

Nanoscale Casting Using Supercritical Fluid

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Porous silica fibers were synthesized by templating activated carbon fibers using supercritical fluid as a solvent. A precursor of silica, tetraethyl orthosilicate was dissolved in supercritical CO₂ and attached to the base-activated carbon. The base-activated carbon in the sample coated with SiO₂ was removed by calcination or O₂-plasma treatment. Not only the fibrous macro shape, but also the meso structure of the base-activated carbon fiber were faithfully replicated in the silica products. These results suggested the great advantage of supercritical fluid for fabricating ceramic replicates of templates with complex structure, such as activated carbon. We have demonstrated that activated carbon with micropores acts not only as a mold for macroscopic shape control but also as a template for nanoscale structure control, when a supercritical fluid was used as a solvent. The advantage of the supercritical fluid as a medium for replication is attributed to the inability of the supercritical fluid to produce a condensed phase.

Introduction

Replication is one of the most important processes in biological,¹ chemical,^{2–5} and industrial mass production⁶ systems. In these processes, templates or molds are used for structure or shape control. In DNA replication, a molecular template is used.¹ Recently, mesoporous materials have been made by using surfactant aggregation templates.^{2–3} Satishkumar et al. have reported oxide nanotubes prepared using carbon nanotubes as templates.⁵ They immersed carbon nanotubes into a liquid silica source, followed by the removal of the carbon nanotubes by calcination. Although micro- or mesoscale structure could be controlled in these processes, other processes are necessary for macroscopic shape control. In metal or plastic casting⁶ by using molds, only the macroscopic shape can be controlled. Materials have not only their own shapes but also their characteristic nanoscale structures. Why are such nanoscale structures not replicated? Because the replicating materials cannot penetrate such fine spaces. When we use a liquid phase in the process, the high viscosity of liquid prevents penetration. Even when we use a gas phase, it capillary condenses in the fine spaces.

Supercritical fluids have large solubility,⁷ large diffusion coefficient,⁸ and low viscosity. In addition, they never produce condensed phases that prevent fine replications. In the present work, we have demonstrated the advantage of supercritical fluid as a medium for replicating structure and shape control of materials. We have made silica materials that replicate base-activated carbons.

Experimental Section

A 3 mL portion of tetraethyl orthosilicate (TEOS) was poured into a stainless steel vessel (50 mL). A stainless steel cage with

1 g of activated carbon fibers containing 27 wt % water (OSAKA GAS Chem. Co., commercial name A-20) was set in the vessel. The activated carbon fibers in the cage were not in contact with the liquid TEOS at the bottom of the vessel. The closed vessel was filled with CO₂ and kept at 393 K and 26 MPa for 2 h in an oil bath. After these treatments, the samples were dried at 378 K for 12 h in air, followed by calcination in air at 873 K for 6 h. We also tried to remove the activated carbon by an oxidation process using a YAMATO Scientific O₂-plasma equipment (PC-103, RFG-500) at 500 W in O₂ (160 mL/min).

The results were compared with those prepared by the method of Satishkumar et al.⁵ in which 1 g of activated carbon A-20 was immersed into 30 mL of liquid TEOS, followed by heating at 378 K and further heating at 873 K for 6 h. The results were also compared with those prepared by the CVD method. The sample was prepared without CO₂. A 3 mL portion of TEOS was charged into an autoclave (50 mL). Activated carbon A-20 was set in the cage so that it was not in contact with the liquid TEOS in the vessel, which was kept at 393 K and 26 MPa for 2 h.

Results and Discussion

The porous structures on a nanometer scale are reflected in their sorption properties. Figure 1A shows the nitrogen adsorption–desorption isotherms for A-20 carbon, A-20 carbon coated with SiO₂ in supercritical fluid, and SiO₂ after removal of activated carbon. The corresponding nitrogen adsorption–desorption isotherms in logarithm are shown in Figure 1B. The shapes of the isotherms of A-20 and A-20 coated with SiO₂ in supercritical fluid are identical with each other and show the typical isotherm shape of a microporous material. The N₂ isotherms for the base carbon material A-20 and A-20 coated with SiO₂ in supercritical fluid display well-defined steps at $P/P_0 = 0.06–0.3$, which is indicative of the filling of micropores with an average density functional theory (DFT) pore size of

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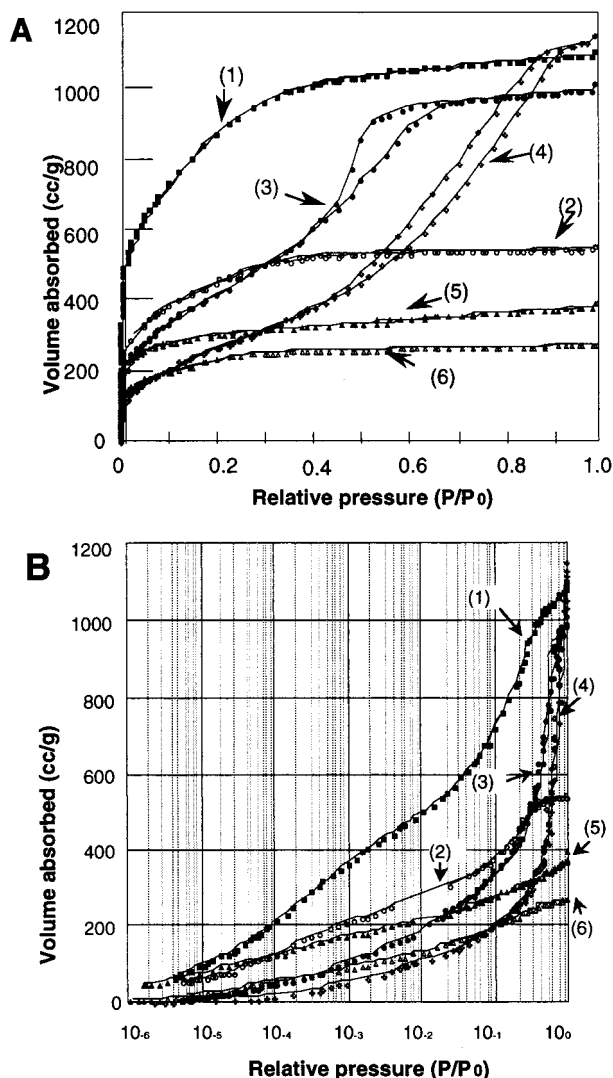


Figure 1. (A) Nitrogen adsorption-desorption isotherms for activated carbon (A-20) (1), A-20 coated with SiO_2 in supercritical fluid (2), sample after removal of A-20 by calcination in air from SiO_2 -coated A-20 in supercritical fluid (3), sample after removal of A-20 by calcination in O_2 plasma from SiO_2 -coated A-20 in supercritical fluid (4), A-20 coated with SiO_2 in liquid SiO_2 precursor, tetraethyl orthosilicate (TEOS) (5), and sample after removal of A-20 by calcination in air from SiO_2 -coated A-20 in liquid TEOS (6). Relative pressure is P/P_0 where P is the equilibrium pressure of the adsorbate and P_0 is the saturation pressure of the adsorbate at the temperature of the adsorbent. Volume absorbed is at STP. Before measurement, each sample was heated at 423 K and 10^{-6} Torr for 3 h. The isotherms were measured at 77 K on a QUANTACROME AUTOSORB-1-MP. (B) Corresponding nitrogen adsorption-desorption isotherms in logarithm.

1.2 nm [Figure 1B(1), (2)]. In contrast, the isotherm for a sample coated with SiO_2 without using a supercritical fluid shows no manifested step in the low P/P_0 region [Figure 1B(5)], which suggests the smaller amount of micropores in the sample. It could be attributed to the surface tension of the liquid TEOS that prevented a penetration into the micropores of the activated carbon. A hysteresis between adsorption and desorption isotherms beyond $P/P_0 = 0.4$ is observed for the two SiO_2 samples after the removal of the activated carbon by calcination in air or in O_2 plasma. The well-defined steps in the $P/P_0 = 0.4$ – 0.9 region and the hystereses indicate the existence of mesopores in the Barret-Joyner-Hallender (BJH) pore size 3.6 and 4.8 nm in the calcined and O_2 plasma treated samples, respectively.

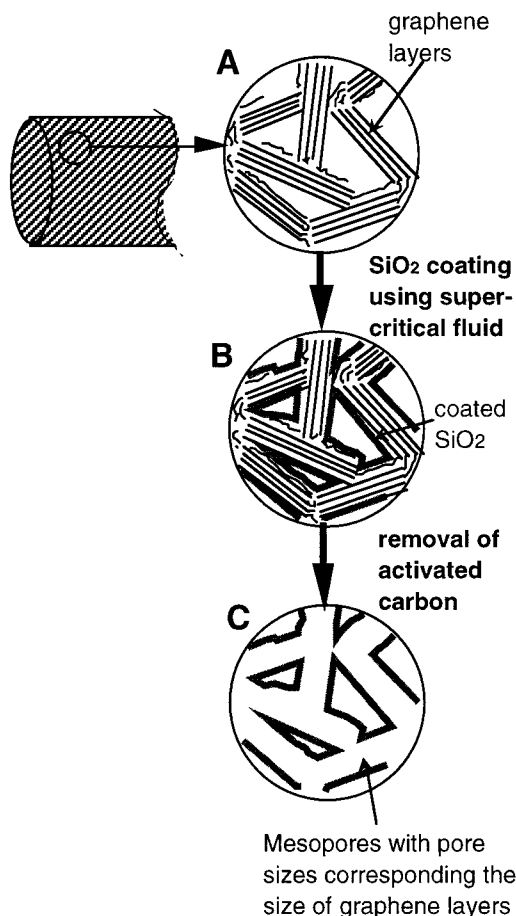


Figure 2. Proposed schematic description of the SiO_2 coating process using supercritical fluid and the formation of SiO_2 castoff skin. Franklin's model for pregraphitic carbon is shown in (A). Stacked graphene layers are represented by straight lines. (B) shows the activated carbon coated with SiO_2 . The surfaces of micropores between graphene layers are coated with SiO_2 using supercritical fluid. After the removal of activated carbon by calcination in air or in O_2 plasma, mesopores with the sizes corresponding with the size of the graphene layers appear, as shown in (C).

Figure 2 shows the proposed schematic description of the SiO_2 coating process using supercritical fluid and the formation of the SiO_2 replicate. The structure of the activated carbon is supposed to be quite similar to Franklin's view⁹ of pregraphitic carbon (Figure 2A). Bent or curved lines represent criss-cross linkages or buckled graphene layers. The spaces between graphene layers are the micropores in the activated carbon. The temperature and the pressure in the vessel in the typical coating process of SiO_2 were 393 K and 26 MPa, respectively, which were beyond the critical temperature (304 K) and the critical pressure (7.38 MPa) of CO_2 . In the SiO_2 coating process, TEOS, the precursor of SiO_2 , dissolved in supercritical CO_2 is supposed to be carried into micropores of the activated carbon. The precursor is presumed to be hydrolyzed with hydroxyl units and adsorbed water molecules on the surface of the activated carbon. The surfaces of the micropores between crystallites were coated by SiO_2 layers whose thickness would be so thin that SiO_2 layers have little influence on the isotherm of A-20 (Figure 1). Removal of carbon fibers with nanometer size yields mesopores in the resultant SiO_2 (Figure 2C). The size of mesopores of these samples corresponds to the size of crystallites. Crystallite sizes along the c -axis (L_c) and a -axis (L_a) of activated carbon were estimated to be 1.4 and 2.5 nm, respectively, which were

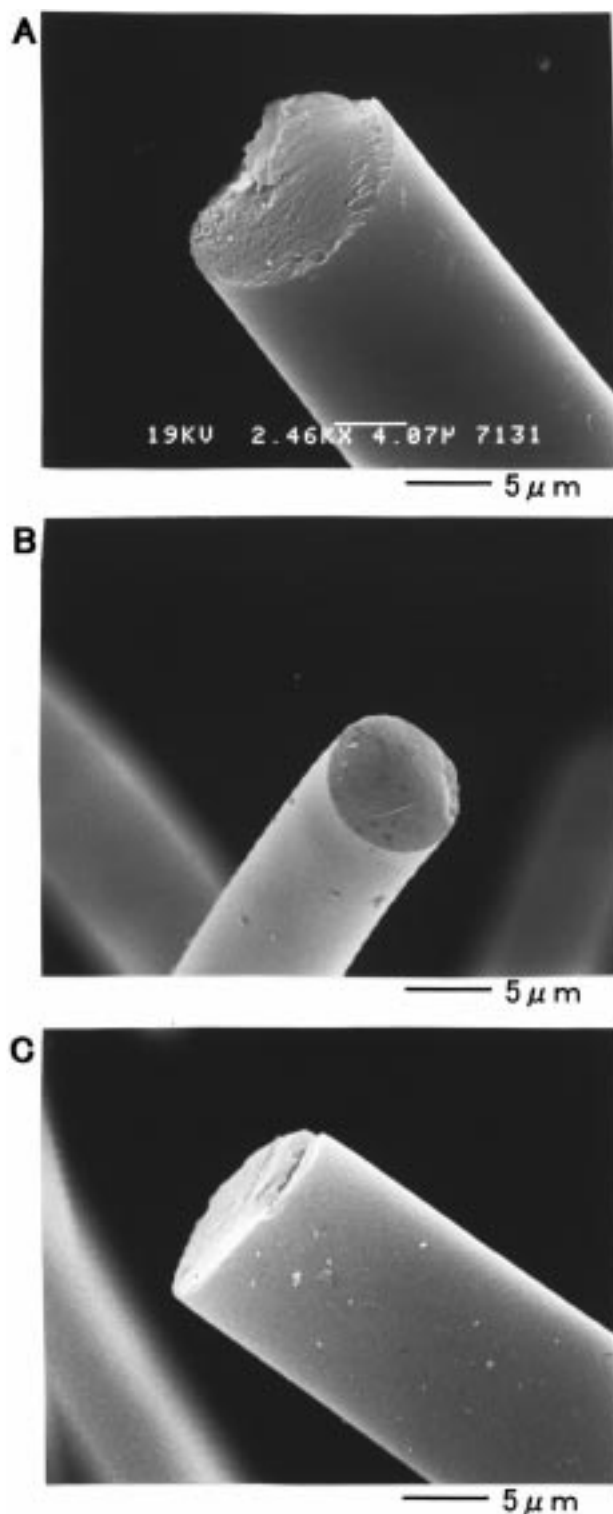


Figure 3. SEM images of (A) activated carbon fiber A-20 (BET surface area 1747 m²/g), (B) SiO₂ fiber after the removal of A-20 by calcination in air from SiO₂-coated A-20 in supercritical fluid (BET surface area 1294 m²/g), and (C) SiO₂ fiber after the removal of A-20 by calcination in O₂ plasma from SiO₂-coated A-20 in supercritical fluid (BET surface area 1180 m²/g) obtained on an AKASHI SIGMA-V scanning electron microscope.

determined from the half widths of 002 and 110 lines in XRD pattern, respectively. The actual sizes of structural units would

be a little bit larger than those estimated with XRD results, because of the disordered structure of activated carbons. The pore sizes in the SiO₂ sample after the removal of A-20 by O₂-plasma treatment are supposed to correspond to the actual sizes of structural units. During the O₂-plasma treatment, the temperature of the sample is about 453 K. The treatment could remove the carbon without significant rearrangement of SiO₂ to yield an extremely faithful replicate of the original microstructures of carbon fibers. The removing of carbon by calcination in air caused shrinkage by some rearrangement in SiO₂.¹⁰ Thus, the size of the pores in the sample calcined in air was smaller than that of the sample treated with O₂ plasma.

The pore size distribution in the resultant SiO₂ replicate was strongly dependent on the size of the crystallite mold. In the case we used other activated carbon (Kureha Chemical Co., commercial name D7) with larger size of the crystallites ($L_c = 5.9$ nm, $L_a = 9.5$ nm) as the base material, the BJH pore size of the SiO₂ after removing activated carbon with O₂-plasma equipment was 7.5 nm. In this case, the pore sizes of SiO₂ are also presumed to correspond to the size of the crystallites of the activated carbon D7.

As shown in Figure 3, the sample calcined in air at 873 K (B) or in oxygen plasma (C) after the treatment in supercritical CO₂ retained the fibrous shape of the base-activated carbon (A). The fibrous shape in the same size can be replicated in the sample calcinated in oxygen plasma. In contrast, a little shrinkage in size can be observed in the sample calcinated in air.

The SiO₂ content in this sample prepared by the CVD method determined from the reduction in the sample weight from at 423 to 1173 K measured on TGA was less than 1/3 of that of the sample prepared using supercritical CO₂. This result would indicate that a good quantity of TEOS could be dissolved in supercritical CO₂.

We have demonstrated that activated carbons could be fine casting molds to control the micro- to macroscale structure of materials. And we also confirmed that such a faithful reflection in the nanoscale structure is realized by using the supercritical fluid as a solvent. Such an advantage of the supercritical fluid as a media would be attributed to the property that the supercritical fluid cannot produce a condensed phase.

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