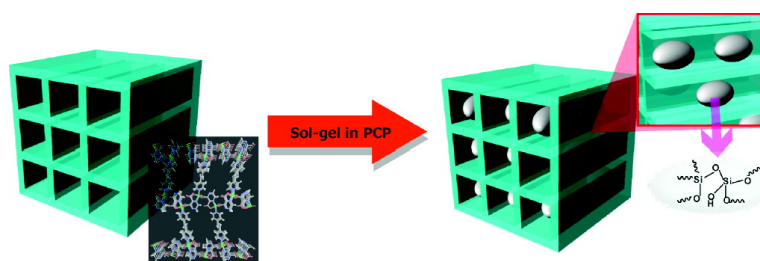


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Sol–Gel Synthesis of Low-Dimensional Silica within Coordination Nanochannels

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Porous coordination polymers (PCPs) prepared by self-assembling processes from metal ions and organic ligands have been extensively developed because of their wide applications in gas storage, molecular recognition and separation, and catalysis, utilizing their advantageous pore characteristics.¹ One promising idea in this area is the preparation of inorganic nanomaterials in the pores of PCPs. The use of nanoporous matrices as host media for the formation of nanosize metals or metal oxides is of considerable interest for specific nanosize properties and host–guest synergistic functions.² Recently, a few pioneering studies on the formation of metal nanoparticles utilizing PCP channels have been reported.³ For example, PCPs composed of redox-active Ni²⁺ in the frameworks produced nanoparticles from corresponding metal ions without an extra reduction process.^{3a,b} Small metal particles with significant catalytic activity were also prepared when a PCP host containing organometallic precursors was treated with H₂ gas.^{3c,d} Thus, fabrication of host–guest composites based on nanoparticles and PCPs may lead to potential applications ranging from fundamental physical studies to trace molecular detection and high-surface-area catalysis.

Silica nanoparticles and nanostructures provide unprecedented material platforms to accomplish many nanoscale functions.⁴ Many of the advances in silica nanochemistry are based on its transparency, stability, dielectric properties, hydrophilicity, and opportunities for introducing multiple functionalities.⁴ However, detailed properties of silica materials of ~1 nm are not clear because of the difficulty of precision control of the silica growth in this region (where size of SiO₄ tetrahedron = 0.26 nm).⁵

In this communication, we report on the fabrication of silica in one-dimensional subnanochannels of coordination pillared layer structures [Cu₂(pzdc)₂(L)]_n (pzdc = pyrazine-2,3-dicarboxylate, **1a**; L = 1,2-di(4-pyridyl)ethylene, **1b**; L = pyrazine)⁶ using a sol–gel reaction of tetramethoxysilane (TMOS, molecular size ca. 6.0 Å) in mild ambient conditions. First, this reaction was performed in the channels of **1a** (pore size = 10.3 × 6.0 Å²) as follows. The monomer TMOS was fully adsorbed in the channel by immersion of **1a** in TMOS, followed by removal of excess TMOS external to the host crystals under reduced pressure. The adduct (**1a**⊃TMOS) was then left under an H₂O atmosphere for hydrolysis of TMOS inside the pore and was heated at 60 °C to induce polymerization. Further condensation was achieved by heating the material under vacuum at 110 °C to provide a composite **1a**⊃silica. We measured X-ray powder diffractions (XRPD) of **1a**, **1a**⊃TMOS, and **1a**⊃silica and found that the host framework of **1a** was completely maintained during the reaction (Figure 1a). Certain changes of the relative peak intensities observed in the profiles are

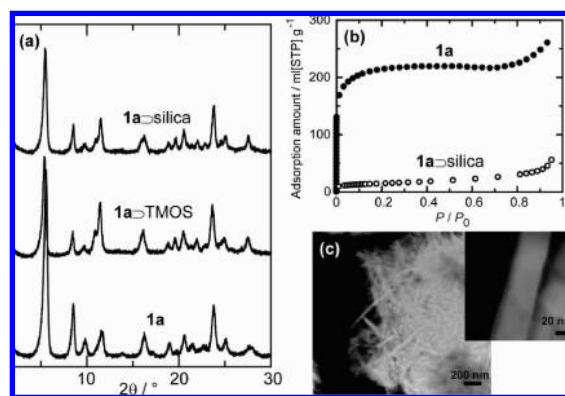


Figure 1. (a) XRPD patterns of **1a**, **1a**⊃TMOS, and **1a**⊃silica. (b) N₂ adsorption isotherms of **1a** and **1a**⊃silica at 77 K. (c) HAADF-STEM images of **1a**⊃silica.

ascribed to the inclusion of TMOS or silica in the channels.^{6b,7} Nitrogen adsorption measurement of **1a**⊃silica showed a drastic decrease in the adsorption amount compared with that of **1a** alone, suggesting that the resultant silica particles inhibited the diffusion of N₂ into the one-dimensional channels (Figure 1b). Scanning electron microscope (SEM) measurements and analysis of particle size distribution by laser light diffraction showed that the particle size, shape, and surface of **1a** were not changed during the sol–gel reaction. Transmission electron microscope (TEM) images of **1a** and **1a**⊃silica revealed that the appearance of the material was almost the same before and after the reaction. In addition, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of **1a**⊃silica did not show contrast for silica aggregates, suggesting homogeneous dispersion of silica within the channels (Figure 1c).⁸ Thus, in this system, the sol–gel condensation successfully proceeded only inside the channels, without destruction of the host framework or deposition of silica particles outside the pores.

Quantitative analysis of **1a**⊃silica by X-ray fluorescence (XRF) showed that number of Si atoms per unit cell of **1a** was 0.94. This value is consistent with the loading amount of TMOS in **1a**⊃TMOS (TMOS per unit cell of **1a** was 0.93), as determined by thermogravimetric analysis (TGA), indicating that the sol–gel condensation proceeded quantitatively in the channel. Next, we examined the sol–gel reaction of TMOS in a different host, **1b**, with narrower channels (pore size = 4.0 × 6.0 Å²). However, in this experiment, almost no silica was embedded in the channel after the reaction (number of Si atoms per unit cell of **1b** = 0.03, as detected by XRF), suggesting that TMOS cannot access into the small channels of host **1b**.

The thermal stability of **1a**⊃silica was studied using TGA (Figure 2a). **1a**⊃silica was found to be stable up to 238 °C, which is higher

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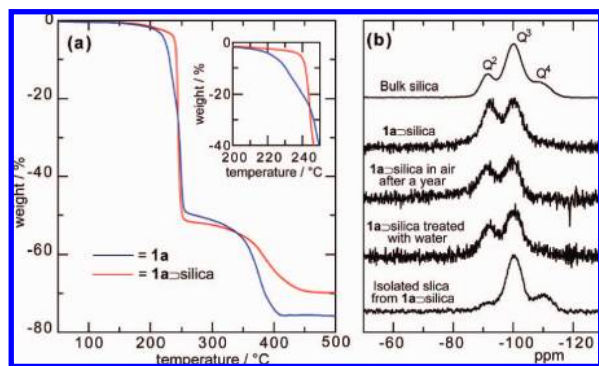


Figure 2. (a) TGA profiles of **1a** and **1a**⊃silica. The inset shows difference of the decomposition temperatures. (b) ^{29}Si MAS NMR spectra of various samples. Chemical shifts are relative to external tetramethylsilane (TMS).

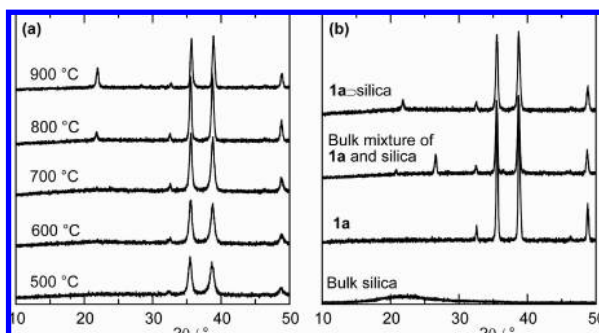


Figure 3. XRPD patterns of (a) **1a**⊃silica annealed at different temperatures and (b) various samples annealed at 800 °C. Peaks corresponding to CuO ($2\theta = 32.5, 35.5, 38.7, \text{ and } 48.8^\circ$), cristobalite ($2\theta = 22.0^\circ$), and quartz ($2\theta = 20.8 \text{ and } 26.6^\circ$) are detected.

than the onset temperature (214 °C) of decomposition for **1a** alone. Such an increase in the thermal stability of a host has not been observed in previous PCP–organic host–guest systems. Thus, hybrid formation with inorganic silica has a remarkable effect on the host PCP stability.^{2c,9}

To understand the degree of silica condensation, ^{29}Si magic angle spinning (MAS) NMR measurements were performed (Figure 2b).¹⁰ A reference sample of bulk material, prepared under similar conditions, exhibits an intense peak for the Q^3 unit at -100 ppm, along with peaks assignable to Q^2 and Q^4 at -92 and -109 ppm, respectively (where $\text{Q}^n = \text{Si}(\text{OSiX})_n(\text{OH})_{4-n}$). Despite the relatively low resolution in the spectrum of **1a**⊃silica, because of the existence of paramagnetic Cu^{2+} ions, the spectrum clearly shows that the domain of Q^2 increases and the fully cross-linked Q^4 unit was undetectable in the channels of **1a** compared with that of bulk silica. Interestingly, this low-dimensional silica structure in **1a**⊃silica has been stable over 1 year in air and was not seriously changed upon treatment with water. However, removal of the host matrix from **1a**⊃silica in EDTA solution immediately allowed further condensation of the active silanol moiety. These results clearly show that, unlike bulk systems, the growth of silica is effectively constrained, and the resultant low-dimensional silica is stably restricted in the channels of **1a**.^{2c,11}

In conventional bulk silica, crystal phase transformation of silica to cristobalite occurs above 1470 °C, and quartz is formed below 867 °C at ambient pressure.¹² However, a unique crystal transformation of the nanosized silica in **1a** was observed when **1a**⊃silica was annealed in air. The XRPD patterns of **1a**⊃silica (Figure 3a) treated at different temperatures show that one diffraction peak attributed to cristobalite appeared, even above 800 °C. However, the diffractions for crystalline silica were not detected in the XRPD profiles of **1a** or

bulk silica calcined at 800 °C (Figure 3b). A few previous papers have reported the ability of Cu^{2+} to promote the crystallization of silica,¹³ so we annealed a bulk mixture of **1a** and silica at 800 °C, but the resultant sample consisted only of quartz and CuO (Figure 3b). Thus, the unique crystal transformation to cristobalite observed at low temperature (~ 800 °C) is a likely cause of the miniaturized particle forms with the increase in favorable nucleation sites.^{14,15}

In conclusion, we have achieved for the first time a sol–gel reaction inside PCP channels without damaging the host structure or depositing the silica particles outside the pores. Interestingly, the labile structure of the nanosized silica can be prepared in the PCP channels, and a drastic decrease of the crystallization temperature for silica was observed because of its minute formation. Because an enormous range of metal oxide materials with significant functionalities can be prepared by the sol–gel reaction, our methodology will contribute to new preparation systems not only for subnanometal oxides¹⁶ but also for functional nanohybrids between PCPs and metal oxides.

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Supporting Information Available: Detailed experimental procedures, crystal structures of hosts, SEM, TEM, and particle size distribution. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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