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Deposition of Thin Nanoporous Silica Layers on Solid Surfaces

Makoto Ogawa,*[†,‡] Naoki Shimura,[†] and André Ayral[§]

Graduate School of Science and Engineering and
Department of Earth Sciences, Waseda University,
Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan,
and Institut Européen des Membranes,
UMR no. 5635 CNRS-ENSCM-UMII, Université Montpellier
II, CC047, Place Eugène Bataillon,
34095 Montpellier Cedex 5, France

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After the successful preparation of mesostructured and mesoporous silica films by the solvent evaporation method,[1,2] the preparation of mesoporous silica films has been extensively investigated partly as a result of the wide range of applicabilities of mesoporous silica films as low-*k* material for semiconductor electronics,[3] nanoreactors for photochemical reaction,[4] and membranes.[5] In addition to the solvent evaporation method, the deposition of the mesoporous silica layer from acidic aqueous solution and vapor phase has been reported to prepare mesoporous silica layers with high structural regularity or controlled thickness on flat substrates.[6,7] Here, we report a novel synthetic way to deposit a homogeneous nanoporous silica thin layer on a variety of solid surfaces from flat substrates to micrometer size powders and, as to the materials, from oxides and hydroxides to organic polymers from basic solution. To the best of our knowledge, there are few reports on the preparation of mesoporous silica films using basic conditions.[7−9] Martin et al. and Nishiyama et al. prepared mesoporous silica films by ammonia vapor after the gel deposition.[7,8] Nishiyama et al. reported the deposition of mesoporous silica on a membrane by hydrothermal treatment.[9] These syntheses are apparently different from the present one, deposition of a homogeneous film under mild conditions from basic solution. The present reaction is very simple, where substrates (both plate and powder) were put into a homogeneous solution containing tetraethoxysilane (TEOS), hexadecyltrimethylammonium chloride (C16TAC), methanol, water, and ammonia and allowed to react at room temperature or 3 °C for several hours. The present synthesis is a new and versatile method to prepare nanoporous silica thin layers on a solid substrate especially when the reported procedure is not applicable: a substrate with complex morphology and/or being unstable in acidic solutions such as hydrotalcite and ZnO.

The deposition of the nanoporous silica layer was conducted by the following procedure: C16TAC (0.211 g), deionized water (17.7 g), methanol (100 mL), and a 28% aqueous ammonia solution (7.2 g) were mixed, and the solution was shaken for 15 s at room temperature. TEOS (0.368 mL) was added to this solution, and then the mixture was shaken for another 3 s. The molar ratio of TEOS/

[†] Graduate School of Science and Engineering, Waseda University.
[‡] Department of Earth Sciences, Waseda University.
[§] Université Montpellier II.

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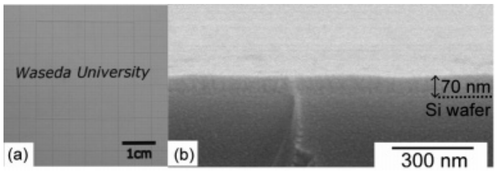

Figure 1. Photograph and SEM image of the mesoporous silica films on (a) borosilicate glass and (b) Si wafer (cross-sectional view).

C16TAC/deionized water/methanol/ammonia was 1:0.4:774:1501:72. The procedure is very similar to that used for the preparation of nanoporous silica spherical particles.[10] A borosilicate glass plate (30 × 30 × 0.2 mm) was subsequently soaked into the solution and aged at room temperature for 20 h. After the aging, the films were washed with methanol and were dried in air for 1 day.

The weight of the substrate increased by 0.2 mg after the reaction, indicating the deposition of silica on the substrate. The thickness of the film is 100 nm as determined by the surface profilometer. The photograph of the film is shown in Figure 1a. When the reaction was repeated for three times, the thickness of the film became 300 nm, showing the possibility to control the thickness with such high accuracy. Silica was not deposited on the substrate when the reaction was conducted in the absence of C16TAC, indicating the role of the interactions between C16TAC and the substrate surface, which is probably an electrostatic one.

The calcination did not affect the morphology of the film. The film density was determined by the weight of the calcined film to be 1.1 $cm^3\ g^{-1}$. From the nitrogen adsorption isotherm,[11] the BJH pore diameter[12] and BET surface area[13] are determined to be 2.4 nm and 930 $m^2\ g^{-1}$, respectively. When the alkyltrimethylammonium chlorides with different alkyl chain lengths (abbreviated as C*n*TACs, where *n* denotes the carbon number in the alkyl chain) were used, transparent films with similar thickness also formed and the pore size depended on the alkyl chain length: 2.0 (C12TAC), 2.25 (C14TAC), and 2.8 nm (C18TAC).

Similarly, the nanoporous silica layer with the thickness of about 70 nm and with disordered mesostructure formed on a silicon wafer as seen by the cross-sectional scanning electron microscopy (SEM) image (Figure 1b). From the nitrogen adsorption isotherm,[11] the BJH pore diameter[12] and BET surface area[13] are determined to be 2.25 nm and 700 $m^2\ g^{-1}$, respectively. These values were different from those of mesoporous silica films deposited on borosilicate glass. A thin layer with disordered mesostructure also formed on polymeric substrates (30 × 30 mm) including polytetrafluoroethylene (PTFE), polypropylene, and polyethylene by the same experimental procedure. The SEM image of the silica−surfactant films on PTFE is shown in Figure 2 as a typical example. Thus, the present methodology enabled us to synthesize mesoporous silica thin films with the thickness of 100 nm on a wide variety of substrates.

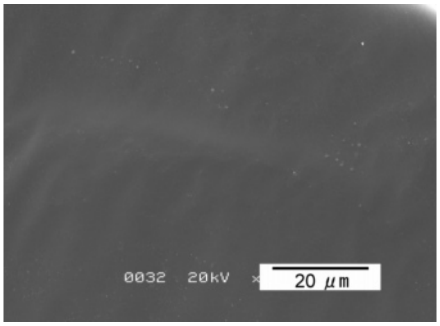

Figure 2. SEM image of the silica−surfactant films on PTFE.

The adhesion between the silica−surfactant films and the substrate was investigated by a Scotch tape peeling test with scotch2526 (3 N cm^{-2}; Sumitomo 3M, Ltd.). The films deposited on borosilicate glass and Si wafer passed the test. However, the films deposited on PTFE, polypropylene, and polyethylene were peeled off. These results suggest the difference in the interactions between the substrate and the mesoporous silica layer.

The above-mentioned results motivate us to deposit a thin nanoporous silica layer on powders to prepare core−shell particles. Hydrotalcite, a layered double hydroxide with the chemical formula of $M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2(A^{n-})_{x/n}\cdot mH_2O$,[14] was used as the core particle. Layered double hydroxides are a class of anion exchanger consisting of a positively charged brucite-like layer and the charge compensating interlayer exchangeable anion. In addition, well-shaped platy particle is available. Hydrotalcite possesses such useful functions as catalytic and adsorptive ones so that the coating on the particle surface is expected to modify the compatibility with other materials and to impart molecular sieving functions toward substrate selective adsorption and reaction.

By simply mixing hydrotalcite, which was prepared according to the reported procedure,[15] with the above-mentioned precursor solution (TEOS, C16TAC, methanol, water, and ammonia) at 3 °C, hydrotalcite was homogeneously coated with thin layer of silica−surfactant hybrid materials. The core−shell particle was calcined in air at 500 °C to remove surfactant to prepare mesoporous silica coated hydrotalcite. The nitrogen adsorption isotherm[11] of the calcined product is shown in Figure 4a. The pore diameter[12] and the BET surface area[13] are 2.5 nm and 140 $m^2\ g^{-1}$, respectively. In addition, by dissolving the hydrotalcite from the resulting core−shell particle, hexagonal shaped mesoporous silica platy particle with the BJH pore diameter[12] and the BET surface area[13] of 2.3 nm and 700 $m^2\ g^{-1}$ was successfully obtained (Figure 4). The pore size distribution was narrow as shown in Figure 4b. The X-ray diffraction (XRD) pattern of the mesoporous silica particles showed no diffraction peaks, suggesting the disordered mesostructure (data not shown). Throughout the procedures (hydrotalcite, silica−surfactant coated hydrotalcite before and after the calcination, mesoporous silica formed after the dissolution of the core Mg−Al oxide), hexagonal shaped platy morphol-

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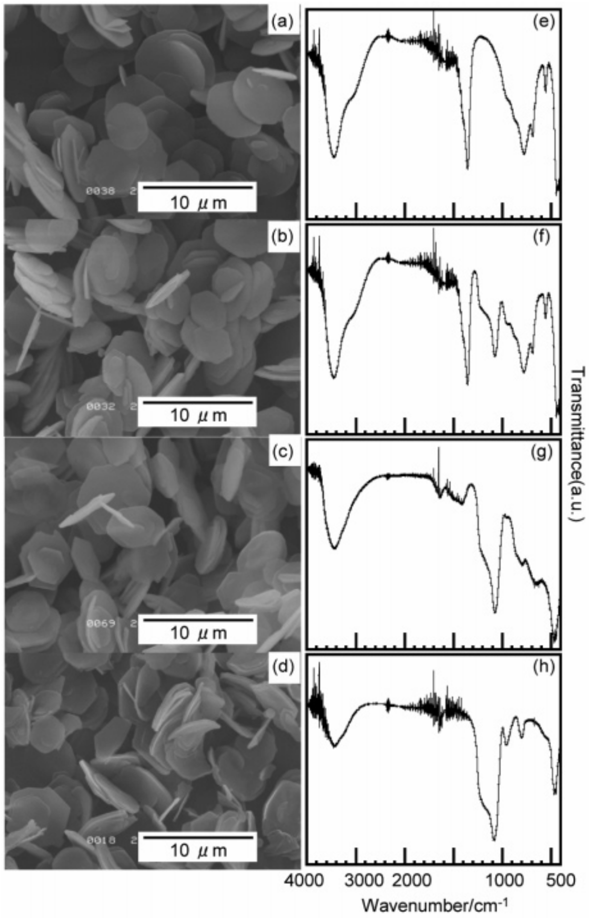

Figure 3. SEM images (a−d) and IR spectra (e−h) of (a and e) hydrotalcite, silica−surfactant coated hydrotalcite (b and f) before and (c and g) after the calcination, and (d and h) mesoporous silica prepared by the acid treatment.

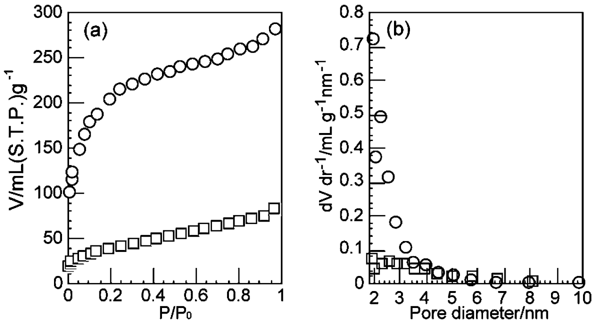

Figure 4. Nitrogen adsorption isotherms (a) and BJH pore size distributions (b) of (squares) hydrotalcite−mesoporous silica and (circles) mesoporous silica hollow particles.

ogy was retained without any loss of size and regularity as shown by the scanning electron micrographs (Figure 3a−d). The reactions (hydrotalcite, silica−surfactant coated hydrotalcite, decomposition of hydrotalcite, and removal of the Mg−Al mixed oxides) were confirmed by the changes in the XRD patterns (data not shown) as well as those of infrared spectra. (Figure 3e−h) The preparation of mesoporous silica particles in controlled shapes is a topic of interest,[4,16] and recently mesoporous silica tubes and spheres were reported using needlelike calcium carbonate particles

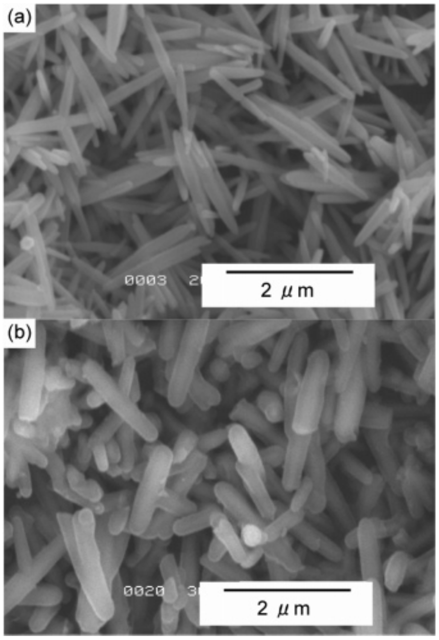

Figure 5. SEM images of (a) ZnO and (b) ZnO mesoporous silicas.

and Latex as the template.[17,18,] The present platy particle is a new form of mesoporous silica and may find applications in cosmetics, lubricant, and so on. Because layered double hydroxides with variable compositions and particles size are available, the complexation with silica is worth investigating further toward controlled size and shapes of mesoporous silica plates as well as functional hybrid particles.

As to the silica coated particles, there are many reports on the preparation and characterization.[19] However, there are few reports on the particle coating with mesoporous silicas.[17,20,21] Mesoporous silica coating is regarded as a way to modify the surface properties of powders as well as to impart new functions such as molecular sieving on catalysts and adsorbents. Zinc oxide particles[22] were successfully coated with mesoporous silica layers by the same procedure to show the versatility of the present method. The scanning electron micrograph of the mesoporous silica coated needlelike zinc oxide is shown in Figure 5. A thin layer also formed on poly(methyl methacrylate) spherical particles with a diameter of about 600 nm. Thus, it was shown that the present method is applicable to coat particles of oxides, hydroxides, and organic polymers.

In summary, it was shown that the homogeneous nanoporous silica thin layers formed on various substrates by simply dipping the substrates in an aqueous solution containing TEOS, alkyltrimethylammonium chloride, ammonia, and methanol. The present method is a versatile way to prepare mesoporous silica layers on a flat substrate and to coat particles due to the very simple procedure, mild reaction conditions, and reproducible results.

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