Ordered mesoporous silicon carbide (OM-SiC) *via* polymer precursor nanocasting†

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Ordered mesoporous SiC with high specific surface area (650–800 m^2 g^{-1}) and well ordered pore structure was obtained *via* nanocasting of polycarbosilanes into SBA-15 and subsequent conversion of the polymer at 1300 °C.

Silicon carbide is an important semiconducting material with high temperature mechanical stability, high hardness and excellent heat conductivity.[1] Besides being a crucial component in structural ceramics, it has also been considered as a catalyst support, especially in exothermic reactions to avoid hot spot formation by using supports with high heat conductivity.[2] However, commercially available silicon carbide has a low specific surface area and is therefore not suitable for catalytic applications. New methods were developed for the preparation of high surface area SiC by using activated or mesostructured carbons as templates.[2,3] For materials with higher specific surface areas (up to 620 m^2 g^{-1}), infiltration of high surface area silica with silicon carbide was employed. Chemical vapour infiltration into SBA-15 was used to prepare mesoporous SiC with surface areas up to 580 m^2 g^{-1} and high temperature stability up to 1300 °C.[4,5] Infiltration of nano-sized silica spheres[6] with polycarbosilanes (PCS) resulted in the preparation of silicon carbide materials with surface areas up to 620 m^2 g^{-1} and disordered pore structure. The PCS used was of high molecular weight (solid at room temperature) and thus the precursors need to be dissolved in organic solvents.

We found that direct infiltration of liquid low molecular weight precursors into ordered mesoporous silica SBA-15, produces ordered mesoporous SiC with even higher specific surface area up to 801 m^2 g^{-1}. The possibility of direct melt impregnation was recently discovered as a method for the preparation of ordered mesoporous carbons.[7] In the present work, low molecular weight PCS (M_w = 800, mp 80 °C) was condensed in the pores of large pore SBA-15.[8] The solvent-free method is essential for a complete infiltration and pore filling producing highly stable SiC with enhanced surface area. After the infiltration, the composite was heated for crosslinking and then transferred to the high temperature furnace and heated in argon to 1300 °C. The composite was washed with HF solution in order to dissolve the mesoporous matrix SiO$_2$, resulting in highly ordered mesoporous SiC (SiC-800).

A second material (SiC-SMPT-10) was obtained using a similar preparation procedure but with a liquid polycarbosilane precursor (SMPT-10).

According to low angle XRD patterns SiC-800 is ordered on the mesoscopic scale (Fig. 1a) and one peak is detected (d = 8.3 nm). On the other hand, also nano-crystalline cubic β-SiC is detected in wide angle measurements (Fig. 1b).

According to nitrogen physisorption measurements (Fig. 1c) the material has a high specific surface area of 648 m^2 g^{-1} and a narrow pore size distribution with an average pore diameter of 3 nm (Fig. 1d). An even higher surface area was measured for SiC-SMPT-10 (801 m^2 g^{-1}), also with narrow pore size distribution and an average pore diameter of 3 nm. In contrast to SiC-800, the low angle X-ray diffractograms of SiC-SMPT-10 showed two weak peaks at 2θ = 1.06° (d = 8.3 nm, as in the case of SiC-800) and a second one with similar intensity at 2θ = 1.83° (d = 4.8 nm). The presence of the second peak may indicate the formation of tubular structures, similar as reported for CMK-5, an inverse replica of SBA-15, with hexagonal ordered nanopipes.[9–11] In the host matrix SBA-15, the position of the (100) peak was at 2θ = 0.87 (d = 10.2 nm) caused by contraction of the silica host (18%)

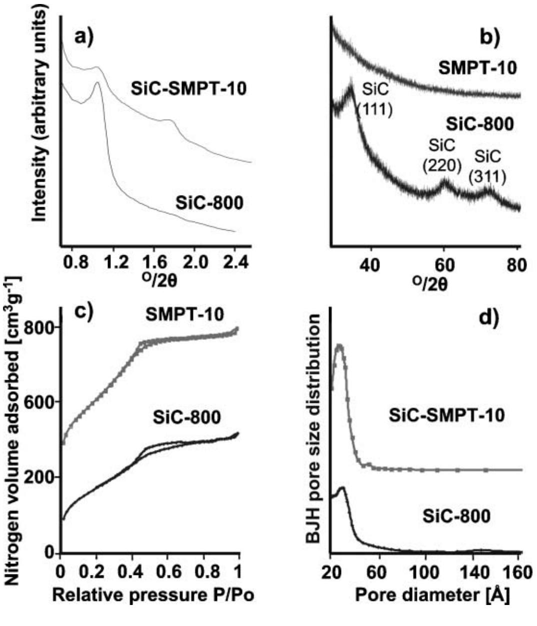

Fig. 1 a) Low angle X-ray diffraction patterns, b) wide angle X-ray diffraction patterns, c) nitrogen physisorption isotherms (200 cm^3 g^{-1} offset), d) BJH pore size distribution (from ads. branch) of OM-SiC.

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† Electronic supplementary information (ESI) available: IR spectra of the mesoporous silicon carbide materials SiC-800 and SiC-SMPT-10. See DOI: 10.1039/b603284b

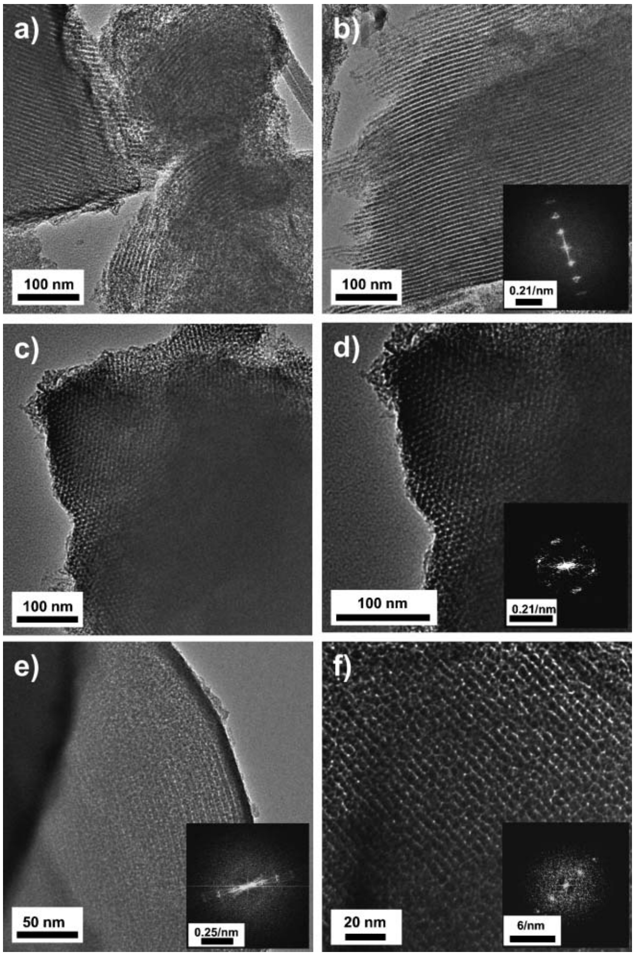

Fig. 2 Transmission electron micrographs of SiC-800 (a–d) and SiC-SMPT-10 (e,f). Insets show the corresponding Fourier transformations.

due to the high temperature pyrolysis process. The total pore volumes measured ($P/P_0 = 0.95$) for both samples were also high: 0.48 $cm^3\ g^{-1}$ for SiC-800 and 0.58 $cm^3\ g^{-1}$ for SiC-SMPT-10. Significant differences with respect to the precursor used were observed for the SBA-15/SiC composites before HF etching. In case of SBA-15/SiC-800, the specific surface area was still high (90 $m^2\ g^{-1}$), while for the SBA-15/SiC-SMPT-10 composite material, the surface area was extremely low ($<10\ m^2\ g^{-1}$) and no residual mesoporosity was present demonstrating efficient pore filling.

Although the specific surface areas of OM-SiC are higher than for CVD,[4]or autogenic pressure-derived silicon carbides,[5] considerable amounts of free-carbon may be present in polymer-derived SiC increasing the specific surface area due to a lower density of the material. Assuming a density of 3.2 $cm^3\ g^{-1}$ for SiC and 2.6 $cm^3\ g^{-1}$ for silica, an inverse replica of SBA-15 with a surface area of 610 $m^2\ g^{-1}$ should yield SiC with a surface area of 496 $m^2\ g^{-1}$, which is lower than the observed value. Thermal gravimetric analysis in air shows SiC-800 to loose 12 wt% at 600 °C due to the oxidation of free-carbon. Similar data were reported for the oxidation of ordered mesoporous carbons.[12] An additional weight gain of 4 wt% was observed in between 600 °C and 1300 °C due to the silicon carbide oxidation. The net result from TG was a mass loss of 8 wt%. Elemental analysis revealed a carbon content of 35 wt% close to the theoretical value (30 wt%), but also considerable amounts of oxygen were detected (14 wt%). The latter is caused by the presence of oxycarbide species on the surface of SiC. The oxycarbide can substantially contribute to the bulk chemical composition in case of high surface area materials.[13] In IR spectra Si–C bonds are detected in both materials (833 cm^{-1}), and a less intensive peak indicating the presence of Si–O bonds (1046 cm^{-1}) as well (electronic supplementary information, ESI).† For higher heating rates employed (100 °C min^{-1}) the measured amount of carbon was lower (28 wt%), but also a lower ceramic yield of 54% was observed as compared to 77% obtained in the 50 °C min^{-1} heating ramp.

Transmission electron micrographs reveal an ordered pore structure of the mesoporous SiC (Fig. 2). Ordering in SiC-800 was detected perpendicular (Fig. 2a,b,d), and along the pore axis (Fig. 2c,d). The *d*-spacing was estimated from the Fourier transformed images to be 8.1 nm (Fig. 2b). Fig. 2d and its Fourier transformed picture confirm the hexagonal pore symmetry. In case of the SiC-SMPT-10 sample the contrast was low, but in addition to the (100) (Fig. 2e) also the (110) *d*-spacing could be measured (4.6 nm, Fig. 2f).

Summarizing, we have presented an efficient method for the preparation of ordered mesoporous silicon carbide materials using direct melt infiltration of low molecular weight polycarbosilanes. The resulting materials have a high surface area, narrow pore size distribution and high mesopore volume.‡

Notes and references

‡ In the typical synthesis procedure 1 g of SBA-15 was placed in a glass reactor, dehydrated at 150 °C in vacuum for 1 h, flushed with argon and cooled down to room temperature. Subsequently, 1.25 g of polycarbosilane (PCS, Aldrich) was added and heated rapidly to 320 °C in an inert atmosphere. The sample was stirred several times and left at the same temperature for 12 h. The infiltrated sample was cooled down, transferred to a high temperature oven, and heated in argon to 1300 °C with a heating ramp of 50 °C min^{-1} for 2 h.

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