Tin-Doped Resorcinol-Formaldehyde Aerogel with Decanano-Cell Structure

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Tin-doped resorcinol-formaldehyde (RF) aerogel was synthesized through immersion of tin (IV) alkoxide in RF gel and drying with supercritical carbon dioxide. The obtained density was 150-280 mg/cm^3, depending on the synthesis conditions. Despite the tin doping, the density is similar to that of undoped aerogel, implying that the shrinkage was suppressed. The cells were ~50 nm in size, much finer than undoped RF. Such characteristics were discussed as they relate to chelate formation between tin (IV) and RF ligands.

Keywords: RF aerogel, doping, shrinkage, tin alkoxide, cell size

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Aerogel is a low-density gel-like material in which water is replaced with air by supercritically drying the gel using liquid CO_2. Its characteristic is an existence of continuous porosity and a unique class of low-density foams with ultrafine adjustable cell size [1]. In particular, high-quality resorcinol-formaldehyde (RF) aerogel has a low density and a small cell size compared to laser spot size and sometimes with laser wavelength. Therefore, it is useful for laser targets to produce laser plasmas [2–4]. A density of 10 mg/cm^3 is required for the second stage of FIREX (Fast Ignition Realization Experiments) [4]. However, in the case of 100 μm thin membrane, the density of RF aerogel was higher than 160 mg/cm [3, 5–8] due to shrinkage from RF gel. The density increased because of shrinkage during the solvent exchange and supercritical CO_2 extraction processes. Doping of tin into aerogel has been required to produce tin plasma, for example, in extreme ultraviolet generation [9, 10]. In this study, we carried out tin doping using tin alkoxide. The obtained tin-doped aerogel shows that both tin doping and suppression of shrinkage of the RF aerogel occurs.

The RF solution was prepared by the methods described earlier [6, 8]. The obtained 78 mL of RF solution was mixed with 20 mL of a 1.8 g/L aqueous benzoic acid solution, and the resulting solution was put into a mold with 100 μm thickness. This mold was sealed by a clip, and occurred upon reheating the solution to 70°C for 2 hours. After the gels were cured, the water in the RF hydrogel was exchanged with 2-propanol (IPA) several times over 2 days. The gel was placed into an excess amount of IPA solution of 10-50 wt% tin (IV) tert-butoxide (TB) and then washed by IPA. The tin-doped RF gel was placed in a pressure vessel. The solvent of the gel was exchanged by liquid carbon dioxide via liquid CO_2 flow for a day. Then the pressure vessel was heated above the critical point of carbon dioxide (T_c = 31°C, P_c = 7.6 MPa). After slow venting of the pressure vessel, RF aerogels were obtained. These aerogels were characterized by scanning electron microscopy (SEM), element analyses, and density measurements.

The resulting aerogels are abbreviated as 10 wt%TB, 25 wt%TB, and 50 wt%TB based on the synthesis conditions. The compositions are as follows:

10 wt%TB:
$[[(C_6H_4O_2)_{0.73}/(CH_2)_{0.12}/(CH_2OH)_{0.17}]_{0.548}/(SnO_2)_{0.107}$
$(\text{-OH})_{2.02}][[(108.11)_{0.61}/(14.04)_{0.22}/(31.02)_{0.17}]_{0.548}/$
$(159.71)_{0.107}/(17.01)_{2.02}]$:calcd. C 18.08, H 2.61, Sn 25.34; Found. C 18.08, H 2.61, Sn 25.34
25 wt%TB:
$[[(C_6H_4O_2)_{0.73}/(CH_2)_{0.12}/(CH_2OH)_{0.17}]_{0.616}/(SnO_2)_{0.097}$
$(\text{-OH})_{1.979}][[(108.11)_{0.61}/(14.04)_{0.22}/(31.02)_{0.17}]_{0.616}/$
$(159.71)_{0.097}/(17.01)_{1.979}]$:calcd. C 20.00, H 2.67, Sn 22.95; Found. C 20.00, H 2.67, Sn 22.95
50 wt%TB:
$[[(C_6H_4O_2)_{0.73}/(CH_2)_{0.12}/(CH_2OH)_{0.17}]_{0.834}/(SnO_2)_{0061}$
$(\text{-OH})_{1.992}][[(108.11)_{0.61}/(14.04)_{0.22}/(31.02)_{0.17}]_{0.834}/$
$(159.71)_{0.061}/(17.01)_{1.992}]$:calcd. C 27.01, H 3.16, Sn 14.59; Found. C 27.01, H 3.16, Sn 14.59

After doping with tin, the volume of the RF gel decreasedto 70% of the original value. The next step, supercritical fluid extraction, induced shrinkage to 70% of the decreased volume. Although the density of the RF aerogel was prepared with 70 mg/cm^3, the density of the obtained RF aerogel was estimated to be 158 mg/cm^3, and the RF aerogel doped with tin had a higher density than that of the

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Table 1 Characteristics of tin-doped and undoped RF aerogel.

synthesis condition of TB	amount of tin (wt%)	density (mg/cm^3)	cell size (nm)
10 wt%	25.34	290	51
25 wt%	22.95	170	52
50 wt%	14.59	150	67
None	0	160	290

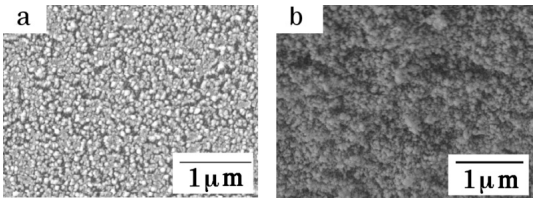

Fig. 1 SEM images of (a) the exterior surface and (b) a cross section of bulk of RF aerogel doped using 10 wt%TB.

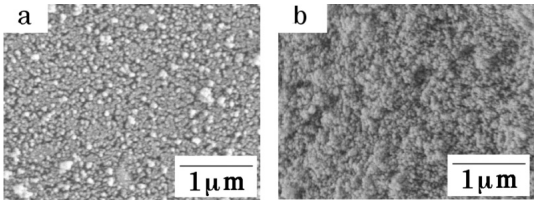

Fig. 2 SEM images of (a) exterior surface and (b) a cross section of bulk of RF aerogel doped using 25 wt%TB.

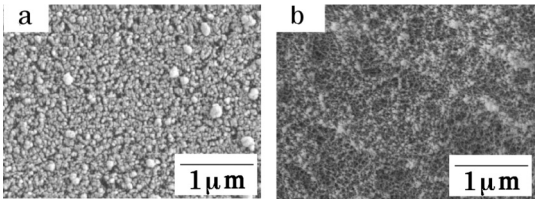

Fig. 3 SEM images of (a) exterior surface and (b) a cross section of bulk of RF aerogel doped using 50 wt%TB.

gel concentration of 70 mg/cm^3, as shown in Table 1.

The amount of tin in the aerogels decreased with TB in IPA. This inverse tendency is attributed to chelate formation between tin (IV) and RF, as described below.

Figures 1-3 show SEM images of the exterior surface (a) and a cross section of bulk (b) after supercritical CO_2 extraction. On the exterior surface, ~100 nm particles, which may be of SnO_2, are observed, whereas no such particles are seen in the cross-sectional views for any of the cases. An SEM image of undoped RF aerogel is seen in Refs. 6 and 7. The average cell size, C, was estimated by counting the number of cross-points (N_{cross}) on a 10 μm line (eq. (1)) [6].

$$C = 10\,\mu m/N_{cross}. \quad (1)$$

The C and density values are summarized in Table 1. The densities of aerogel decrease with increasing TB concentration, and, thus, the cell size increases slightly. Although the density of the 50 wt%TB-RF aerogel are nearly the same, the cell size of the undoped RF aerogel (290 nm) is 4.5 times that of the RF aerogel containing 50 wt% tin (67 nm).

The decrease in density is consistent with the decrease in the amount of tin, and both have an inverse tendency with the concentration of TB in IPA. This discrepancy can be explained by a chelating formation between tin (IV) and RF. When TB attaches to a ligand group of the side chain of RF polymer, such as OH or COOH, hydrolysis happens from Sn–O–Bu to form a Sn–O–RF coordination bond. In the case of low TB in IPA, other Sn–O–Bu bonds also hydrolyzed with vacant ligands of RF, and stabilized not to release from RF, which is chelate formation effect. On the other hand, in the case of high TB, the population of vacant ligands is not sufficient to form chelates, inducing easy removal of tin during the next step of washing by IPA. The chelate induces not only a large amount of tin introduction, but also refines the cell structure to a 50 nm cell size. The structure size would be due to a three-dimensional crosslinking network formation process [11]. A recent report on polystyrene-based gel revealed a relation between the number of crosslinkers and cell sizes, where more crosslinkers induced smaller cell size, and the relation was explained by a motion of the free side chain to increase the cell size [12].

To summarize, tin (IV) plays the role of a crosslinker through chelate formation. The shrinkage from the gel was smaller than that of the undoped aerogel, and the cell size was likewise smaller (~50 nm). The density and tin amount showed an inverse tendency to the concentration of TB in IPA, which was also explained by the chelating effect of tin.

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