Synthesis of Self-standing Mesoporous Organosilica Films

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The mesostructured self-standing films with homogeneously distributed phenylene in the framework were synthesized using evaporation-induced coassembly of surfactant and 1,4-bis(triethoxysilyl)benzene. The addition of methyltriethoxysilane and dimethyldiethoxysilane to control the siloxane cross-linking network improved the flexibility and strength of films substantially. Thus obtained films also maintain their morphology with mesostructure even after calcination at 300 °C.

Hybrid organic–inorganic mesoporous organosilicas homogeneously integrated organic molecules within the pore walls were first reported in 1999.[1–5] These materials were synthesized from bridged organosilane precursors $(R'O)_3Si–R–Si(OR')_3$ and the choice of the bridged organic groups "R" is important to control the chemical and physical properties of the resulting hybrid materials. Extensive researches have been conducted by extending this approach using a variety of bridging organosilanes for potential applications in the field of catalysis, templates for nano-cluster synthesis, and selective adsorbents. Recently, the synthesis of periodic mesoporous organosilicas having phenylene and biphenylylene bridged groups with crystal-like pore wall structures was reported.[6,7] These materials have hexagonal arrangement of one-dimensional (1D) channels and unique pore walls structure exhibiting structural periodicity in the pore walls along the channel direction with spacings of 0.76 and 1.19 nm, respectively. These periodic mesoporous materials having aromatic groups in the pore walls can be easily functionalized by various chemical modifications for practical uses. For instance, sulfonic acid fuctionalized mesoporous materials could serve as a potential solid acid catalyst because of its easy recovery and reusability.[6] Furthermore, materials with high loading of sulfonic acid groups also used in fuel cells as an electrolyte.

Film is an attractive morphology and directly applicable to a variety of applications such as sensor, coating, and electrolytes. Especially, the film without a substrate (self-standing film) should expand the application window of these materials to new fields.[8,9] Ogawa et al. first reported the concept of the self-standing films with detailed synthesis of highly ordered mesoporous silica film.[10] They controlled these conditions of the evaporation-induced self-assembly (EISA) process to improve the strength of films. However, the calcined films were too brittle to be suitable for practical applications.

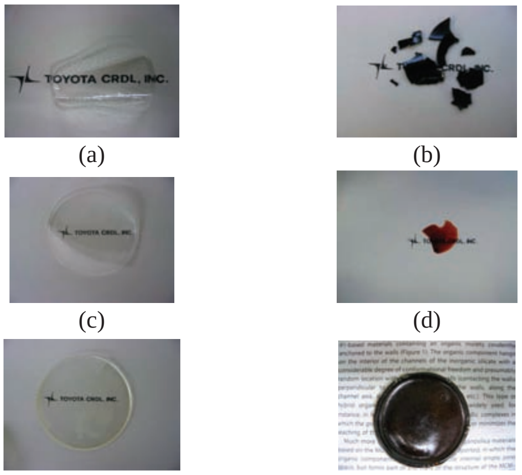
In this study, we report the syntheses of mesopstructured self-standing films with homogeneously distributed phenylene groups in the framework using evaporation-induced coassembly of surfactant and 1,4-bis(triethoxysilyl)benzene (**BTEB**). Furthermore, the improvement in flexibility and strength of films were obtained by adding methyltriethoxysilane (**MTES**) or dimethyldiethoxysilane (**DMDES**) as an additive for control of siloxane cross-linking unit.

The typical synthesis of self-standing hybrid films is as follows. Octadecyltrimethylammonium chloride (C_{18}TMACl, 1 mmol), water (1.52 mmol), 2 M HCl aqueous solution (1 mmol), and ethanol (22 mmol) were mixed together in a bottle and stirred for 2 h at room temperature. Pre-mixed precursors of **BTEB**, **MTES**, and **DMDES** were added to the above solution and further stirred for 2 h. The amount of each precursors added is listed in Table 1. After the reaction, the solution was cast on a flat Teflon vessel and the vessel was cured at 80 °C for 1 d. The solidified film was peeled off from the Teflon vessel to obtain the self-standing film containing surfactant (as-made film). The removal of surfactant from as-made film was carried out by calcination in air at 300 °C for 2 h.

Table 1. The mixture composite of precursors

Entry no.	**BTEB** /mmol	**MTES** /mmol	**DMDES** /mmol
1	2.5	—	—
2	0.83	3.3	—
3	0.83	—	3.3

As-made films of all samples were transparent and continuous as shown Figures 1a, 1c, and 1e. Thicknesses of the films are a few hundred micronmeter. For example, the film thickness of Entry 3 before calcinations was 300 µm. The self-standing film composed of only phenylene-bridged framework moieties (Entry 1) was rigid and brittle. But the films containing methyl-capping units (Entries 2 and 3) were flexible and the strength of films was also improved. Entry 3 containing dimethylsilane unit was the most flexible. The elastic modulus of the Entry 3 measured by dynamic viscoelasticity instrument was 2.2×10^7 Pa, which was almost the same elasticity to usual rubbers. Morphologies of the films after calcination at 300 °C are shown in Figures 1b, 1d, and 1f. The film containing dimethylsilane unit



(a) (b) (c) (d) (e) (f)

Figure 1. The photographs of self-standing films: (a) Entry 1, (b) Entry 1 calcined at 300 °C, (c) Entry 2, (d) Entry 2 calcined at 300 °C, (e) Entry 3, (f) Entry 3 calcined at 300 °C.

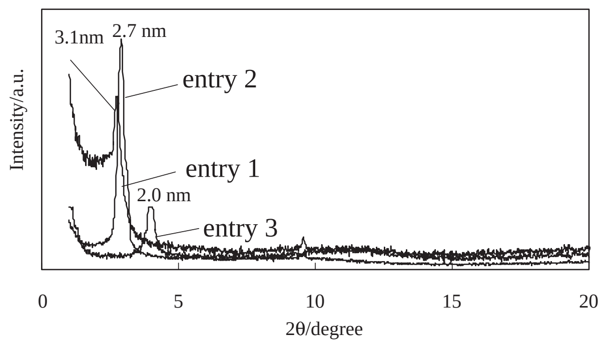


Figure 2. XRD patterns of self-standing films after calcination at 300 °C.

(Entry 3) retained its morphology and flexibility even after calcination at 300 °C (Figure 1f). The brown color of the film after calcination suggests the existence of a small amount of carbon residue. Figure 2 shows the XRD patterns of calcined films. The ordered mesostructures were preserved for all the samples even after removal of surfactants. It suggests that the films have no lamellar structure but 3D-ordered mesostructure. The exact mesophase of the films are difficult to be determined due to the lack of XRD peaks.

Figure 3 exhibits the nitrogen adsorption isotherms of the calcined films. The nitrogen adsorption isotherm of Entry 1 is characteristics of mesopores materials (type IV). The Brunauer–Emmett–Teller (BET) surface area and pore size were found to be 885 m^2/g and 2.0 nm, respectively.[11] Whereas, type I isotherm characteristic of microporous materials was observed for Entries 2 and 3. The BET surface areas of these films were 1228 and 1079 m^2/g, respectively. The pore size of these microporous materials could not be calculated owing to their narrow size but it is estimated to be under 2 nm based on XRD results.

The effective removal of surfactant from as-made films was also confirmed by IR spectroscopy. The absorption bands at 2850 and 2920 cm^{-1} corresponding to the symmetric and asymmetric vibrations of $–CH_2$ chain were observed for as-made samples; however, no such band were noticed after calcinations at 300 °C. The ^{29}Si MAS NMR spectrum of the calcined film (Entry 3) shows D signals $[\mathit{Si}C_2(OH)_n(OSi)_{2-n}]$ ($n = 0$, 1) and T signals $[\mathit{Si}C(OH)_m(OSi)_{3-m}]$($m = 0$, 1, 2) indicating that all of Si species are covalently bonded to carbon atoms. Furthermore, the very small signals due to SiO_4 species such as Q^3 $[\mathit{Si}(OH)(OSi)_3]$ and $Q^4[\mathit{Si}(OSi)_4]$ which give signals between −90 and −120 ppm also confims that the most of chemical bond between phenylene and silicon atom remains intact during the synthesis process.

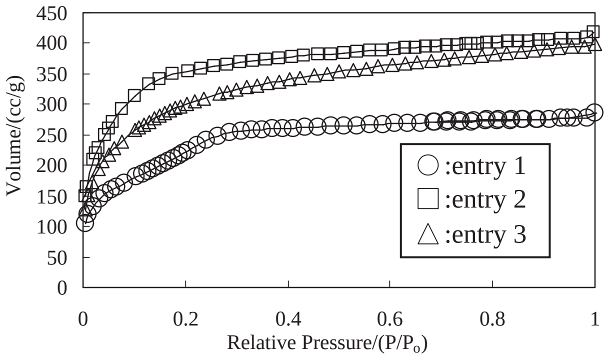


Figure 3. Nitrogen adsorption isotherms of self-standing hybrid mesostructured films.

The film with methylsilane unit (Entry 2) became rigid and crushed into pieces after calcination at 300 °C. However, its morphology (self-standing film) was stable up to 200 °C. On the other hand, Entry 1 composed of only phenylene framework could not retain its morphology even up to 100 °C. It is well known that increasing the condensation of siloxane network makes the film more rigid. Thus, heating at high temperature accelerates the hydrolysis and condensation of remaining silanol groups in the framework and increases siloxane network as well as rigidity. Therefore, it is likely that the introduction of **MTES** or **DMDES** would limit the siloxane cross-linking chemically, and thereby affords the desired flexibility. Thus, the observed experimental results show that **DMDES** (linear-capping unit) was a suitable reagent for increasing the flexibility as well as keeping its morphology and mesostructure even after calcination at 300 °C.

The thin film formation has pronounced the effect over the ratio of **BTEB** and methyl-capping reagents (**MTES** and **DMDES**) and the optimized ratios are given in the Table 1. The use of increased amount of both methyl-capping reagent and **BTEB** leads to mesostructure loss and rigidity, respectively. This implies that the level of cross-linking plays a crucial role and use of an appropriate amount of a suitable methyl-capping reagent would produce a stable self-standing mesoporous film with desired flexibility.

In summary, we have successfully prepared mesostructured self-standing films with homogeneously distributed phenylene groups in the framework using evaporation-induced coassembly of surfactant, **BTEB** and methyl capping reagent (**MTES** or **DMDES**). Improvement in both flexibility and strength of films was achieved by adding methyl-capping reagent as an additive to control the fundamental cross-linking unit of mesoporous framework. The mesoporous self-standing film obtained from **BTEB** and **DMDES** showed the required flexibility up to at 300 °C and possessed high surface area.

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11 The pore sizes of calcined films were calculated by BJH method.

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