Fast fabrication of mesoporous SiC with high and highly ordered porosity from ordered silica templates

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Three-dimensional (3D) mesoporous SiC samples with highly ordered porosity were prepared using three different routes. The essential difference was in the first step in which sacrificial uniform silica spheres were packed into ordered three-dimensional arrays using: i) sedimentation, ii) centrifugation and iii) electrophoretic deposition (EPD) methods. Regardless of the method used, the quality of arrays was quite high and reproducible. The prepared silica arrays were infiltrated with a pre-ceramic polymer precursor. The infiltration step was followed by a thermal curing step, a pyrolysis step at 850 °C in an Ar atmosphere and, finally, removal of the silica templates by etching with a 3 M NaOH solution. The final products were porous 3D SiC samples with typical volumes around 1 cm^3 and a pore size of 240 or 650 nm. The synthesized porous SiC was characterized using SEM, TEM and XRD methods.

Key words: Silica, Silicon carbide, Sacrificing template method, Electrophoretic deposition, Porous material.

Introduction

Porous SiC ceramics show unique characteristics such as a low specific weight, low thermal conductivity, controlled permeability, high chemical stability and thermal shock resistance, high surface area and high specific strength. On these bases, they have found many applications including filtration of molten metal, filtration of solid particles from diesel engine exhaust gases, filtration of hot corrosive gases in various industrial applications, gas-burner media, membrane supports for hydrogen separation and light-weight structural parts for high temperature applications [1-5]. Ceramic foams are also used as catalyst supports, thermally-insulating materials, fire protection materials and thermal protection systems in the space shuttle [6, 7].

The numerous applications have triggered intense research into well-defined porous SiC self-standing materials. For example, porous SiCN and SiC with a 3D ordered porosity have been prepared using a colloidal silica template (colloidal crystals) in combination with polycarbosilane as a precursor for SiC ceramics [8, 9]. Furthermore, the pore characteristics of the porous SiC samples achieved have been tailored using different sizes of sacrificial silica spheres [10]. Besides latex, silica spheres are the most investigated type of particles for colloidal crystal assembly, as they can be obtained both highly monodispersed [11] and relatively cheaply.

Many methods have been developed for the preparation of colloidal crystals. Among the ones that have been used most frequently are gravity sedimentation [12], centrifugation [13], vertical deposition [14], electrophoresis [15], template deposition, and controlled drying [16]. As regards silica-based templates for the preparation of porous SiC, however, only the gravity sedimentation has been used [12, 17]. In this method, colloidal suspensions are placed in a container, and then sedimentation occurs driven by gravity. Obviously, this is a very slow process and thus of limited interest for use in real applications. Additionally, this method has very little control over the morphology of the top surface because the ordering forces are generally much weaker. Similarly, the final number of layers of the 3D crystalline arrays is difficult to assess with this method. Finally, the structure of the crystalline lattice usually consists of many randomly oriented domains, so it is not easy to obtain a uniform surface arrangement of particles.

It is well known that the process of gravity sedimentation can be improved via centrifugation [18]. In particular, the processing time can be reduced by one or even two orders of magnitude (from more than a week to about 1 h), but the dimensions of the parts produced still remain limited. The properties of such rapidly grown silica templates are here investigated in significant detail. We also demonstrate that the process for forming highly ordered bulk silica templates can be significantly enhanced by the use of electrophoretic deposition (EPD). The EPD method is based on an electric-field which induces deposition of electrically charged particles from the suspension onto an electrode [19-21].

Experimental Section

Preparation of monodispersed colloidal spheres
Silica nanospheres were synthesized following the Stöber-

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Fink-Bohn method (Stöber *et al*. 1968) [22] starting from tetraethyl orthosilicate (TEOS 98%, Aldrich), deionized water, ammonia (25%, Merck), and absolute ethanol (99.9%, Riedel-de Haën) as precursor alkoxide, hydrolyzing agent, catalyst and solvent, respectively. Two mother solutions were prepared, one containing ammonia-water and another one other containing TEOS- ethanol. The two solutions were mixed in a thermostatically controlled water bath (50 ± 1 °C). After 60 minutes, the resulting spheres were separated from the liquid phase by centrifugation and then ultrasonically dispersed in deionized water. The procedure was repeated three times. Then the particles were dried in an oven at 50 °C. Note that using this method, the final particle size critically depends on the reagent concentrations, molar ratio and reaction temperature, so that difficulties are usually encountered in obtaining both a good control of the sphere size in a wide dimensional range and monodispersity with a size distribution as narrow as possible. Nevertheless, quite good monodispersity has been achieved, as shown in the results and discussion section. In the present paper we apply the conditions described to well-defined silica particles having dimensions of either 240 or 650 nm.

Formation of three-dimensional (3D) arrays of colloidal spheres

To form colloidal crystals by gravity sedimentation, colloidal suspensions of SiO_2 particles (240 nm in diameter) in water (2 wt%) were placed in a container, and then the particles were left until fully sedimented. The sedimentation rate depends on the size of the particles. In our case it took typically about three weeks until full sedimentation was observed.

In the second set of experiments, the same suspensions were loaded into tubes and then centrifuged at about 4500 rpm for 5 minutes.

For the EPD experiments, stable ethanol suspensions containing 2 wt.% of silica particles (650 nm in diameter) were prepared. Zeta-potential and conductivity that play a key role in EPD were measured by a ZetaProbe device (ColloidalDynamics, USA). The deposition was performed at a constant DC voltage of 20 V for 5 minutes or 5 V for 5 and 20 minutes. Electrodes made of steel, both of dimensions : 30 mm × 10 mm × 0.2 mm, were vertically immersed in the suspension in the EPD cell. The distance between the electrodes was 1.5 cm. Before deposition, the electrodes were thoroughly cleaned in acetone using an ultrasonic treatment, washed with distilled water, and dried with compressed air.

The crystals formed by gravity sedimentation, centrifugation or EPD were left to dry, first at 50 °C for 24 hours and then at 700 °C for 7 hours.

Infiltration of PCS

The three-dimensional (3D) SiO_2 samples obtained in the previous steps were vacuum infiltrated with allylhidrido polycarbosilane (AHPCS) with the commercial name SMP-10 (Starfire SystemsInc., USA) following the processing scheme suggested by Iveković *et al*. [23]. Prior to infiltration, the polymer was agitated with a magnetic stirrer in order to degas the polymer and heated to 60-80 °C to decrease its viscosity from ~0.1 Pas at room temperature to 0.03-0.02 Pas. The samples were evacuated to 1000-500 Pa and then infiltrated with the polymer using a pressure difference between the chambers with the polymer and the sample. After polymer impregnation, multiple heat treatments were necessary: Before pyrolysis, the polymer was cured in a tube furnace in air at 400 °C for 1 h in order to achieve appropriate cross-linking of the polymer. The pyrolysis was carried out in an inert argon atmosphere at 850 °C for 1 h. During the pyrolysis, the AHPCS transforms into amorphous SiC, while during the crystallisation step carried out in an inert argon atmosphere at 1600 °C for 2 h, the amorphous SiC transformed into crystalline SiC. Thus, a composite structure composed of SiO_2 nanospheres embedded in SiC ceramic was formed.

Preparation of mesoporous SiC with high and highly ordered porosity

In the case of the 240 nm silica particles, SiO_2 was removed by etching with a 3 M NaOH solution at 60 °C for 24 h. In the case of the bigger particles, the procedure was the same except that the etching time was prolonged up to 30 h.

Characterisation

The samples were observed by a scanning electron microscope (FE-SEM Zeiss SUPRA 35VP) and a transmission electron microscope (JEOL JEM-2100). The domain size was estimated by measuring the equivalent area with highly densely packed ordered structure.

Results and Discussion

Fig. 1 shows SEM images of the as-prepared mono-dispersed Stöber *et al*. silica particles with a diameter of 650 nm and 240 nm (+/− 50 nm). Beside the electro kinetic and electric properties of the system, our experience shows that a narrow particle size distribution has an important influence on the packing into 3D arrays and helps minimize the density of defects in such arrays.

The aqueous suspensions of the 240 nm, as well as of the 650 nm silica spheres were highly stable and naturally settled very slowly. As summarised in Table 1, three weeks were needed to form a deposit appoximately 1 cm^3 in size. Under centrifugal force (centrifugation), the process was significantly faster and the size of about 1 cm^3 was formed already in five minutes. Approximately the same size was obtained in 5 minutes using the EPD method from an ethanol suspension. The surface area of the deposit is related to the surface area of the electrodes, while the deposition rate decreases with an increasing thickness and increases with deposition time. Up to a 1 cm thick deposit can be prepared in a reasonable time.
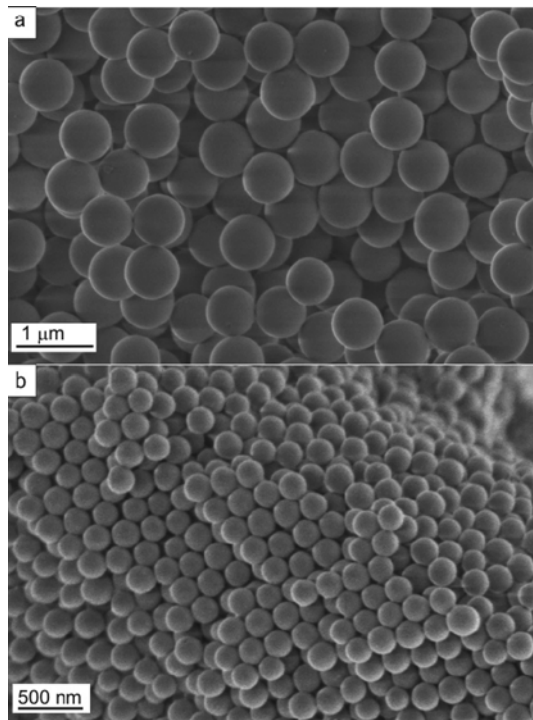
Fig. 1. SEM images of SiO$_2$ particles prepared according to the Stöber et al. procedure, a) 650 nm silica particles, b) 240 nm silica particles.

Table 1. The effectiveness of three different techniques of assembly of SiO$_2$ spheres with a diameter of 650 nm.

Forming technique	Time to form	Size of the compact (cm^3)	Average domain size (µm^2)
Gravitational sedimentation	3 weeks (650 nm) 6 months (240 nm)	1-10	100-600
Centrifugation	5 minutes	1	100
EPD	5-10 minutes	0.6-1	100

It has to be pointed out that the success of the EPD process is highly sensitive with respect to the surface charge of the particles in the suspension and, also, to its conductivity [24]. Despite the high dielectric constant of water, its drawback is electrolysis (a significant side reaction) that causes bubble formation during EPD. For this reason, ethanol suspensions rather than aqueous suspensions were prepared. Furthermore, with the aim to optimise the process, the suspension with the highest apparent zeta-potential (−117 mV) but moderate conductivity (0,5 mS/cm) was used in EPD. It has been reported that the size of domains decreases with a decrease in the zeta-potential; in the worst case, particle ordering is completely lost when the zeta-potential is too low. This occurs due to deposition of large floccules instead of individual particles which corrupts the arrangement of particles [21].

The microstructures of the SiO$_2$ colloidal crystals (compacts) formed from well-dispersed suspensions using the three techniques mentioned above are illustrated in Figs. 2(a)-(c), respectively.

A careful analysis of the micrographs shown in Fig. 2(a) to (c) and numerous similar micrographs obtained in this study shows that by using a well-dispersed suspension all three methods give 3D silica arrays of similar quality. The average domain size is 100 µm^2 but could be as big as 600 µm^2. In all cases dense packing is observed through the entire layer thickness, regardless of the direction of a break. In all the samples, similar types of defects such as point defects, missing lines or rows, steps, etc. are observed. The density of point defects is primarily dependent on the width of the silica particle size distribution and less on the preparation method. The density of non-point defects is also similar in all cases - there are about 100 defects within 1 mm along the given direction on the surface of each 3D array in Fig. 2.

Due to its simplicity, only the centrifugal sedimentation was used for preparation of porous SiC ceramics. The
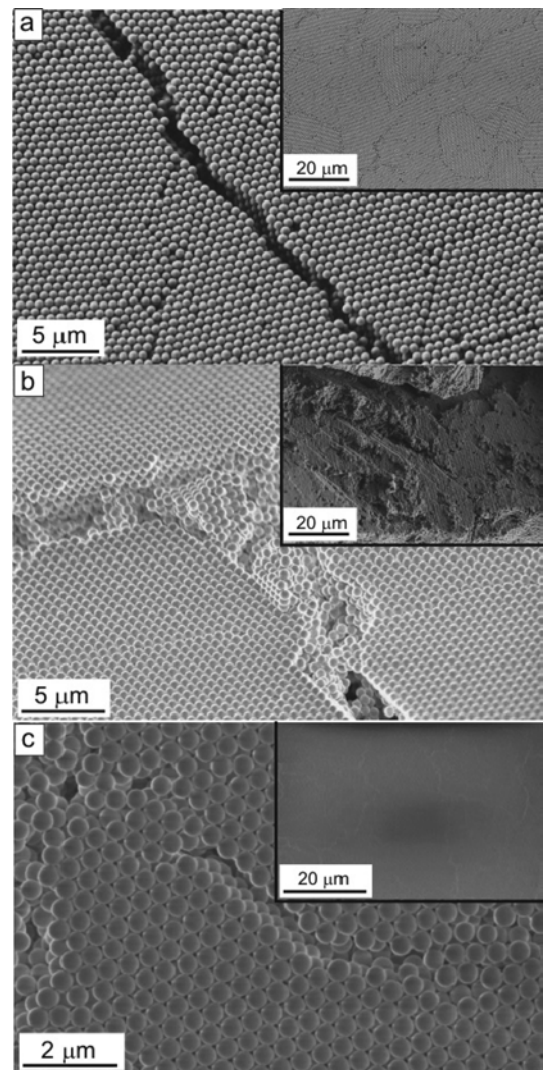

Fig. 2. SEM images of three-dimensional (3D) arrays of SiO$_2$ at different magnifications prepared by a) gravity sedimentation, b) centrifugation and c) the EPD method.

compacts were infiltrated with a pre-ceramic polymer AHCPS and thermally treated as described in the experimental section. Figs. 3(a) and (b) shows the macroscopic view of the pyrolised samples (heat treatment at 850 °C) of the composite material consisting of SiO_2 spheres embedded in SiC ceramics. As evident from Fig. 3(a), the spaces between silica spheres are completely filled with the SiC phase.

The formation of SiC was confirmed by XRD, which also confirmed that after heating at 850 °C amorphous SiC was present, while during heat treatment at 1600 °C it crystallised to form β-SiC. For the purpose of this investigation the degree of crystallinity was not an essential feature so in further experiments we used the samples treated at 850 °C. EDS analysis in Fig. 4 shows the presence of Si, O and C. A certain amount of Na is probably due to the treatment using NaOH. The Cu is due to the microscopic mesh.

In order to get an inverse material, silica was disolved from the SiO_2/SiC composites. The typical time needed to dissolve all the silica across the composite volume of about 1 cm³ was about 24 h (using 3 M NaOH at 60 °C). Shorter times led to remainders of silica within the porous matrix of SiC (example is shown in Fig. 5(c)).

SEM images of SiC porous materials obtained after dissolution of 240 nm or 650 nm silica spheres from the SiO_2/SiC composite are illustrated in Fig. 5(a)-(d). The pores remained ordered and intact. The pore size distribution in the inverse materials obtained is apparently narrow
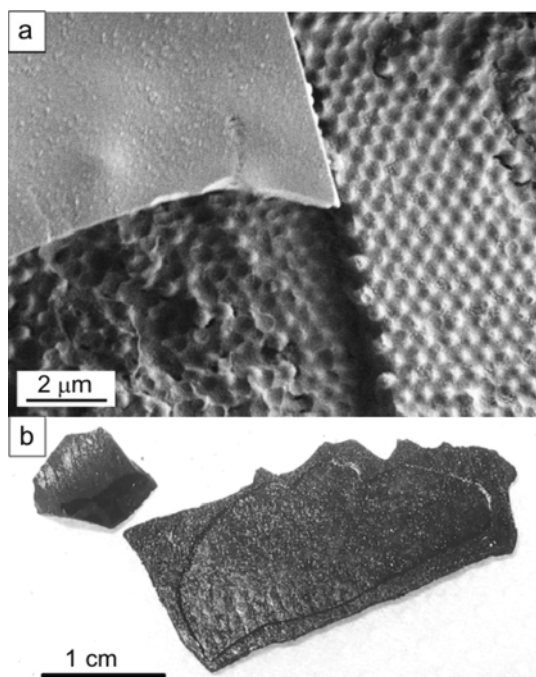

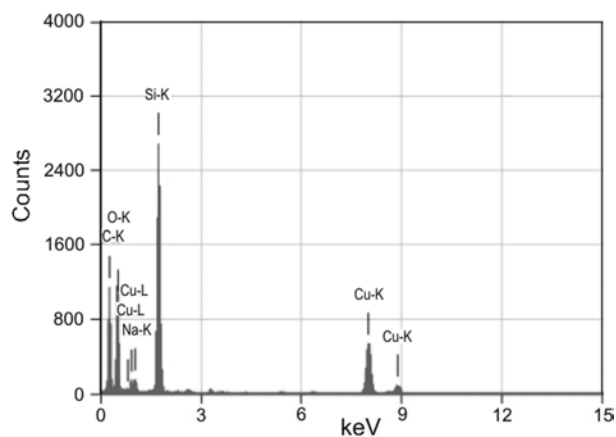**Fig. 3.** SiO_2/SiC composite material. a) SEM image, b) macroscopic view.

Fig. 4. EDS analysis of SiO_2/SiC composite obtained after 1h at 850 °C (for detail see the experimental section).
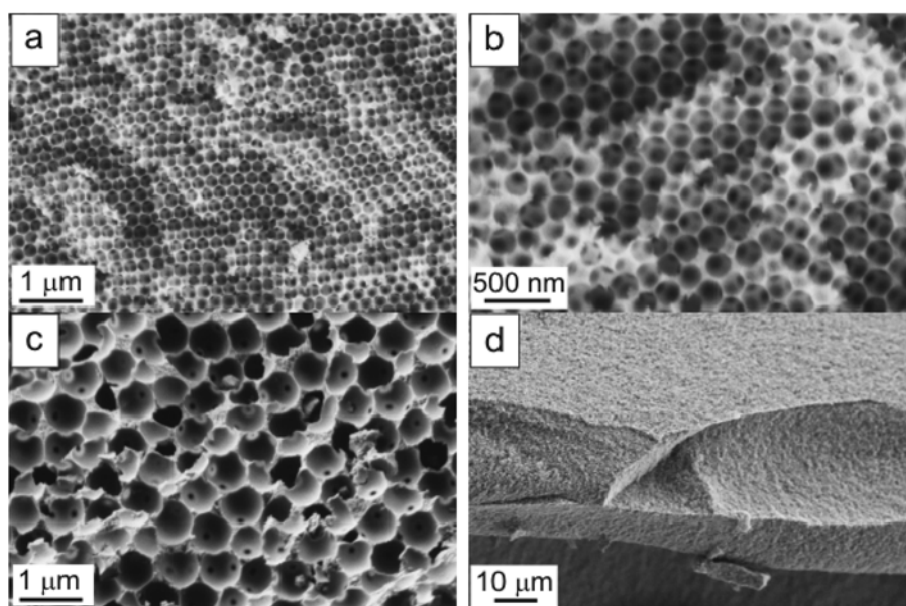

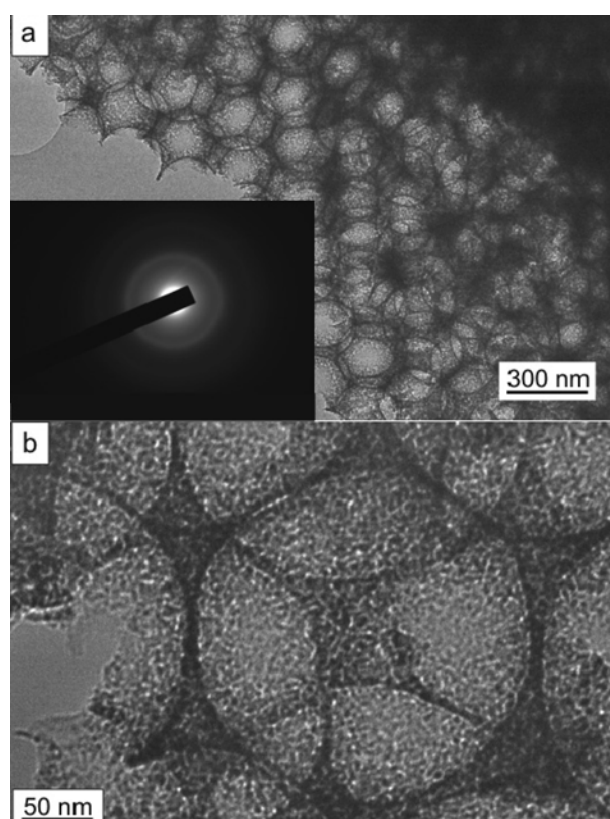**Fig. 5.** SEM images of SiC porous material using a),b) 240 nm and c), d) 650 nm silica spheres.

Fig. 6. TEM images of the porous SiC from a silica template, with a pore diameter 200 nm, and an electron diffraction pattern.

Fig. 7. HR-TEM images of porous SiC. For the sake of clarity, two different regions showing the porous nature of samples are displayed.

and corresponds to the diameter of the silica spheres. The struts are dense and without voids that are characteristic of the foam-replication technique. Although the thickness of the pore walls is in the order of several nanometres, relatively good mechanical stability is preserved as indirectly seen from the compact macroscopic structure shown in Fig. 5(d). The porous samples retained their incandescent properties (as indicated in Fig. 3(b)).

Figs. 6(a)-(b) show TEM images of the obtained porous SiC. The dark areas in Fig. 6(a) and (b) represent the SiC framework and the light areas correspond to the void spaces. The electron diffraction pattern (inset of Fig. 6(a)) is characteristic for nanocrystalline material (uniform diffuse rings), where the presence of an amorphous phase is highly probable. This is also evident from the HR-TEM (high-resolution transmission electron microscopy) micrographs in Fig. 7(a) and (b).

Conclusions

We have demonstrated that highly-ordered three-dimensional mesoporous SiC can be prepared from 3D templates of ordered silica spheres. The latter can be prepared using different techniques, such as gravity sedimentation, centrifugation or electrophoretic deposition. The advantage of the latter two methods is that they are much faster (carried out in 5-10 minutes) than the former one (up to half a year). The quality of samples (degree of
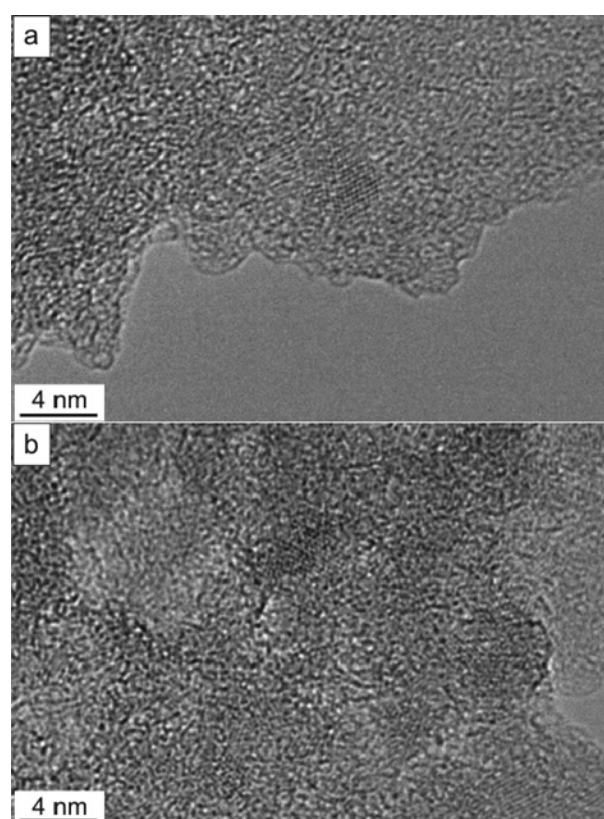
order/concentration of defects), however, is comparable in all three cases. Typical volumes of individual samples are of the order of 1 cm^3, but with slight adjustment pieces of up to 10 cm^3 can be prepared. The final samples contain rather pure and ordered, mechanically robust, porous SiC with very small minimum thickness of walls (several nm). The degree of crystallinity of SiC can be tuned by the final temperature and time of the thermal treatment.

Acknowledgements

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