Squarely Mesoporous and Functional Nanocomposites by Self-Directed Assembly of Organosilane**

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Mesoporous silica nanocomposites attracted increasing attention in recent years due to their wide applications in many fields, such as optoelectronic devices, catalysis, and drug delivery.[1–4] These porous materials are normally synthesized by co-assembling bridged silsesquioxanes and surfactants, followed by the removal of surfactant molecules.[2–4] Self-directed assembly of bridged silsesquioxanes which exploits non-covalent interactions generally produces mesoscopically ordered lamellar solid materials.[5–15] To the best of our knowledge, mesoporous materials by self-directed assembly of bridged silsesquioxanes have not been reported to date.

Recently, porphyrin derivatives are attracting increasing attentions not only because of their versatile optical and electrochemical properties as well as high chemical and thermal stabilities,[16,17] but their interesting assembly to form desirable structures, mainly due to the large and flat conjugated tetrapyrrole macrocycle.[18,19] Here we explores the unique assembly behavior of porphyrin-bridged silsesquioxane and first reports the synthesis of mesoporous materials by a directed assembly of organosilane, without using any surfactant. Particularly, the resultant mesopores are uniform and show a square structure, which provide them with potential applications as separation media that combine both shape selectivity and enantioselectivity.[20]

The building molecule, porphyrin-bridged silsesquioxane (PBS, Fig. 1), was readily synthesized by reacting 4,4',4",4'''-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid) with γ-isocyanatopropyltriethoxysilane in tetrahydrofuran.[21] It is well-known that disk-shaped macrocycle structure can make PBS molecules to stack together easily. As a result, the engineered building blocks organize into closely stacked and highly ordered superstructures after evaporation of the solvent from PBS tetrahydrofuran/H_3O^+ solutions. As shown in the optical micrograph at Figure 2a, the solvent evaporation (air dry in minutes) leads to the formation of flake-like and

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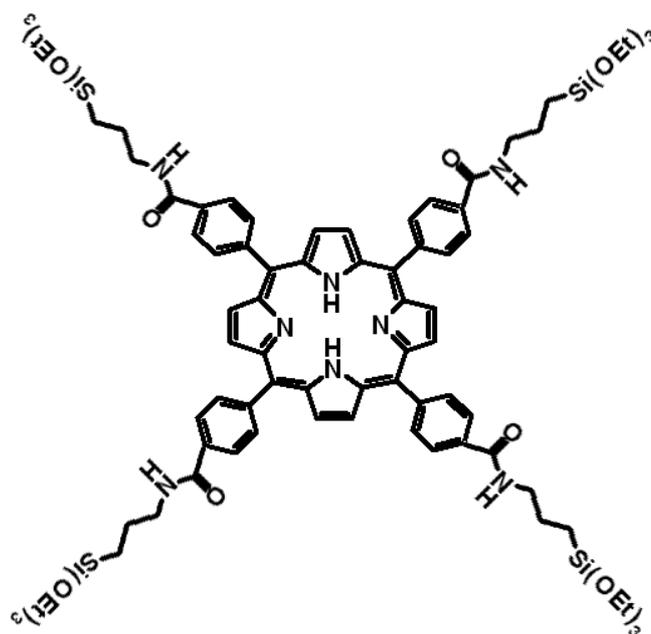Los Angeles, CA 90095 (USA)

Figure 1. Structure of the PBS building molecule.

transparent films. X-ray diffraction analysis (Fig. 2b) demonstrates the ordered lamellar structure in the films with a d-spacing of 2.07 nm which can be related to the length of bridging organic units of the building blocks. A side view of transmission electron microscopy (TEM) (shown in Fig. 2c) further confirms the ordered lamellar structure with an inter-lamellar distance of 2.1 nm. This value agrees well with that obtained from XRD analysis.

Mesoporous structure of hybrid thin films is demonstrated in Figure 3. Due to the unique chemical structure of PBS molecules, they assemble in a square arrangement during the evaporation of solvents, producing mesopores among PBS stacks inside the materials (schematically shown in Fig. 3a). Atomic force microscopy further confirms this square and porous organization (Fig. 3b). In addition, the N_2 adsorption isotherms indicates that the average diameter of these mesopores calculated through the BJH model is ~ 1.7 nm (Fig. 3c), which agrees with the results from the atomic force microscope image in Figure 3b. It should be noted that the film sample had been repeatedly evacuated and flushed with N_2 for several times before the nitrogen adsorption/desorption characterization. So the observed square pores are indeed derived from the unique assembly of PBS building molecules,
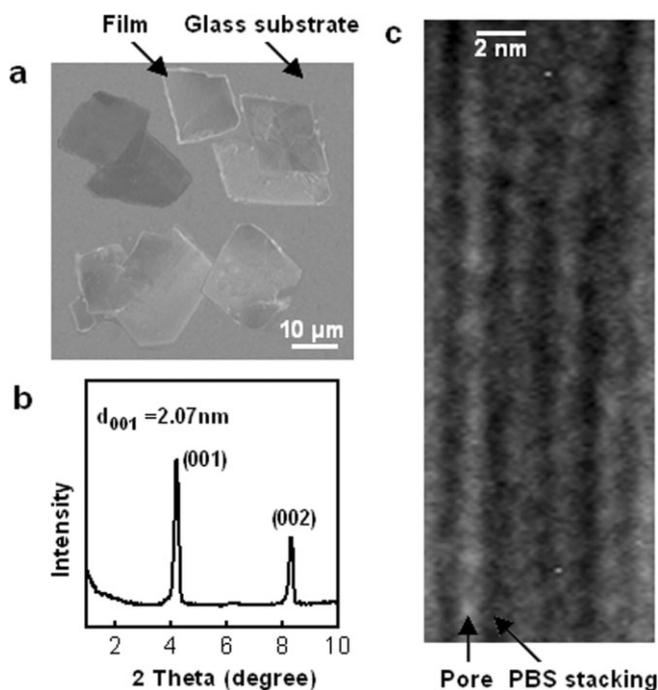
Figure 2. Flake-like and transparent porphyrin/silica nanocomposite films with a highly ordered mesostructure. a) Optical microscopy image. b) X-ray diffraction pattern on the lamellar structure with a d-spacing of 2.07 nm. c) TEM images of the stacked PBS building blocks.

not due to the vacancy left by solvent molecules during the test.

As clearly demonstrated by the experimental results, this hierarchical assembly is a time-dependent process in which more complex structures are progressively formed upon sequential self-organization of basic building blocks.[16] To investigate this viewpoint, we have studied a series of nanocomposite films derived from PBS with different incubation periods in tetrahydrofuran acid solutions. If the as-prepared

mixture solution is immediately coated on glass substrates, the resultant films exhibit no peaks from XRD measurements. In addition, no ordered lamellar structure is found from TEM analysis. On the other hand, if the PBS solution is incubated for a longer period of time, e.g., 30 minutes, two weak and broad peaks corresponding to (001) and (002) planes appear from XRD analysis (Fig. 4a). With the further increase of incubation time, the peaks become sharper and stronger. Both the peak intensity and the sharpness saturate after incubation of 3 hours, indicating that the PBS building molecules have reached their preferred patterns.

The time-dependent assembly is further confirmed by UV-vis spectra (Fig. 4b). It is well known that nanocomposites show better optoelectronic property by the formation of a more ordered structure.[6] For films prepared by immediately coating the PBS solution on glass substrates, only one weak peak at 440 nm is detected. With the increase of incubation time over 30 min, another four small peaks between 500 and 700 nm appear as well except for the main adsorption at a wavelength around 440 nm. Particularly, increase in the incubation time not only leads to stronger adsorption peaks at the longer wavelength but a red shift of the main adsorption around 440 nm.

The versatile optical and electrochemical properties, the possibility to tune these properties by grafting various substituents at their peripheral positions, and their high chemical and thermal stabilities make porphyrin families attractive materials in electronics, optoelectronics, and photonics.[23] For the currently engineered nanocomposites, the ordered silica network provides a much improved alignment for the π-π stacking of the porphyrin moieties,[24,25] favoring a better optoelectronic performance of the conjugated systems. As expected, the UV-vis spectra of porphyrin/silica fibers are significantly different from those of the corresponding PBS solutions. Figure 5a compares the optical spectra of hybrid films of porphyrin-bridged silsesquioxane, and of its tetrahydrofuran solution. Absorption peaks assigned to porphyrin rings between 300 and 700 nm shift to the longer wavelengths after formation of highly ordered assemblies. Such red-shifted phenomena have been observed in other self-assembled conjugated systems, which are believed to be from the ordered molecular organization that allows more efficient π–π stacking and energy transport among the building blocks.[26] In addition, by complexing various metal ions into the center of largely conjugated porphyrin macro-cycles, the porous films show much improved electrical conductivities. The electrical conductivity for nanocomposites without ion complexation is typically about 10^{-7} S cm^{-1} at room temperature. After complexed with metal ions in the center of conjugated porphyrin
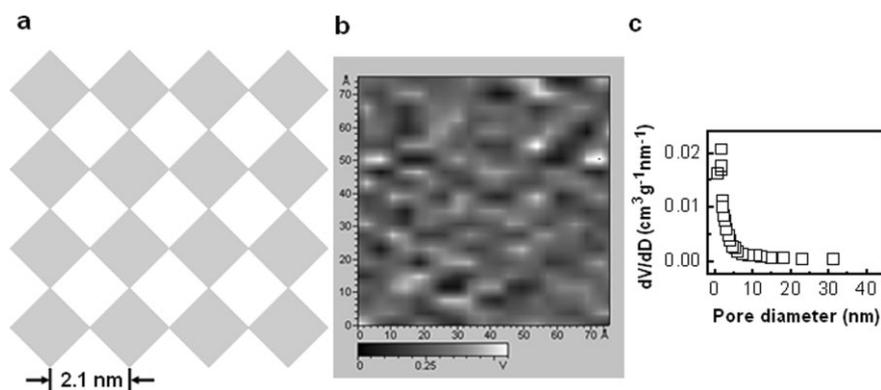

Figure 3. a) Schematic illustration of the formation of mesoporous structure by a square arrangement of PBS building molecules. b) AFM on side view of the squarely mesoporous structure of porphyrin/silica nanocomposites. c) BJH (Barret–Joyner–Halenda) pore diameter distribution from nitrogen adsorption/desorption [22].
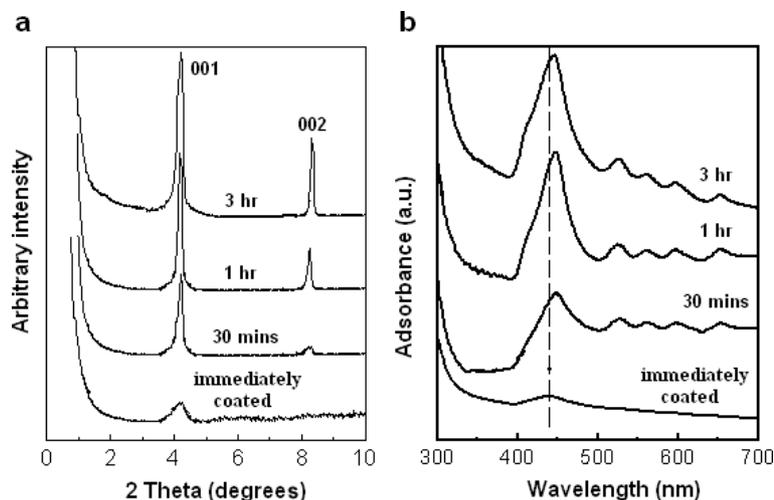
Figure 4. Time-dependent assembly of PBS building molecules characterized by a) X-ray diffraction analysis and b) UV-vis spectra. The nanocomposite films were prepared using different incubation time, i.e., immediately coated, 30 min, 1 h, and 3 h.
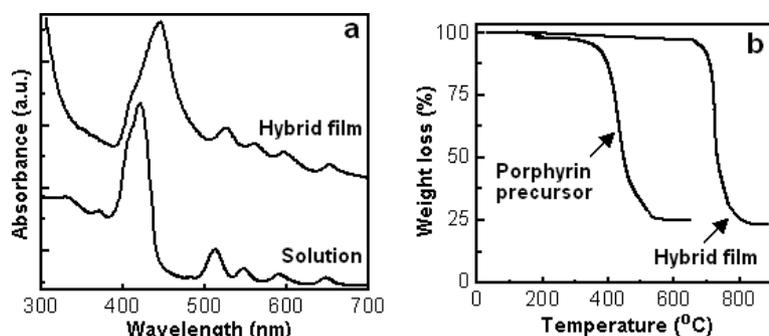

Figure 5. Much improved properties of the nanocomposites. a) UV-vis spectra for the PBS solution and the derived hybrid nanocomposite film after incubation of 3 h. b) Thermogravimetric analysis of the porphyrin precursor, 4,4',4'',4'''-(21H, 23H-porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid), and the hybrid nanocomposite film.

macrocycles, the electrical conductivities of derived nanocomposites are several hundred times larger than those without complexation. For example, the films complexed with Zn^{2+} and Fe^{2+} show electrical conductivities of 5×10^{-4} and 4×10^{-4} S cm^{-1}, respectively, at room temperature. Furthermore, the hybrid nanocomposites provide improved thermal stability.[24,27] As shown in Figure 5b, the porphyrin precursor undergoes bulk decomposition at about 500 °C, while the nanocomposites lose the bulk weight at much higher temperature (~ 800 °C).

In summary, we have demonstrated a novel synthesis of squarely mesoporous porphyrin/silica nanocomposite films through the self-direct assembly of bridged silsesquioxane. Due to the formation of robust silica networks around conjugated porphyrin moieties, the resultant mesoporous materials exhibit excellent optoelectronic properties and good thermal stability, providing unique platforms for many applications.

Particularly, this research provides an efficient synthetic paradigm to a family of functional and mesoporous materials through a neat one-step process, compared to the lengthy operation in a co-assembly approach.

Experimental

Synthesis of Porphyrin-Bridged Silsesquioxane: Two precursors, 4,4',4'',4'''-(21H,23H-porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid) and (3-isocyanatopropyl)-triethoxysilane, were added into a multi-neck flask with the solvent tetrahydrofuran. The flask was repeatedly evacuated and flushed with argon gas. The mixture was stirred for several minutes under argon atmosphere, then refluxed in an oil bath. The reaction was held overnight. After cooling down to room temperature, the product was washed with petroleum ether to remove the excess (3-aminopropyl)triethoxysilane.

Preparation of Mesoporous Films: In a typical synthesis, the bridged silsesquioxane (0.17 mmol) was dissolved in THF (1.5 mL). A solution of HCl (0.1 M, 1.0 mL) was added and the mixture was treated with ultrasound at room temperature for different time, i.e., immediately coated, 30 min, 1 h, and 3 h. Thin uniform nanocomposite films were, prepared by casting the resultant solution on the glass substrate followed by evaporation of solvents.

Characterizations: The morphology study was conducted by a visible microscopy (on an Olympus IMT-2 inverted microscope connected to a high-resolution monitor (SONY) and an S-VHS VCR through an Optronics CCD camera). The nanocomposites were further characterized by transmission electron microscope (JEOL 2010 microscope operated at 120 kV), atomic force microscope (Q-Scope 250 Quesant) and powder X-ray diffraction (XRD) patterns (Siemens D500 diffractometer operating at 40 kV, 30 mA, Cu-Kα radiation, $\lambda = 0.15406$ nm). Thermal analysis was conducted on a Thermogravimetric Analyzer (TGA) 2950 by TA instruments run at 15 °C min^{-1} from 25 to 1000 °C with argon sweep gas. The electronic properties were examined using UV-vis spectrophotometer (Beckman DU 640B Ultraviolet-visible). The electrical conductivity was recorded over a frequency range of 10 to 1×10^7 Hz using a Solartron 1260 gain phase analyzer. The resistance was taken at the frequency that produced the minimum imaginary response.

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