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Mesoporous Polysilsesquioxanes

Mesoporous Organic–Inorganic Hybrid Materials Built Using Polyhedral Oligomeric Silsesquioxane Blocks**

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It has been well-recognized that many natural organisms exhibit elegant hierarchical porous architectures, which endow them with very unique properties. Inspired by nature, substances that are "made porous" have been one of the most intensively investigated topics involved in the approaches to construct hierarchically dimensioned materials.[1] Vast potential applications can be envisaged for such well-organized porous materials in the fields of catalysis, adsorption, photonics, electronics, and so on. Among the various approaches, the stepwise assembly of predefined nanoscale building blocks is an intriguing strategy for building hierarchical porous materials that can be finely designed and synthesized by tuning the primary building blocks with specific functionality and structure.[2]

Polyhedral oligomeric silsesquioxanes (POSS) are ideal building blocks for constructing organic–inorganic hybrid materials. Built through stable siloxane bonds and surrounded by organic peripheries, POSS compounds embody both organic–inorganic characteristics and cagelike structures in one small nanoentity.[3] The hybrid materials made from POSS are usually prepared by blending or covalently bonding POSS to a polymer matrix, which usually results in phase-separated composites.[4] Early attempts to build homophase materials from sole POSS units mainly used the X-ray radiation induced polymerization,[5] coupling of different POSS cages by hydrosilylation,[6] or by using R_2SiCl_2 and other organic molecules as cross-linkers.[7] However, it is highly anticipated but still a challenge to use POSS as the sole building blocks for constructing hierarchical organic–inorganic hybrid materials with well-defined porous architectures and specific functions.

Herein, we present a new strategy for synthesizing organic–inorganic hybrid materials with hierarchical structure by using predefined POSS units as the only building blocks. We weaved the POSS units into an infinite mesoporous structure by a block-copolymer-assisted coassembly method.[8]

A POSS precursor, OVPOSS-SILY (compound **2**, Scheme 1), bearing hydrolyzable peripheries, was synthesized by Pt-catalyzed hydrosilylation of an octavinyl-substituted POSS octamer (compound **1**, OctavinylPOSS, denoted hereafter as OVPOSS, Scheme 1) with triethoxysilane ($HSi(OEt)_3$).[9] A substoichiometric amount of triethoxysilane relative to the vinyl groups was employed (6:1 $HSi(OEt)_3$/**1**), with the intention of retaining the vinyl groups in OVPOSS-SILY so that they could be further modified. NMR and MALDI-TOF mass spectra show that compound **2** appears as a mixture of POSS with different degrees of vinyl substitutions. The average number of the remaining vinyl groups per cage is estimated to be 2.3 (Figure S1–S3 in the Supporting Information). The hybrid material was synthesized by coassembly of OVPOSS-SILY with P123 and subsequent condensation of OVPOSS-SILY around the P123 micelles (Scheme 1). Extraction of the occluded P123 is expected to generate mesopores penetrating the polymerized POSS framework. The resulting hybrid material is denoted as MesoPOSS.

Figures 1 a and 1 b display the nitrogen-sorption isotherms and the corresponding pore-size-distribution curve of MesoPOSS, respectively. A type IV isotherm with a steep hysteresis loop at relative pressure P/P_0 of 0.5–0.6 can be observed, indicating that this sample has mesoporous structure with uniform pore size. The Barrett–Joyner–Halenda (BJH) pore-size-distribution curve further confirms the uniform mesopore size centered at 4.40 nm. The sample exhibits a BET surface area as high as 960 $m^2 g^{-1}$ with a total pore volume of 0.91 $cm^3 g^{-1}$. The microporous volume (micropore size: ca. 0.51 nm) is estimated to account for about 35% of the total pore volume from micropore analysis based on the Horvath–Kawazoe (HK) method. However, it is difficult to distinguish the micropores between the densely cross-linked POSS units from the ones that originate from the polyethylene oxide chains of the template. Thus, the porosity from

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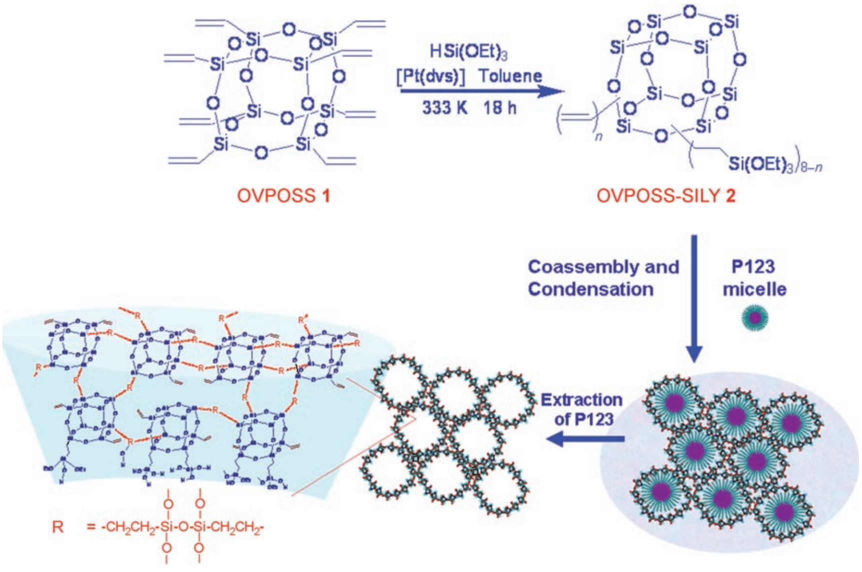

Scheme 1. Synthesis of the POSS compound OVPOSS-SILY and the mesoporous hybrid material MesoPOSS; dvs = divinyltetramethylsidiloxane.

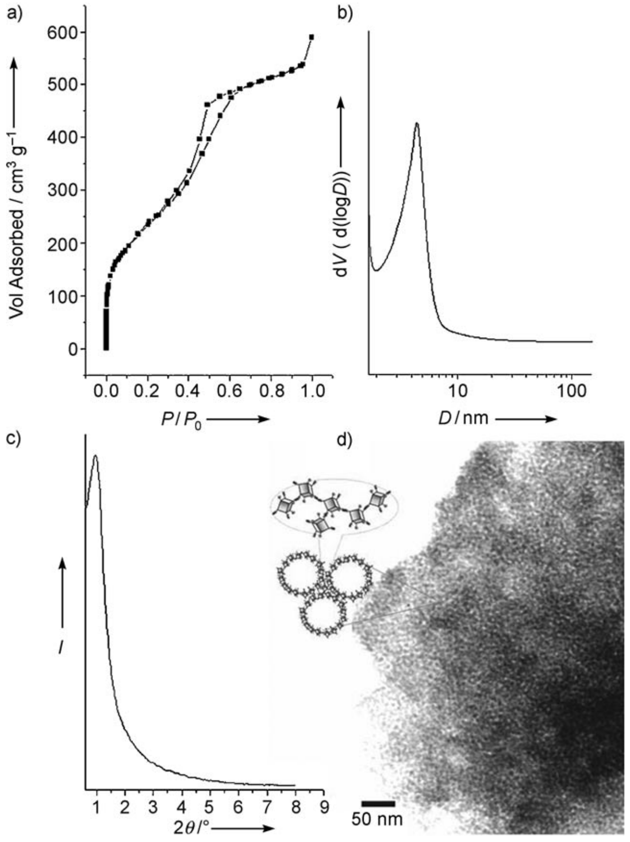

Figure 1. a) Nitrogen-sorption isotherm (standard temperature and pressure), b) BJH pore-size distribution (*D*: pore diameter), c) PXRD pattern, and d) TEM image of the mesoporous hybrid material MesoPOSS.

the mesopores that are generated by the block-copolymer scaffold is at least about 65 % of the total pore volume.

A sharp diffraction peak at $2\theta = 0.95°$ is observed in the XRD pattern of MesoPOSS (Figure 1 c), suggesting that this material has a mesostructure similar to that of MSU materials synthesized with the same type of block copolymer.[8a] Since the size of POSS compounds is estimated to be around 1–2 nm,[3] OVPOSS-SILY represents one of the largest organosilane building blocks for the synthesis of mesoporous hybrid materials thus far. Considering the steric hindrance, it is difficult for such a rigid and hydrophobic block to highly cross-link into an infinite and stable network while still possessing the flexible configuration needed for the coassembly around the micelles with high curvature. Butanol and NaCl were added during the synthesis to aid the formation of the mesostructure by reducing the hydration of poly(ethylene oxide) groups of P123 and enhancing the interaction between POSS and the P123 micelles.[10,11] Without butanol and NaCl, no mesoporous materials were obtained. The TEM image of MesoPOSS clearly shows the branched uniform wormlike channels distributed homogeneously throughout the bulk phase (Figure 1 d). This observation is consistent with the XRD result and confirms that MesoPOSS has an MSU-like mesostructure.

Shown in Figure 2 are the IR spectra of OVPOSS, OVPOSS-SILY, and MesoPOSS. The existence of the vinyl group in OVPOSS-SILY and the hybrid material MesoPOSS was confirmed by the bands at 1604, 3030, and 3065 cm^{-1}. The band at 1604 cm^{-1} is assigned to the C=C stretching vibration, while the bands at 3030 and 3065 cm^{-1} are assigned to the C–H stretching vibrations of the -CH= and =CH_2 units in the vinyl groups, respectively.[12a] Both OVPOSS-SILY and MesoPOSS exhibit the symmetric and asymmetric C–H vibrations

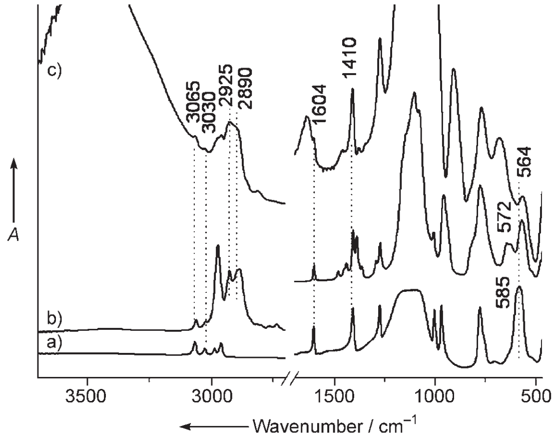

Figure 2. FTIR spectra of the POSS compounds a) OVPOSS, b) OVPOSS-SILY, and c) the mesoporous hybrid material MesoPOSS.

of the bridging ethylene group at 2890 and 2925 cm^{-1}, respectively.[10] The band at 585 cm^{-1} observed for OVPOSS can be assigned to the skeletal vibration of the silsesquioxane double four-membered ring (D4R) of the cubic core.[13] A red shift of this band is observed for OVPOSS-SILY (572 cm^{-1}) and MesoPOSS (564 cm^{-1}). The gradual variation in this band reflects the stepwise structural transformations around the D4R.

In Figure 3 the CP MAS ^{13}C and ^{29}Si NMR spectra of MesoPOSS are shown. Three sets of signals can be observed in the ^{13}C NMR spectrum. The signal at $\delta = 5.0$ ppm can be assigned to the carbon atoms of the bridging ethylene group, Si-CH$_2$CH$_2$-Si, in accordance with previous reports.[10] The signals for -CH=CH$_2$ appear at $\delta = 130.7$ and 137.0 ppm. The signals at $\delta = 17.0$ and 70.0 ppm are attributed to the P123 residue.[14] The ^{29}Si NMR spectrum of MesoPOSS shows three signals at $\delta = -56.9$, -65.0, and -79.6 ppm, together with a small shoulder at $\delta = -48.9$ ppm (Figure 3b). The signals at $\delta = -48.9$, -56.9, and -65.0 ppm can be assigned to silicon species bridged by -CH$_2$CH$_2$- of T^1 (CH$_2$CH$_2$–*Si*(OSi)(OH)$_2$), T^2 (CH$_2$CH$_2$–*Si*(OSi)$_2$(OH)), and T^3 (CH$_2$CH$_2$–*Si*(OSi)$_3$), respectively (T^n: silicon atom connected to one carbon atom, CSi(OSi)$_n$(OH)$_{3-n}$).[10] The signal at $\delta = -79.6$ ppm corresponds to the T$^{3'}$ (CH$_2$=CH–*Si*(OSi)$_3$) silicon sites attached to the pendant vinyl groups.[12b] No T$^{2'}$ (CH$_2$=CH–*Si*(OSi)$_2$(OH)) silicon species at about $\delta = -70$ ppm could be observed.[12b] This result indicates that the cage structure of the POSS is retained during the synthesis. The combined results of FTIR, ^{13}C MAS NMR, and ^{29}Si MAS NMR clearly show that the POSS building block was successfully weaved in the infinite porous structure of MesoPOSS without obvious alteration of the characteristics and structure.

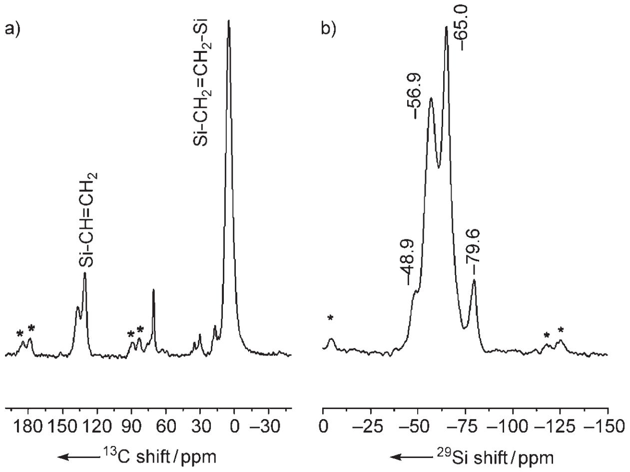

Figure 3. a) CP MAS ^{13}C NMR and b) CP MAS ^{29}Si NMR of the mesoporous hybrid material MesoPOSS; *: side bands.

The above characterizations show that MesoPOSS features three-dimensionally connected mesopores with uniform pore size, as well as multifunctionalities derived from the rigid inorganic cubic D4R core, hydrophobic ethylene groups bridged in the mesoporous framework, and reactive vinyl groups protruding in the pore.

One of the advantages provided by the mesoporous structure is the enhanced exposure of interior active components. With the aim of endowing more functionality to MesoPOSS, the vinyl groups hanging in the mesopore were treated with 4-bromoacetophenone through Heck coupling.[15] Figure 4 shows the IR spectra of 4-bromoacetophenone, MesoPOSS, and MesoPOSS-PM (after Heck coupling). Compared with MesoPOSS, the IR spectrum of MesoPOSS-PM displays new bands at 588, 800, 1363, 1562, and 1674 cm^{-1} in addition to the vibrations attributed to the species derived from -CH$_2$CH$_2$-, -CH=CH$_2$, and D4R. The band at 800 cm^{-1} can be assigned to the C–H deformation vibration of the aromatic ring. The C–H deformation of the methyl group of the acetophenone unit can be found at 1363 cm^{-1}. The bands at 1562 and 1674 cm^{-1} can be attributed to the C=C stretching of the aromatic ring conjugated with the carbonyl group and the C=O stretching of the carbonyl group conjugated with the aromatic ring, respectively. The IR results show the successful modification of the vinyl group of MesoPOSS. In addition to using the Heck reaction, new functional groups could also be generated from the vinyl groups by bromination, epoxidation, hydroformylation, and metathesis, among other methods. Future efforts could be made to incorporate chiral ligands by modifying the vinyl groups and incorporate metal atoms into the POSS cage for catalysis.

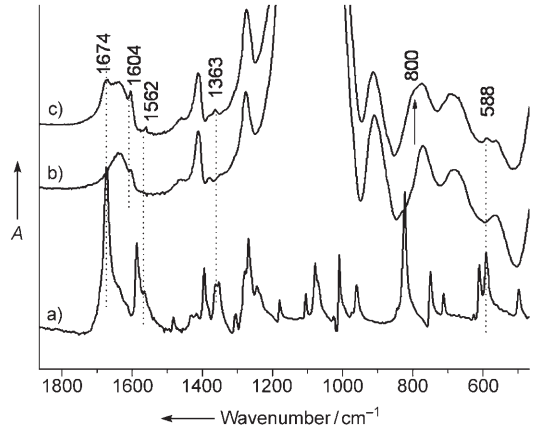

Figure 4. FTIR spectra of a) 4-bromoacetophenone, b) the mesoporous hybrid material MesoPOSS, and c) MesoPOSS-PM (MesoPOSS modified with 4-bromoacetophenone).

In summary, a mesoporous organic–inorganic hybrid material was successfully synthesized by using POSS building blocks. This hybrid material has hierarchical architecture and functionality, as evidenced by the existence of branched uniform mesopores, the cubic silsesquioxane cage, the bridging ethylene groups, and the pendant vinyl groups. The pendant vinyl group hanging in the mesopore can be transformed into groups with new functionality. By combining the versatile coassembly strategy with the rich POSS chemistry, many other novel hierarchical hybrid materials with potential applications could be synthesized.

Experimental Section

MesoPOSS: In a typical synthesis, P123 (0.50 g) and NaCl (1.64 g) were dissolved in aqueous HCl ($0.1\,\text{M}$, 18.75 g). The mixture was stirred for 2 h at 313 K. A solution of **2** (0.58 g) in butanol (0.5 mL) was slowly added to the P123 solution with vigorous stirring. The resulting mixture was further stirred for 20 h at the same temperature, with subsequent hydrothermal treatment at 373 K for 24 h. The white precipitate was finally recovered by filtration. To extract the porogen species, the sample (1 g) was stirred in an ethanol solution (200 mL) containing HCl (1.5 g) at 328 K for 24 h. This process was repeated once. Finally, the sample was washed with ethanol in a Soxhlet apparatus for another 24 h, and dried under vacuum.

Characterization: MALDI-TOF mass analysis was performed with a Voyager-De STR instrument. NMR spectra of POSS compounds were recorded on a Varian GEMINI 300 spectrometer. ^{29}Si and ^{13}C CP MAS NMR spectra were recorded on a Bruker DMX500 spectrometer. Infrared spectra were recorded on a Nicolet Nexus 470 IR spectrometer as KBr pellets. X-Ray powder diffraction (XRD) patterns were recorded on a Rigaku D/Max 3400 powder diffraction system by using $\text{Cu}_{K\alpha}$ radiation with a wavelength of 0.1542 nm. The nitrogen-sorption experiments were performed at 77 K on a Quantachrome Autosorb 1 system. Samples were degassed at 393 K for 5 h prior to the measurements. Transmission electron microscopy (TEM) was performed with a JEM-2010 at an acceleration voltage of 100 kV.

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