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Synthesis of Machinable Optical Monolith of Forsterite-PMMA Organic-Inorganic Nanocomposite through a New Synthetic Strategy

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Many experimenters were attracted by the sol-gel method, because it could be a good synthetic tool for preparing their sample in an exotic morphology such as thin film,[1] preformed monolith,[2] uniformly sized particles,[3] or highly porous monolith.[4] Therefore, in some sense, the method should be considered to have very high processability. But, considering the usefulness of the final products in a practical application, a weak point of the method should also be dealt. The problem is that the mechanical properties of the sample prepared by the method are very poor. During the drying process, shrinkage occurs in an unacceptably large extent.[5] If hastily dried, the sample develops cracks.[6] The monolith experiences warping which render the method useless in preparing a sample in exact dimension.[7] From the reason, the maximum dimension acceptable is ~1 mm thick for a

monolith, and ~1 μm for a thin film. Most of all, the sol-gel product has very poor mechanical strength, and is not machinable at all. Without an additional heat treatment, the product disintegrates in polar solvents, and readily breaks by small stress.

These problems had been tackled by various ways. Drying Control Chemical Agents (DCCA) were used to get a crack-free monolith.[8] Solvent was removed in its critical state to get a shrinkage- and crack-free monolith.[9] But, still the mechanical properties of the products were poor. Recently, in an effort to circumvent these problems, a new kind of approach came up as a promising synthetic tool. Rather than to prepare simply the inorganic sol-gel product, the method was modified to produce nano-structured organic-inorganic composite materials. This new kind of organic-inorganic composite was refered as a CERAMER (CERAmic+polyMER)[10] or ORMOCER (ORganically MOd-

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ified CERamic).[11] In the case the inorganic moiety was silica, it was being called ORMOSIL (ORganically MOdified SILica). Unlike in the conventional sol-gel process, the thickness of the film could build up to several μm. The mechanical strength was largely improved that some were actually commercialized as a protective or antireflective films on lenses or as contact lenses.[12]

Usual synthetic strategy to the composite was to secure chemical bonding between inorganic and organic moieties, by modifying the sol-gel reactants by exchanging one or two alkoxy ligands with other organic ligands whose unsaturated bonds could be polymerized via organic polymerization.[13] The composite could also be prepared by physical blending without such chemical bonding between those two moieties. Some prepared such composite by introducing organic monomers into the pores of the dried gel (silica xerogel) and in-situ polymerizing the monomers.[14] Still, most of the problems described for the sol-gel method should be dealt while the xerogel monolith was prepared. Novak and coworkers synthesized the composite by infiltrating organic monomers into the network structure of aerogel.[15] It was observed that organic polymers with no H-bonding functional group, such as PMMA, leached out from the network during hypercritical treatment, and the composite could not be made with PMMA.

We report newly devised synthetic strategy to prepare a monolith of organic-inorganic composite made from forsterite (Mg_2SiO_4) and poly(methyl methacrylate) (PMMA) via modified sol-gel route. Previously, none was reported on the preparation of the composite between forsterite and PMMA. Main goal of the study was to get monolithic lenses with acceptable mechanical and optical properties, and into it intentionally to put a dopant with an optical activity. By introducing inorganic moieties into organic polymer, we tried to alter the environment around the dopant.

Synthetic scheme was schematically shown in the Figure 1. The polymerization was carried out first in the inorganic component by usual sol-gel reaction (hydrolysis and condensation). Then, the polymerization in the organic component was carried out by radical polymerization of methyl methacrylate (MMA). The forsterite (Mg_2SiO_4) gel network, the inorganic moiety of the composite was synthesized by the H_2O_2-assisted sol-gel method.[16] This forsterite gel was an alcogel whose pores in the inorganic network of the gel were filled with a mixture of methanol, ethanol, and water. The key step in this synthetic strategy was to exchange alcohol solvent in the pores of the alcogel with MMA, thereby preparing an "organogel" which included MMA in its pores, instead of alcohol. The solvent exchange was carried out by centrifugally washing the forsterite alcogel several times with undiluted MMA, thereby gradually raising the MMA content relative to the alcohol. After being aged for 1-2 weeks, the inorganic moiety of the alcogel was separated from solvent by centrifuge. The supernanatant was discarded. The inorganic moiety was redispersed in MMA, and the same collection was repeated several times. Inorganic loss through the supernatant was negligible. Therefore, solvent composition could easily be selected by adjusting the number of centrifugation and relative amount of MMA addition. Final composition of the solvent in the "organogel" of this study was calculated to be >99% MMA with a trace
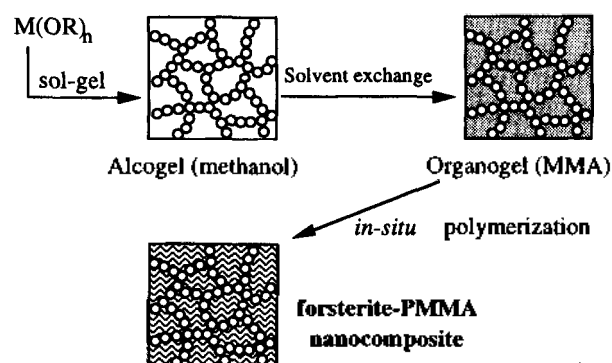

Figure 1. A pictorial scheme which shows the synthesis of forsterite-PMMA composite by exchanging alcohol in the forsterite alcogel with MMA, then by radically polymerizing the MMA.

of alcohol. Then the MMA infiltrated into the inorganic gel network was in-situ polymerized by radical polymerization by incubating the "organogel" in 45 °C oven. By this manner, all that problematic drying steps were skipped. A solid block of the forsterite-PMMA composite prepared was further cut into a desired shape and polished if necessary.

In order to see the pore characteristics of the inorganic gel network, the alcohol solvent was removed in its critical state in order to minimize a variation in the inorganic network structure. By hypercritical drying method,[17] the solvent was extracted at 265 °C and 1000 psi, and an aerogel of forsterite was prepared. The aerogel had very big surface area, exhibiting the BET surface area of 800 m^2/g. Figure 2 shows the accumulated pore distribution of the forsterite aerogel, obtained from nitrogen adsorption-desorption isotherm which exhibited the type IV of mesoporous solids, with a hysteresis near to the type H2 which indicated the shape of the pores was near to the ink-bottle.[18] The dimension of the pore was in a mesopore range of 100-500 Å with fairly broad size distribution. Contrary to the highly porous aerogel, the BET surface area of the composite was 5.8 m^2/g. The isotherm obtained from the forsterite-PMMA composite was type II which was typically observed for a nonporous solid.[18] The weight fraction of the inorganic moieties assessed by elemental analysis, thermal analysis, and ICP/MS was in a range 4-8%. The theoretical fill calculated from the porosimetry results came out to be about 11 weight %. Considering the structural variation of the network during the hypercritical drying was not significant,[19] we assumed that liquid MMA filled these pores which were occupied previously by alcohol. This observation indicated the pores were completely filled with PMMA which was in-situ polymerized from MMA infiltrated into the pores.

The forsterite-PMMA composite had hybrid mechanical properties. Measurement carried out by a microindenter showed the hardness of the composite was 3.1 Kg/mm^2. Comparing the hardness of the sole PMMA was 2.7 Kg/mm^2, and that of the xerogel monolith was 32.6 Kg/mm^2, the hardness of the composite was near to the property of the organic component. Whereas a block ($20\times4\times1$ mm^3) of sole PMMA was unbreakable (Modulus of Rupture up to 200 MPa) during three-point bending test, the composite broke at MOR of around 140 MPa, which indicated the strength of the composite was much weaker than the or-
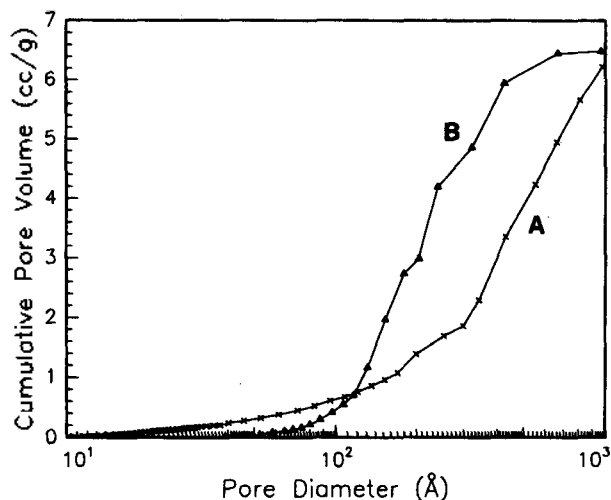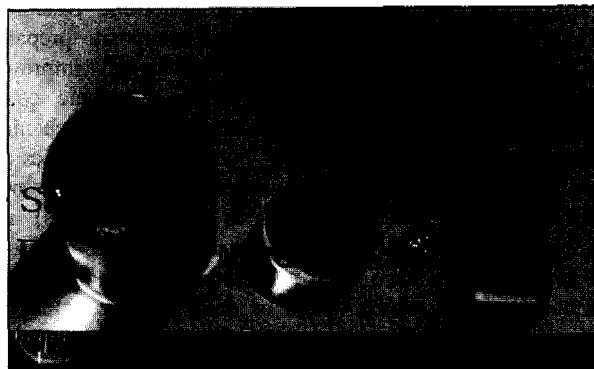
Figure 2. Accumulated pore volume obtained from nitrogen adsorption-desorption isotherms. The pore size distribution measured by adsorption (A) is very different from that measured by desorption (B).

Figure 3. A picture shows, a preform of the forsterite-PMMA composite prepared by using a cylindrical mould (A), a lens fabricated by cutting and polishing the moulded preform (B), a xerogel monolith prepared by carefully drying the forsterite alcogel of same volume as that used in getting the lens (C), and a block of the composite fabricated by cutting and polishing the moulded preform (D).

ganic counterpart. Though, comparing to the weakness of the xerogel monolith of forsterite, the improvement of the mechanical strength by PMMA incorporation was immense. The bending test could not even be performed on a block of the forsterite xerogel because it was too weak. Even if the extent was small, the thermal stability of the composite was also observed to be better than sole PMMA. The melting temperature of the composite observed by thermal analysis was about 30 °C higher than that of the sole PMMA.

Unlike the xerogel monolith prepared by the sol-gel method, the forsterite-PMMA composite was machinable. The picture in the Figure 3 showed a transparent lens cut out of a cylindrical mould of the forsterite-PMMA composite, which was compared to a xerogel monolith made by carefully drying forsterite alcogel. Large extent of shrinkage (of around 75%) experienced by xerogel was manifested by relatively small size of the monolith (same volume of gel was used for making both composite lens or the monolithic xerogel). Because the content of the composite was high in organic, the mechanical properties resembled those of PMMA. The composite could be cut into a block or any shape of lenses, and its surface could be polished in usual way. Its surface could be preformed into a concave or convex shape by using a mould. By adopting extra monomers on top of the mould, the extent of the shrinkage of the composite during polymerization was almost negligible (cf. the extent of the shrinkage occurred was less than 1%).

The UV-vis spectrum taken from a lens (3 mm thick) of composite was compared to the one obtained from the sole PMMA in the Figure 4. Compared to the air, the transparency in the visible range was about 88%. The transparency which was compared to the sole PMMA was near 98%. Apparently, the shoulder in the ultraviolet region indicated the transparency in the region was actually improved. Considering the high transparency up to the ultraviolet region, it could be conceived that domain of the inorganic moieties should be very small, and considered to be in a nano-range.[13] Most of all, the transparency was not
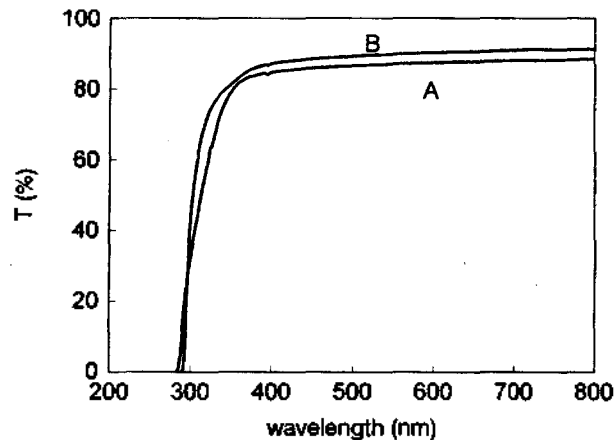
Figure 4. Transparency of the forsterite-PMMA composite measured by taking a UV-vis spectrum. The spectrum obtained from a lens of the composite (A) was compared to the one obtained from a lens of the sole PMMA (B).

lost by cycles of heating and cooling up to 200 °C. The loss of the transparency by being heated around 200 °C was observed in many ORMOCER samples with high inorganic content, and speculated to be caused by Si-OH sites still remained in the sample.[20] By getting FTIR spectrum from xerogel powder of forsterite which was thoroughly washed with MMA (under inert atmosphere) and dried under vacuum, the possible ligand exchange on the surface of the inorganic network was eliminated. The lack of the chemical bonding between inorganic moiety and PMMA was previously reported.[21] Therefore, without any chemical bondage between the inorganic and organic moieties, phase separation was expected to occur. Therefore, the good optical transparency of the composite suggested that the domain of the inorganic moieties was in a size of nanometer range, which conformed to the formation of nanocomposite. If the size of the domain were larger than 100 nm, the lens should become opaque by phase separation upon being heated.[22]

In summary, a new synthetic strategy of preparing an organic-inorganic composite from "organogel" was successful-

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ly applied on the preparation of a monolithic forsterite-PMMA nanocomposite. The monolithic composite prepared had very good optical transparency, and largely improved mechanical characteristics relative to the inorganic counterpart, and most of all it was machinable. The mechanical property of the composite had hybrid characteristics of those inorganic and organic moieties. Doping of the optically active materials (either ions or macromolecules) into this new forsterite-PMMA nanocomposite is in progress, and some dopants have been successfully incorporated into this host material, which would be dealt in forthcoming report.

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22. A composite synthesized with colloidal gel (turbid gel) showed scattering in blue region, which was caused by larger size of the inorganic moiety: unpublished result by authors.

# Design and Synthesis of Furoxan Derivatives as Probe for the Nitric Oxide Generation

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Nitric oxide (NO),[1] known to be the smallest biomolecule up-to-date, is involved in various physiological activities such as vasodilation[2] and tumoricidal and bactericidal activities.[3] More interestingly, it mediates a signal transduction in the brain.[4] Due to these diverse biological actions, the NO precursors have been a main subject of interest in the treatment of NO-related diseases. Furoxan (Furazan *N*-Oxide) **I** has been known to release NO by interacting with a thiol compound such as cysteine and glutathione *in vivo*.[5] We also reported the NO generation from various furoxan derivatives by the electron impacted fragmentation.[6] The biochemical mechanism for NO generation from the furoxan, however, is not explored exactly in the molecular level.

To probe such a biochemical mechanism and to develop a potential NO-precursor for biomedical study, we designed thiol containing furoxan derivatives **IIa** and **IIb** expecting the NO generation by the intramolecular sulfide-nitronate interaction.[7] Here, we wish to report a synthetic method of the furoxans **IIa** and **IIb** containing protected thiol.

IIa n=1, IIb n=2
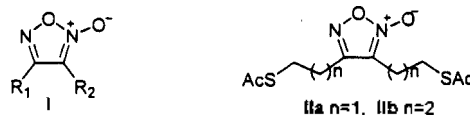
The furoxans **IIa** and **IIb** were prepared through dimerization of the corresponding nitrile oxide as a key step.