$ potential (mV)</th>
<th>Appearance of SiO$_2$–PVA composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>0.5</td>
<td>monolithic, no cracks</td>
</tr>
<tr>
<td>2.6</td>
<td>0.7</td>
<td>monolithic, no cracks</td>
</tr>
<tr>
<td>3.3</td>
<td>-1.6</td>
<td>monolithic, no cracks</td>
</tr>
<tr>
<td>4.2</td>
<td>-15.6</td>
<td>monolithic, some cracks</td>
</tr>
<tr>
<td>5.4</td>
<td>-29.5</td>
<td>many cracks</td>
</tr>
<tr>
<td>7.4</td>
<td>-48.0</td>
<td>small pieces</td>
</tr>
</tbody>
</table>

Table 1. pH and zeta potential of SiO$_2$ suspension and appearance of SiO$_2$–PVA composite prepared from the suspension

![Table 1](image3.png)
Table 2. FT-IR absorption bands and their assignment for (a) PVA, (b) fumed silica, (c) SiO$_2$–PVA composite, (d) transparent silica glass obtained by sintering the SiO$_2$–PVA composite at 1100°C in air, and (e) commercially available silica glass

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3431</td>
<td>O–H stretching</td>
<td>3435</td>
<td>O–H stretching in H$_2$O</td>
<td>3433</td>
<td>O–H stretching</td>
<td>3432</td>
<td></td>
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<tr>
<td>2943</td>
<td>CH$_3$ asymmetric stretching</td>
<td></td>
<td>2949</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2910</td>
<td>CH$_2$ symmetric stretching</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1734</td>
<td>C=O stretching</td>
<td>1724</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1653</td>
<td>C=C stretching</td>
<td>1645</td>
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<td></td>
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<td>1437</td>
<td>O–H and C–H bending</td>
<td>1636</td>
<td>O–H stretching in H$_2$O</td>
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<td>Si–O–Si asymmetric stretching</td>
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<tr>
<td>1092</td>
<td>C–OC stretching</td>
<td>1095</td>
<td></td>
<td></td>
<td>Si–OH stretching</td>
<td>975</td>
<td></td>
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<tr>
<td>849</td>
<td>CH$_2$ rocking</td>
<td>806</td>
<td>*Si–O–Si symmetric stretching</td>
<td>804</td>
<td></td>
<td>799</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>475</td>
<td>Si–O–Si bending</td>
<td>470</td>
<td></td>
<td>470</td>
<td></td>
</tr>
</tbody>
</table>

*The absorption band of silica at ~800 cm$^{-1}$ is also assigned to vibrational modes of ring structures of SiO$_4$ tetrahedra.

Fig. 3. TEM image (bright field) and EELS mapping images (silicon, carbon, oxygen) of the SiO$_2$–PVA composite.

Silanol groups (Si–OH) are present on the surface of the SiO$_2$ nanoparticles (fumed silica).

The conditions for silanol groups on SiO$_2$ particles in aqueous solution are governed by the following surface equilibrium depending on the pH value:

$$\equiv\text{Si–OH} + H_2O \leftrightarrow \equiv\text{Si–OH}_2^{+} + OH^-$$

(1)

$$\equiv\text{Si–OH} \leftrightarrow \equiv\text{Si–O}^{-} + H^+$$

(2)

When the pH value of the SiO$_2$ suspension is higher than pI, Eq. (2) shifts to the right. On the other hand, when the pH value of the SiO$_2$ suspension is lower than pI, Eq. (1) shifts to the right. There are a number of attachment points by hydrogen bonding on the SiO$_2$ particle surface at around pI, because most silanol groups exist as unionized Si–OH at pI. PVA molecules contain hydroxyl groups (–CH$_2$–CH(OH)–)–hence, mixing a PVA aqueous solution with a SiO$_2$ suspension at around pI results in PVA molecules adsorbing onto the SiO$_2$ nanoparticle surface by hydrogen bonding between the hydroxyl groups and silanol groups. The SiO$_2$–PVA nanocomposite, which is a homogeneous combination of SiO$_2$ nanoparticles and PVA molecules, is obtained because of the hydrogen bonding. In addition, the nanocomposite prepared from the SiO$_2$ suspension at around pI consists of a strong network built through hydrogen bonding interactions between the silanol groups of SiO$_2$ nanoparticles and the hydroxyl groups of PVA. In previous research, for preparing SiO$_2$–PVA composite film with thickness of ~10 μm, homogeneous dispersed structures were also obtained from a SiO$_2$ suspension at around pI, because of PVA molecules adsorbing onto the SiO$_2$ nanoparticle by hydrogen bonding. In this study, PVA molecules were strongly connected to each SiO$_2$ nanoparticle through hydrogen bonding and the strong hydrogen-bond network may have allowed the nanocomposite to overcome the contraction stress and capillary force of the drying process and then the nanocomposite formed a monolithic structure without cracks.

It was found that a monolithic SiO$_2$–PVA nanocomposite without cracks could be prepared from a SiO$_2$ suspension at pH of about 2–4 (around pI) and PVA aqueous solution. It is important for preparing a monolithic SiO$_2$–PVA nanocomposite to use a SiO$_2$ suspension with a zeta potential absolute value of around zero (See Table 1).

3.2 Transparent silica glass by sintering of SiO$_2$–PVA nanocomposite

We used the monolithic SiO$_2$–PVA nanocomposite prepared from the SiO$_2$ suspension at pH 3.2 for the fabrication of silica glass by sintering. Figure 4 shows the TG and DTA curves of the SiO$_2$–PVA nanocomposite (weight ratio of SiO$_2$–PVA = 80:20). The weight loss below 100°C is due to the evaporation of water trapped in the nanocomposite. Combustion of PVA in the nanocomposite occurred between 200 and 550°C, which resulted in a broad exothermic peak in the DTA curves with a weight loss of ~20%. PVA in the nanocomposite combusted completely below 600°C and weight loss of the sample was not observed above 600°C. Figure 5 shows a photograph of the SiO$_2$–PVA nanocomposite and bodies obtained by heat-treating the nanocomposite at 600, 800, 900, 1000, and 1100°C for 1 h, respectively. Figure 6 shows cross-sectional FE-SEM images.
of the SiO₂–PVA nanocomposite and the heat-treated bodies. Table 3 shows the BET surface area, total pore volume and BJH desorption average pore size of the nanocomposite and heat-treated bodies. The results reveal that the SiO₂–PVA nanocomposite was a mesoporous structure with average pore size of 24.7 nm. Heat-treating the nanocomposite at 600°C, the BET surface area doubled and total pore volume increased due to the combustion of PVA in the SiO₂–PVA nanocomposite. Heat-treating the nanocomposite up to 900°C, we observed no sintering of the SiO₂ nanoparticles. However, sintering of the body heat-treated at 1000°C was clearly observed as the progression of sintering SiO₂ nanoparticles, thereby decreasing the BET surface area and total pore volume. A transparent and dense sintered body was obtained by heat-treating the SiO₂–PVA nanocomposite in air at 1100°C, and the glass state was confirmed by X-ray diffraction measurements. FT-IR absorption spectrum of the nanocomposite [Fig. 2(c)] shows a shoulder at ~975 cm⁻¹, which is attributed to the Si–OH stretching vibration of isolated silanol groups on the fumed silica surface.¹³ In the FT-IR spectrum of the transparent silica glass [Fig. 2(d)], this shoulder becomes weak and the spectrum is analogous to that of commercially available silica glass [Fig. 2(e)]. The results indicate that silanol groups of the fumed silica are reduced by sintering and the structure of the transparent silica glass sintered at 1100°C is similar to that of commercially available silica glass.

After heat-treating the SiO₂–PVA nanocomposite in air at 600°C for 3 h to combust the PVA, transparent silica glass was obtained by sintering it in air at 1100°C for 3 h. Figure 7 shows the transmission spectrum of the silica glass. The optical transmittance exceeds 90% in the visible region and exceeds 85% in the ultraviolet region. Impurities in the transparent silica glass were checked by energy dispersive X-ray fluorescence analysis (XRF), and no other element was observed besides silicon and oxygen. Density of the transparent silica glass is 2.2 g/cm³, and Vickers hardness (Hᵥ) is 777. These values for the glass fabricated by sintering are the same as those of commercially available silica glass.²⁹ We conclude that transparent silica glass can be prepared by sintering a SiO₂–PVA nanocomposite in air at 1100°C.

Table 3. BET surface area, total pore volume and BJH desorption average pore size of the SiO₂–PVA composite and sintered bodies heat-treated at 600, 1000, and 1100°C for 1 h in air, respectively.

<table>
<thead>
<tr>
<th>Heat-treated temperature (°C)</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanocomposite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>147.9</td>
<td>0.93</td>
<td>24.7</td>
</tr>
<tr>
<td>800</td>
<td>278.4</td>
<td>1.41</td>
<td>22.7</td>
</tr>
<tr>
<td>1000</td>
<td>20.8</td>
<td>0.11</td>
<td>13.9</td>
</tr>
<tr>
<td>1100</td>
<td>Dense body</td>
<td>Dense body</td>
<td>Dense body</td>
</tr>
</tbody>
</table>

Fig. 4. TG and DTA curves of the SiO₂–PVA composite in air at a heating rate of 5°C/min.

Fig. 5. (Color online) Photograph of the SiO₂–PVA nanocomposite and bodies obtained by heat-treating the nanocomposite at 600, 800, 900, 1000, and 1100°C for 1 h in air, respectively.

Fig. 6. Cross-sectional FE-SEM images of the SiO₂–PVA nanocomposite and bodies obtained by heat-treating the nanocomposite at 600, 800, 900, 1000, and 1100°C for 1 h in air, respectively.
4. Conclusions

We developed a glass preparation process that uses an inorganic–organic nanocomposite. To obtain monolithic transparent silica glass by sintering SiO$_2$ nanoparticles, we used an inorganic–organic nanocomposite consisting of homogeneously dispersed SiO$_2$ nanoparticles and PVA prepared from a SiO$_2$ suspension and PVA aqueous solution. Formability of the SiO$_2$–PVA nanocomposite was dependent on the pH of the SiO$_2$ suspension, and a monolithic SiO$_2$–PVA nanocomposite without cracks was obtained using a SiO$_2$ suspension at pH of 2–4 (around pI). Monolithic transparent silica glass was obtained by sintering the SiO$_2$–PVA nanocomposite in air at 1100°C. The silica glass is highly transparent from the ultraviolet to the visible range. Density and $H_v$ are equivalent to commercial-grade silica glass prepared by melting method. Thus, the process described herein provides an attractive, low-temperature alternative for fabricating silica glass.

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