

## SYNTHESIS AND CHARACTERIZATION OF HIERARCHICALLY POROUS SILICA WITH POPLAR TISSUE AS TEMPLATE WITH ASSISTANCE OF SUPERCRITICAL CO<sub>2</sub>

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Hierarchically porous silica samples, ranging from mesopores to macropores, were prepared by “nanoscale casting using supercritical (SC) fluids” (NC-SCF) technology and bionics, achieving a biomineralization process in an environmentally friendly and efficient way. These wood-templated SiO<sub>2</sub> samples, having special hierarchical pore sizes from 3.3 nm up to 50 μm, were obtained with SC-CO<sub>2</sub> precursor solution by a wood-silication method. For this method, the precursor, tetraethyl orthosilicate (TEOS), was dissolved in SC-CO<sub>2</sub> and impregnated into poplar tissue cells using SC-CO<sub>2</sub> as a mass carrier. After removal of the wood template by calcination in air at suitable temperatures, the porous silica was obtained. The effects of CO<sub>2</sub> pressure and precursor concentration on the impregnating ratio were studied, and the products were characterized. SEM experimental results showed that the obtained silica had the same external and internal structures of the original wood. XRD and N<sub>2</sub> absorption-desorption results indicated that the silica was amorphous but crystallized with the calcination temperature up to 1000°C, and had a preferable BET surface area being up to 469 m<sup>2</sup>/g (600°C). So this work provides a simple and timesaving route to obtain and control the special microstructure of silica with the aid of a wood template in supercritical CO<sub>2</sub>.

*Keywords:* Supercritical carbon dioxide; Wood template; Silicon oxide; Porous; Hierarchical

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### INTRODUCTION

Porous materials, such as micropores, mesopores, and macropores, are amazing because of the huge surface area or selectivity as well as their functional properties. However, the free-control of microstructures of materials is still the main interest of researchers who are involved with chemistry and material science. Usually the basic methods include hard/soft templates replication, in which the micro-domains are based on multiphase compatibility or aggregation, etc. The synthesis of inorganic frameworks with specified pore networks is of potential importance in all kinds of fields, such as catalysis (Tanev et al. 1994; Burch et al. 1996), separation technology (Barrer 1982), and biomaterials engineering (Ohgushi et al. 1992; Guillemin et al. 1987), lightweight ceramics (Walsh and Mann 1995), electromagnetic absorbing and shielding (Shibata et al. 1997), fuel cell electrode materials, controlled drug delivery devices, and membrane reactors, etc. (Yuan and Su 2006). Ordered arrangements of mesoporous channels in silica-based materials are usually produced by post-treatment for removal of surfactant templates (Kresge et al. 1992; Beck et al. 1992). The

fabrication of inorganic materials with structural hierarchy can be combined by supramolecular and supercellular templates (Davis et al. 1997; Lakes 1993). Hierarchical materials containing both interconnected macroporous and mesoporous structures have enhanced properties compared with single-sized pore materials due to increased mass transport. Bimodal mesoporous–macroporous inorganic materials can be prepared by using a self-assembling surfactant or amphiphilic block copolymer species in conjunction with macrotemplates such as colloidal crystals, polymer foams, bio-celluloses, and emulsions (Yuan and Su 2006).

Materials from nature can be morphologically complex with sophisticated structure and ordering. Now the biological templating method (Tirrell et al. 1994; Dan 2000; Sarikaya 1999; Aksay and Weiner 1998) has succeeded in bridging the materials-biology gap. Recently it has been extended to various bio-templates ranging from biomacromolecules [DNA for metallic nanowires or nanocomposites (Jan et al. 2001; Richter et al. 2000; Le et al. 2004; Numata et al. 2004); block copolypeptides for SiO<sub>2</sub> (Cha et al. 2000)], microorganisms [bacteria for SiO<sub>2</sub>, zeolite and Fe<sub>3</sub>O<sub>4</sub> (Zhang et al. 2000; Davis et al. 1997; Smith et al. 1998); tobacco mosaic virus for SiO<sub>2</sub> or inorganic-organic nanotube composites (Fowler et al. 2001; Shenton et al. 1999); yeast cells for Al<sub>2</sub>O<sub>3</sub> (Towata et al. 2005); marine algae for CaCO<sub>3</sub> (Walsh and Mann 1995)] to plants [woods for carbides such as SiC (Ota et al. 1995; Greil et al. 1998; Qian and Jin 2006; Sieber et al. 2000) and TiC (Sun et al. 2004), oxides like SiO<sub>2</sub> (Shin et al. 2001), zeolite (Dong et al. 2002), TiO<sub>2</sub> (Cao et al. 2004; Huang and Kunitake 2003; Caruso 2004; Ota et al. 2000), Al<sub>2</sub>O<sub>3</sub> (Cao et al. 2004; Rambo and Sieber 2005), Fe<sub>2</sub>O<sub>3</sub> (Liu et al. 2005), Cr<sub>2</sub>O<sub>3</sub> (Fan et al. 2006), and ZrO<sub>2</sub> (Rambo et al. 2004), and composites like SiSiO/C (Zollfrank 2004); cotton for SiC (Krishnarao and Mahajan 1996); cloth or cotton for TiO<sub>2</sub> (Huang and Toyoki 2003)], and animal tissues [butterfly for SiO<sub>2</sub> (Cook et al. 2003); cuttlebone for chitin–silica composites (Ogasawara et al. 2000); Morpho for CaCO<sub>3</sub> (Walsh et al. 1999); eggshell membrane for TiO<sub>2</sub> tube (Yang et al. 2002)] for the preparation of biomimetic materials, such as metallic or nonmetallic oxides with various morphologies of nanowire, nanotube or bulk sample with hierarchical pores. Wood provides an excellent natural template with a hierarchically porous structure. The scales range from millimeter scale of growth rings and vessel pores, the micrometer scale of transversely radiating parenchyma and longitudinal tracheid or fiber, to the nanometer scale of molecular fiber and cellular membrane (Tirrell et al. 1994; Qian and Jin 2006). The materials from biomaterial's hierarchical tissues are available for the tailoring of meso- or macropores. In addition, macroscopic shapes of porous materials are also important for applications such as plastic molding or metal casting in industrial processes (Wakayama and Fukushima 2000), which easily can benefit from morphological characteristics that they inherit from biomaterials.

Supercritical fluids (SCFs) are of great interest because of their unique properties of low viscosity, high diffusivity, and controllable solubility by changing the temperature and/or pressure or by adding suitable modifier (Cooper 2003; Darr and Poliakov 1999; Etesse et al. 1992; Dobbs et al. 1987). Among the SCFs, SC-CO<sub>2</sub> is especially important because it is nonflammable, nontoxic, and inexpensive. Moreover, SC-CO<sub>2</sub> can dissolve most organic small molecules; thus it is expected to carry a quantity of precursors into the fine spaces of the raw matrix. Supercritical fluids have shown their advantages in making nanoscale materials (Johnston and Shah 2004; Pai et al. 2004). Also the novel process for material

synthesis called “NC-SCF” has been developed by Wakayama’s group for activated carbon templated nanoporous materials (Wakayama and Fukushima 2000; Wakayama and Fukushima 1999; Fukushima and Wakayama 1999). Compared with the traditional processes, the high mass-carrying power and controllable dissolvability of precursors in SCFs but without harmful organic solvent residue may give us a surprise in a preferable nanoscale casting or porous materials (Shin et al. 2001; Dong et al. 2002; Liu et al. 2005; Fan et al. 2006). In this study, we adopt the NC-SCF process and the poplar tissue as template for the preparation of hierarchically porous silica. The meso-scale to macro-scale hierarchical replication of the porous structures of silica is confirmed.

## MATERIALS AND METHODS

### Materials

Materials included poplar slices (10×10×6 mm<sup>3</sup>), aqueous ammonia (AP, Luoyang Henghui Chem. Ltd.), HCl (AP, Kaifeng Kaihua reagent Ltd.), ethyl alcohol (AP, 95%, Guoyao group Chem. Ltd.), tetraethyl orthosilicate (TEOS, AP, Guoyao group Chem. Ltd.), CO<sub>2</sub> (99.9%, Zhengzhou Shuangyang gas Co.), and deionized water.

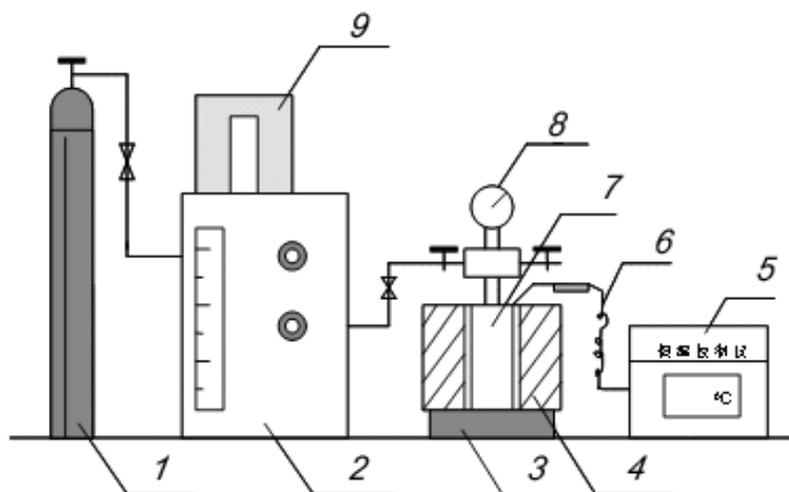
### Main Apparatus and Instruments

A single cylinder injection pump (DB–80) was provided by Beijing Weixing Co. A stainless steel autoclave (50 ml), attached with electric heating collar and thermostatic controller, was supplied by Jiangsu Haiyan instrument plant. A muffle furnace (5–12) was from the Shenyang electric furnace plant.

### Experimental Process of Porous SiO<sub>2</sub>

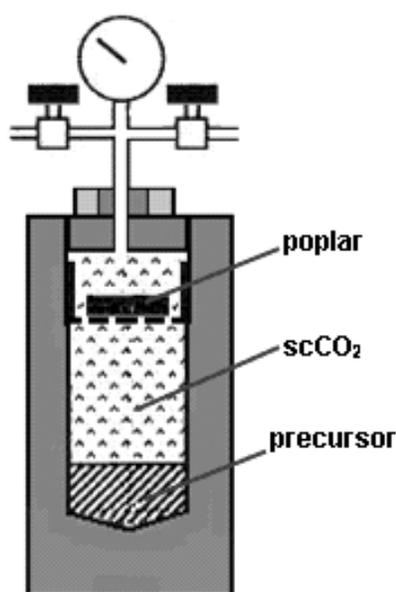
The production of “silicified wood” was performed using the following process: (i) introduction of precursor into wood material via supercritical fluid, (ii) hydrolysis of the precursor in the cell structure to form a silica gel, and (iii) calcination at an appropriate temperature in air. The typical process and conditions were as follows. The raw poplar was cut into slices and extracted by boiling aqueous ammonia (5%) twice, and then HCl (5%), for purification before use.

The experimental apparatus is shown in Scheme 1. TEOS (8 ml) was placed in a stainless steel autoclave of 50-ml capacity. Then the prepared poplar template was placed in a stainless cage fixed at the upper part of the autoclave without touching with liquid TEOS at the bottom, as shown in Scheme 2. Later the autoclave was filled with CO<sub>2</sub>, and the samples were treated under various experimental conditions. After depressurization the sample was immersed in the hydrolyzing solution (the molar ratio of alcohol, water, and HCl is 4:4:1) for 1 h with a few minutes of ultrasonic vibration ahead. The hydrolyzed sample was dried at 80°C for 8 h in normal atmospheres. The poplar tissue template was then removed by calcination at 600 °C, 800 °C, or 1000 °C for 4 h in air.



**Scheme 1.** Experimental equipment.

(1 CO<sub>2</sub> cylinder, 2 injection pump, 3 magnetic stirring apparatus, 4 heating collar, 5 thermostatic controller, 6 thermocouple, 7 autoclave, 8 pressure gauge, 9 ice box)



**Scheme 2.** Schematic illustration of an autoclave and cage used to treat samples in SC-CO<sub>2</sub>.

### Characterization of Porous SiO<sub>2</sub>

Nitrogen adsorption-desorption isotherms were obtained at 0 °C and with an outgas temperature at 100 °C on a surface energy and pore size analyzing instrument, QUANTACHROME NOVA 1000e. The BJH (Barrett-Joyner-Halenda) method on the desorption branch was used to determine the mesopore size distribution. XRD data for porous silica was recorded by RIGAKU MAX-III B, using CuK $\alpha$  radiation and 6°(2 $\theta$ )/min of scanning speed with the 2 $\theta$  range of 10–80°. Scanning electron microscope (SEM) observation was performed using a FEI QUANTA 200 SEM.

## RESULTS AND DISCUSSION

In this study several factors related to coating ratio of precursor on the substrate were studied, e.g. 1) the pressure of the supercritical CO<sub>2</sub> and 2) the concentration of precursor in the impregnation system. The impregnation/coating ratio is identified as follows:

$$\text{coating ratio} = m_c/m_0, \quad (1)$$

where  $m_0$  is the mass of dry poplar slice, and  $m_c$  is the impregnation mass of precursor into the poplar slice.

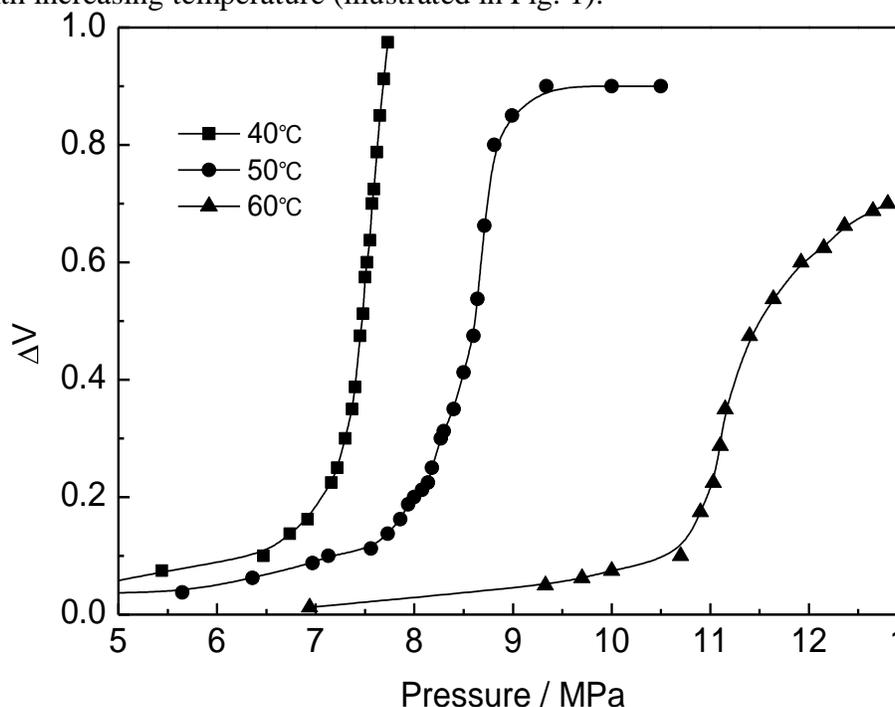
### Compatibility of Precursor and CO<sub>2</sub>

During the SC-CO<sub>2</sub> assisted impregnation/coating process, the precursor should be soluble in CO<sub>2</sub>. Thus it is necessary to study the miscibility of CO<sub>2</sub> in the precursor, and the high-pressure phase behavior of precursor TEOS in CO<sub>2</sub> was first investigated. The extent of miscibility is reflected in the volume expansion of the liquid phase. The volume expansion of the liquid phase  $\Delta V$  at a certain pressure  $P$  and temperature  $T$  is defined by

$$\Delta V = [V(P, T) - V(P^0, T)] / [V_0 - V(P^0, T)] \quad (2)$$

where  $P^0$  represents the atmospheric pressure, and  $V_0$  represents the volumetric capacity of the windowed autoclave (50-ml in our experiment).

The solvent power of SC-CO<sub>2</sub> was enhanced as a function of pressure, but it decreased with increasing temperature (illustrated in Fig. 1).



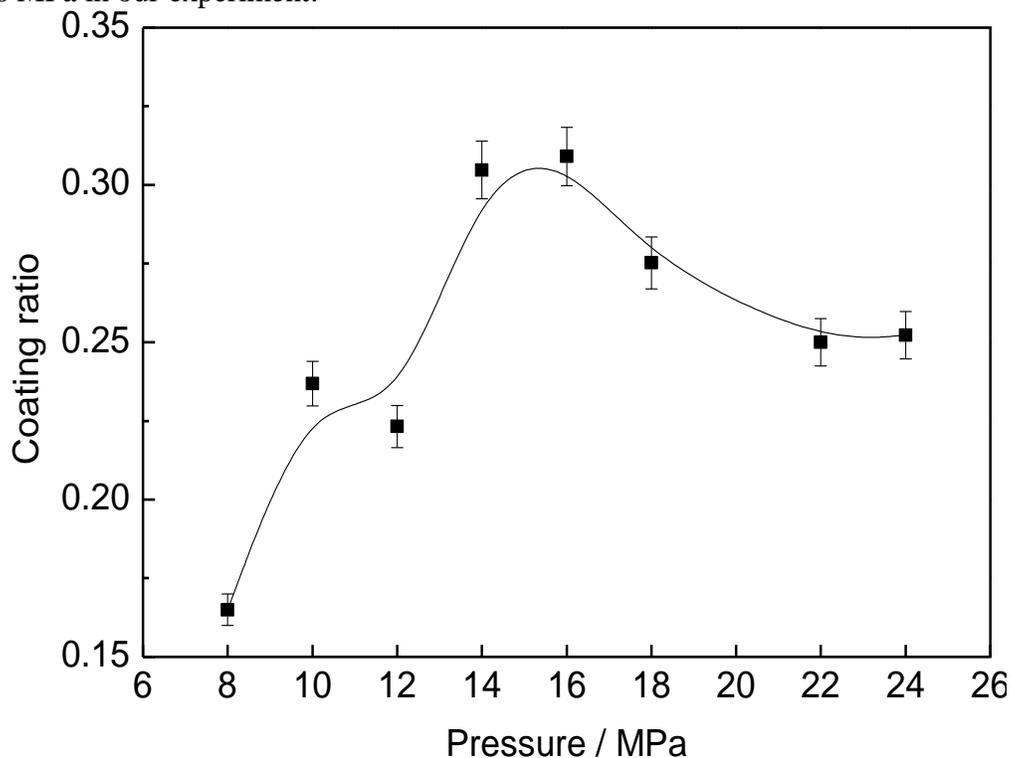
**Figure 1.** Function of biphasic compatibility of precursor TEOS with SC-CO<sub>2</sub> versus CO<sub>2</sub> pressure and temperature. (c=8% v/v)

It can be seen that the miscibility of CO<sub>2</sub> in the precursor increased when the CO<sub>2</sub> pressure rose, while the biphasic compatibility decreased with the temperature rising from 40°C to 60°C, with critically compatible pressures of ca. 7.5 MPa at 40°C, 8.5 MPa at 50°C, and 11.5 MPa at 60°C. These phenomena may be illustrated by the classic physicochemical theory, attributing to the relations of density and dissolvability of SC-CO<sub>2</sub> under various conditions.

## EFFECTS OF EXPERIMENTAL PARAMETERS ON COATING RATIO

### Effects of CO<sub>2</sub> Pressure

The dependence of the coating ratio on the experimental pressure is shown in Fig. 2. The coating ratio increased initially with increasing pressure, reached a maximum at 16 MPa, and then was reduced with further increase in pressure. So there existed a maximum point in the range of our study, and this phenomenon is thus explained: CO<sub>2</sub> is a poorer solvent for the precursor at a low pressure, and so only a limited amount of dissolved precursor (in other words, 8 ml precursor TEOS was not totally dissolved in SC-CO<sub>2</sub> at this stage in our experiment) can permeate into and coat the poplar matrix assisted by SC-CO<sub>2</sub>. With an increase of pressure, the limited amount increases and the coating ratio rises, and this trend is maintained until the dissolution of all TEOS molecules in SC-CO<sub>2</sub> is initially achieved at about 16 MPa in our experiment.

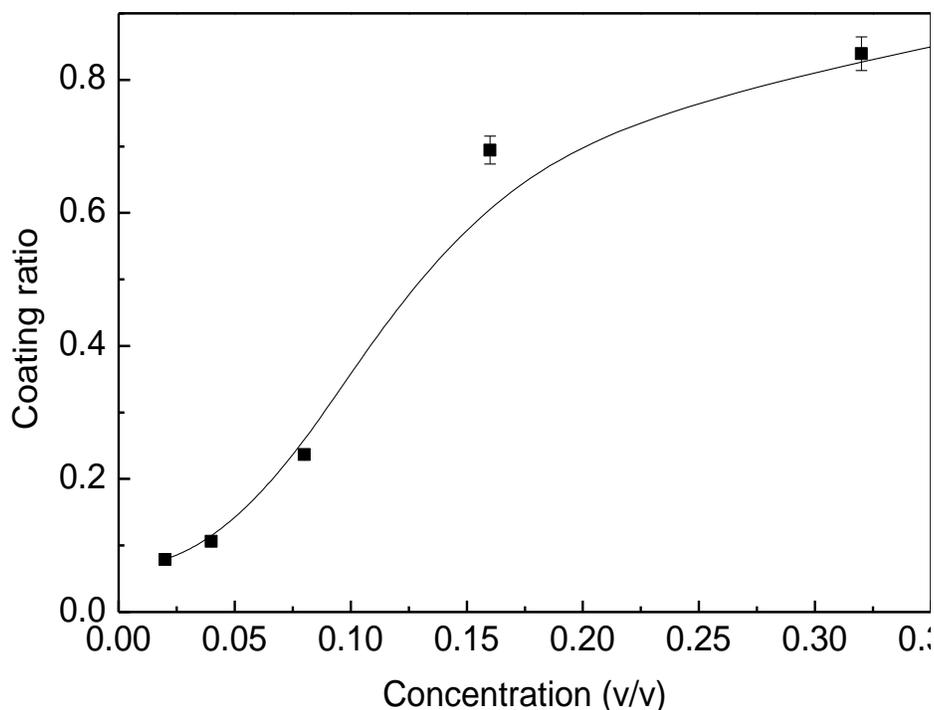


**Figure 2.** Function of coating ratio of precursor TEOS on/poplar tissue matrix on CO<sub>2</sub> pressure. (T=40°C, t=1 h, c=16% v/v)

But when the experimental pressure continues to increase, a larger proportion of precursors remain in the SC-CO<sub>2</sub> fluid phase, not coating or permeating into the poplar matrix because of the enhanced solvent power of SC-CO<sub>2</sub>. That's to say, there is a competition effect between the adsorption of precursors into the matrix and the dissolution of precursors in SC-CO<sub>2</sub> solvent. So we come to a conclusion that, at some intermediate pressures, these binary opposite effects of supercritical solvent on the dissolution of precursor and the coating or permeating into template can be balanced, and the maximum of coating ratio is observed. This phenomenon has also been observed for supercritical impregnation by other scientists (Watkins and McCarthy 1995).

### Effects of Precursor Concentration

Figure 3 shows the dependence of coating ratio upon the concentration of precursor. It was observed from the experimental results that the coating ratio increased continuously with the increase of precursor concentration from 0.02 to 0.32 v/v. It can be suggested that within the range of precursor concentration in this experiment, the precursor/SC-CO<sub>2</sub> binary system is homogeneous, and SC-CO<sub>2</sub> can carry more precursor into the meso- or macropores of the wood template.

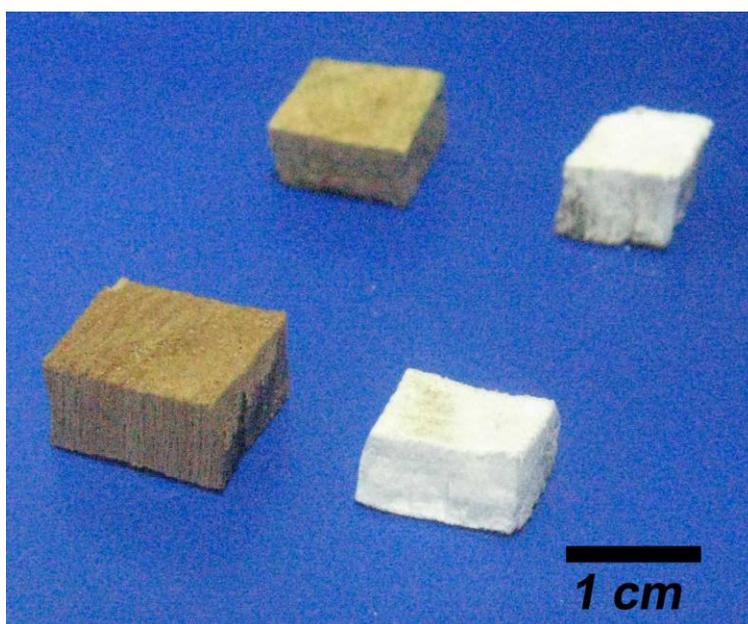


**Figure 3.** Function of coating ratio of precursor TEOS into matrix poplar tissue on TEOS concentration. (P=10 MPa, T=40 °C, t=1 h)

### Morphology of Porous SiO<sub>2</sub>

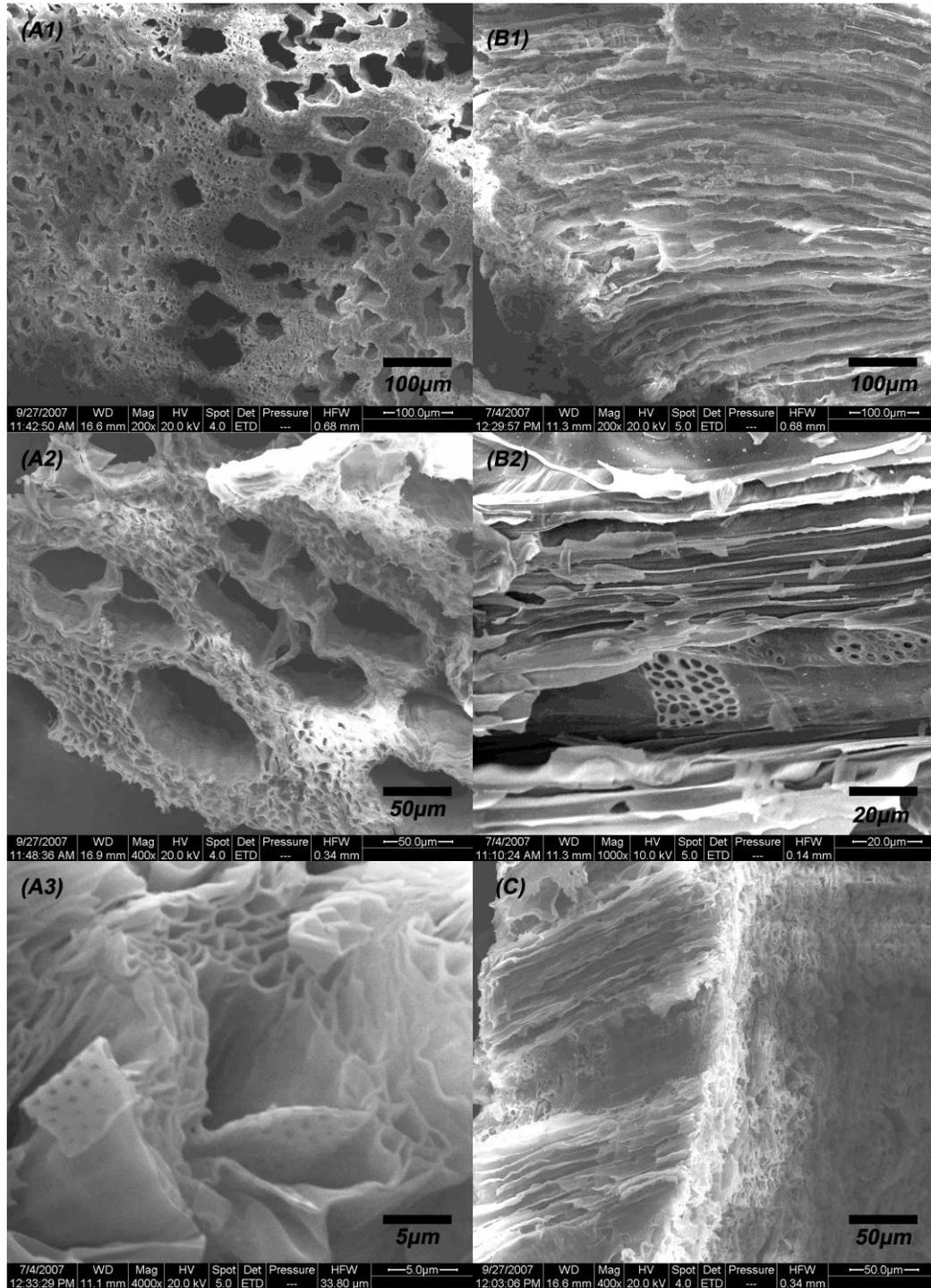
Figure 4 shows a photo of original poplar wood slices, i.e., the template material, and silica replicas. It can be seen clearly that the white silica replicas retained the macroscopic shape of the poplar template, but some volumetric shrinkage was also observed for the calcined samples. On the other hand, the inherited microscopic structures of the poplar tissue

were concomitantly retained in the silica replica (shown in Fig. 5). Figure 5(A<sub>1</sub>,A<sub>2</sub>,A<sub>3</sub>), (B<sub>1</sub>,B<sub>2</sub>) and (C) show the SEM pictures of the transverse, longitudinal-sectional, and side view configurations of poplar-templated silica calcined at 800 °C. The well-aligned porous framework was observed in micron scale, and the pores from vessels with diameters about 5–50 μm and tracheids or fibers with diameters 1–5 μm were kept by the silica. The above-mentioned images show an overall view indicating that pores from cells or fibers were tubular and three-dimensional. The entire cellular structure was well preserved, and adjacent tracheids were linked together by middle lamellae (Greil 2001). In addition to the macrocellular structure, the obtained silica tissue also retained the detailed microstructure of the wood cells (Fig. 6). The faithful replication included the insides of the hollow vessels, and some tinier or finer microstructures, such as mesh-like tissue replicas (A&B in Fig. 6), which were continuous or discontinuous, and the rough inner-surfaces or rings (Fig. 6C) were also maintained. The tracheids, vessels and hollows were replicated within the size range between 1 μm and 50 μm.

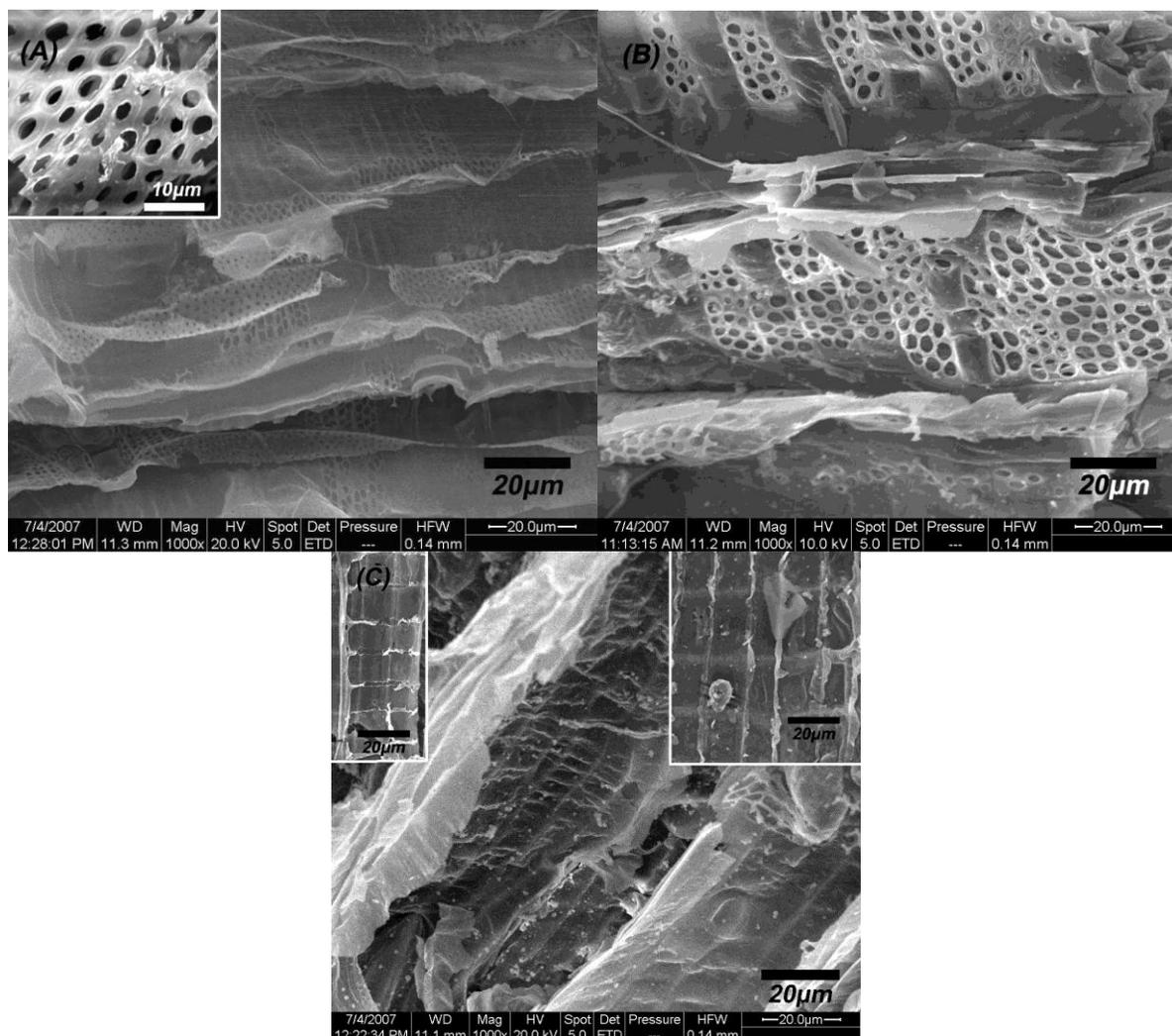


**Figure 4.** The macroscopic shape of the poplar slices and templated silica calcined at 600 °C.

The work shown confirms earlier findings that the porous silica replica inherits the structural features in wood template such as hierarchy, selectivity, and anisotropy (Greil et al. 1998). The SC-CO<sub>2</sub>-assisted replicating process can be illustrated by a mechanistic pathway for the formation of hierarchically porous silica, as shown in Scheme 3: Silica precursors, TEOS, are dissolved in SC-CO<sub>2</sub> and are carried into the hierarchical tissue's hollow microstructures or even nano-cavities of the wood template. The TEOS then hydrolyzes and polymerizes to form a silica network by reaction with hydroxyl units in the hydrolyzing solution. The surface of the vessels, pores, and interstitial spaces of wood template were coated with silica layers. After the removal of template, the silica was left behind, with hierarchical structure corresponding to the size and morphology of the wood tissue.



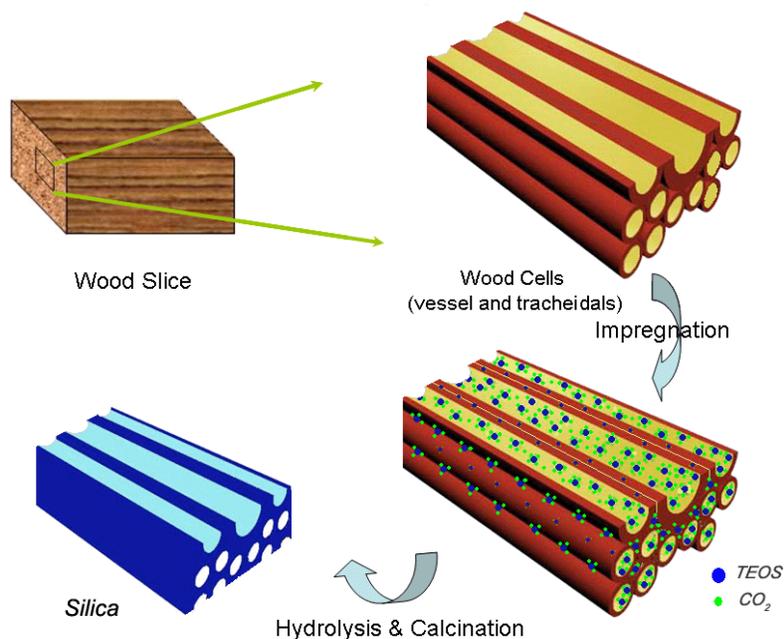
**Figure 5.** SEM images of the A<sub>1</sub>,A<sub>2</sub>,A<sub>3</sub>) cross-section, B<sub>1</sub>,B<sub>2</sub>) axial cross-section, C) oblique view of poplar reproduced silica porous samples calcined at 800 °C. (Impregnation process conducted under the following SCF conditions: P=10 MPa, T=40 °C, c=16% v/v, t=1 h)



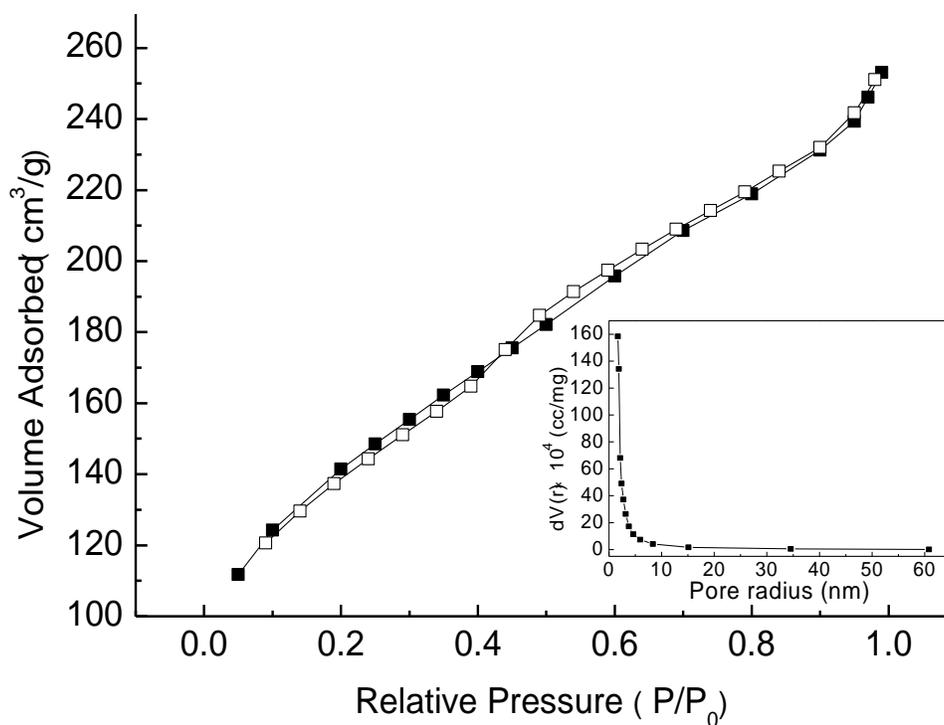
**Figure 6.** SEM views from the longitudinal section of tissular vessels of the poplar template replicated by silica calcined at 800 °C. (Impregnation process conducted under the following SCF conditions: P=10 MPa, T=40 °C, c=16% v/v, t=1 h)

### Porosity of Porous SiO<sub>2</sub>

From N<sub>2</sub> adsorption-desorption measurements, the isotherm and corresponding pore size distribution (PSD) curve for poplar-templated silica calcined at 600 °C are shown in Fig. 7. The sample exhibited a typical IV-type isotherm with a H3-type hysteresis loop on the basis of the IUPAC classification. IV-type isotherms are caused by the capillary condensation of mesopores, and H3-type hysteresis loops are attributed to asymmetric slot-shape mesopores and channels in coincidence with the tubularly characteristic pores or interstitial space in wood templates. The type of isotherm indicates an interconnected mesoporous system and very high pore connectivity according to the percolation theory (Seaton 1991). Further, from the nitrogen adsorption-desorption isotherm, the BET surface area of the porous silica was calculated to be 469 m<sup>2</sup>/g, the total pore volume was 0.392 ml/g, and the PSD curve calculated by BJH method showed that the mesoporous average diameter of the sample was 3.34 nm.



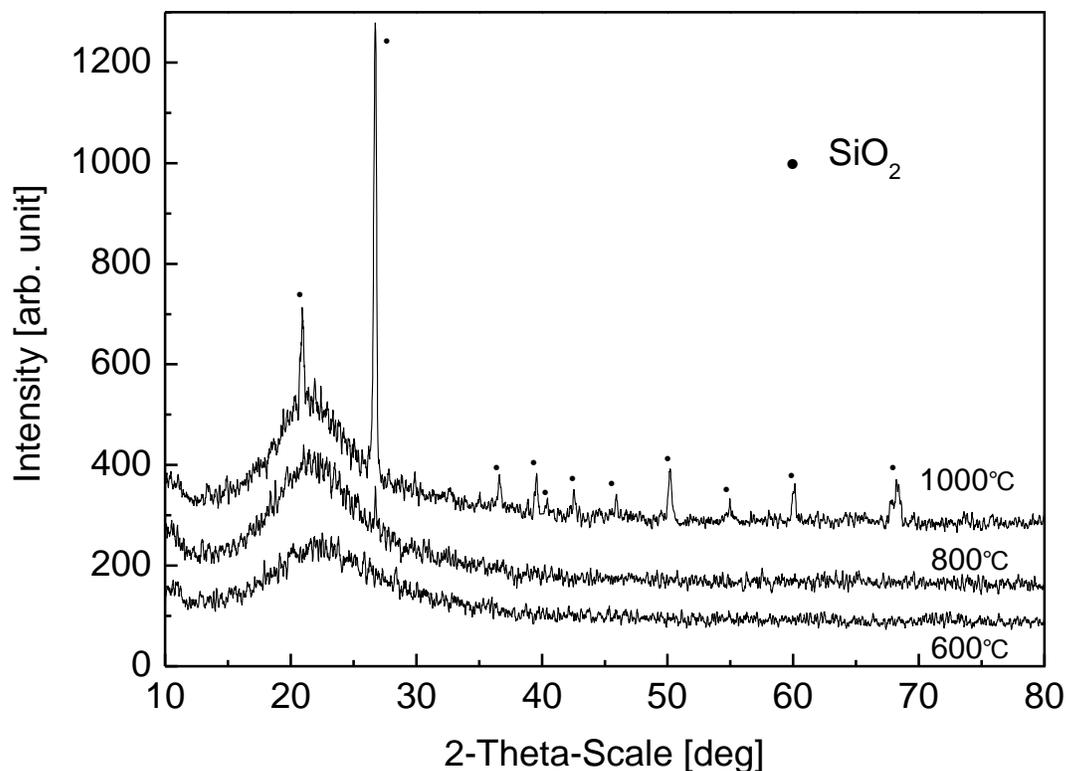
**Scheme 3.** Illustration of fabrication of hierarchically organized silica materials from wood tissue.



**Figure 7.** N<sub>2</sub> adsorption-desorption isotherm and mesopore size distribution curve for porous silica after removal of poplar template by calcination at 600°C in air from silica-coated poplar template in SC-CO<sub>2</sub>. (Impregnation process conducted under the following SCF conditions: P=10 MPa, T=40 °C, c=16% v/v, t=1 h)

### XRD Analysis of Porous SiO<sub>2</sub>

The samples were pulverized for powder X-ray diffraction characterization. In Fig. 8, XRD patterns of all the samples from different calcination temperatures are illustrated. According to these patterns, the original components of wood were removed, and the SiO<sub>2</sub> was confirmed as the single phase. When the temperature rose, the peaks in the XRD pattern from the same wood template became more apparent. Higher temperature led to an increase in the size of the SiO<sub>2</sub> crystallites. It was also found that the silica changed from an amorphous into a crystalline phase with the calcination temperature up to 1000 °C.



**Figure 8.** XRD patterns of poplar-templated silica prepared with the impregnation process conducted under the following SCF conditions of 10 MPa, 40 °C, 16% v/v, 1 h, and calcined at 600 °C, 800 °C, and 1000 °C. (Referenced JCPDS cards No. 50490 & 331161)

### CONCLUSIONS

We have demonstrated the synthesis of mesoporous and macroporous silica, replicating both the macroscopic shape as well as nanoscale and microscale structures of poplar tissue template, using an environmentally friendly coating technology using SC-CO<sub>2</sub> as the carrier medium (Hay and Khan 2002). Supercritical fluid was shown to be an effective solvent assisting the microstructure replication to produce hierarchical materials with designed macroscopic shapes. The process can be applied over a range of structural or functional ceramics or metals whose structures and properties are needed to be controllable. Further, the prepared macroscopic special shape and microscopic hierarchically porous materials may have potential application in building functional materials such as sorbents, sensors, catalysts, or structural supports in catalytic devices.

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