

Direct Synthesis of Carbide-Derived Carbon Monoliths with Hierarchical Pore Design by Hard Templating

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Electronic Supplementary Information (ESI†)

Supplementary Figures

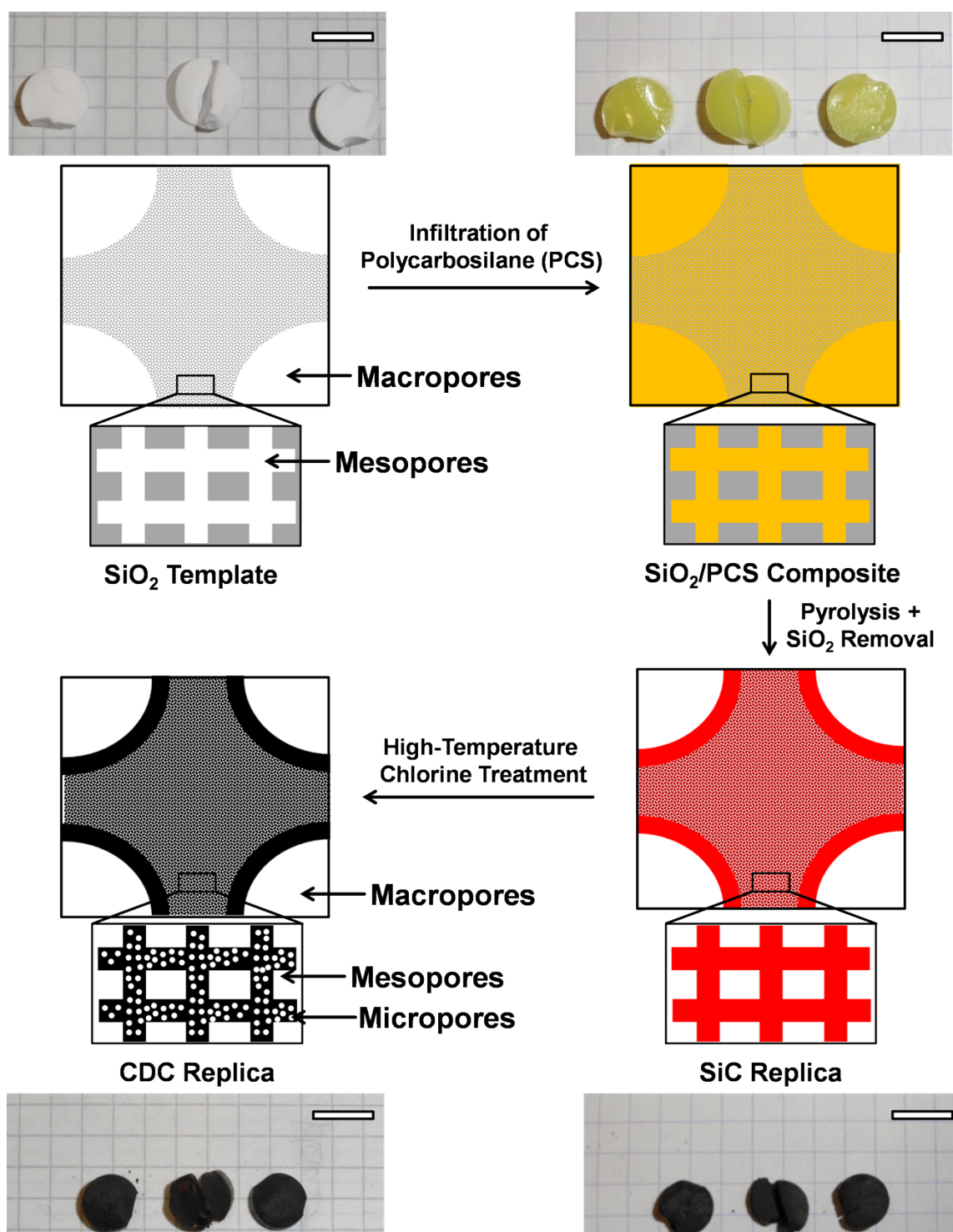


Fig. S1. Schematic of synthesis procedure, pore structure, and photographs at different synthesis stages (scale bar = 1 cm) of the CDC monoliths.

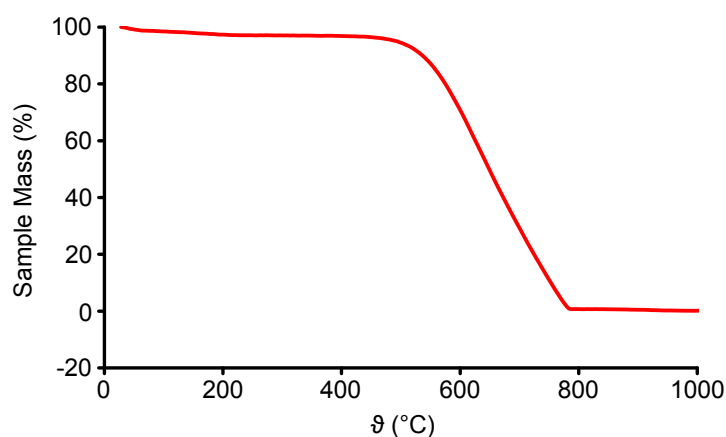


Fig. S2. Thermogravimetric analysis of the CDC monoliths under oxidative conditions (air).

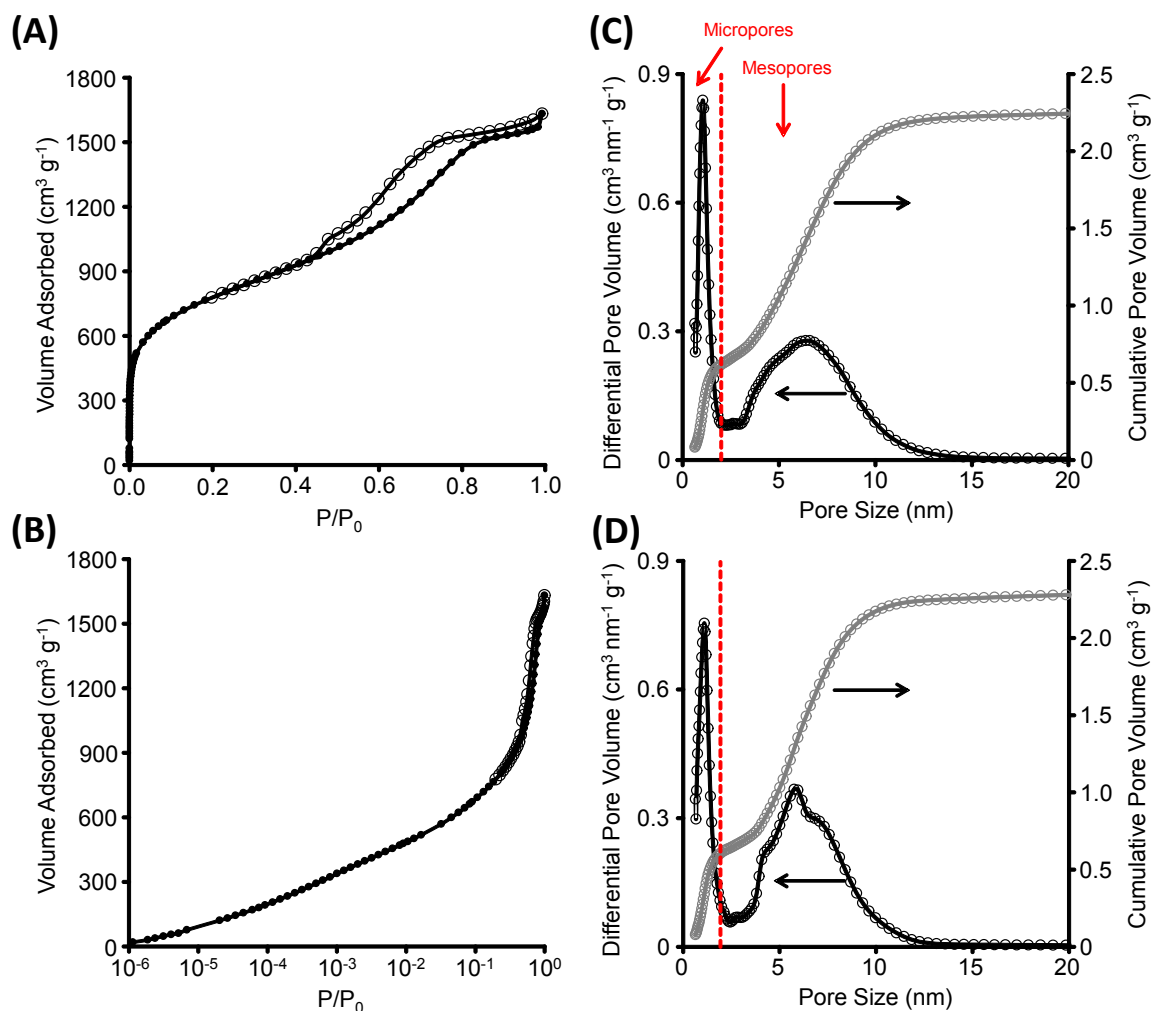


Fig. S3. Linear (A) and semi-logarithmically (B) plotted low-pressure nitrogen adsorption/desorption (filled symbols/empty symbols) isotherms of the CDC monoliths measured at -196°C and corresponding cumulative (grey) and differential (black) QSDFT pore size distributions (nitrogen on carbon with slit/cylindrical pores) obtained from the adsorption (C) and equilibrium (D) kernel.

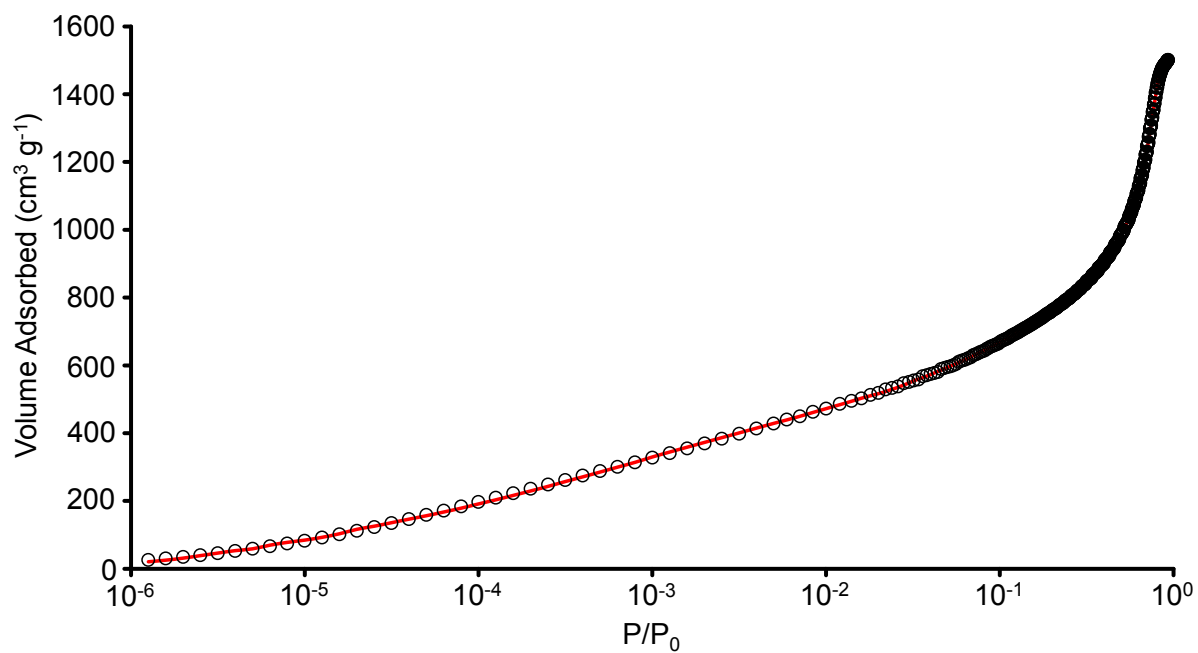


Fig. S4. QSDFT fit between the used carbon slit/cylindrical adsorption branch kernel (straight red line) and the experimental data (nitrogen physisorption, measured at -196 °C; empty circles) for the CDC monoliths.

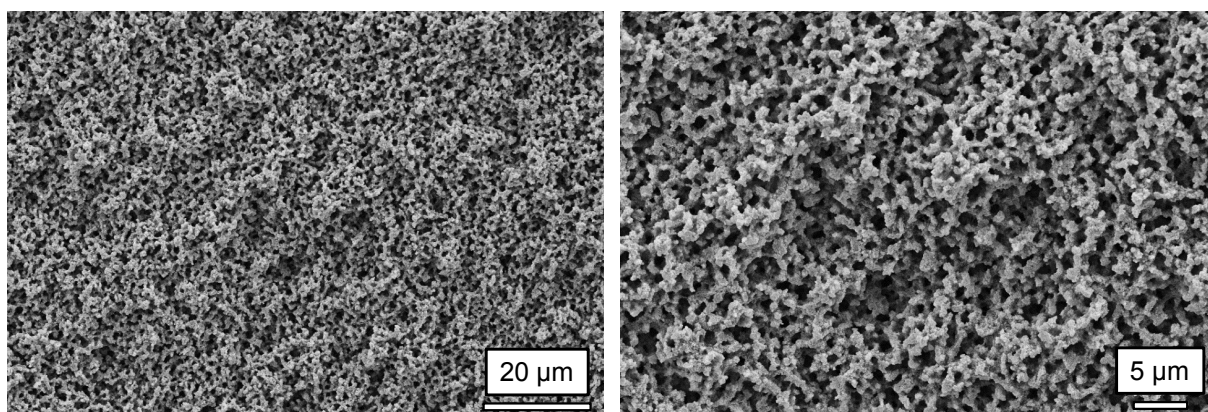


Fig. S5. SEM micrographs of the SiO₂ monolith templates.

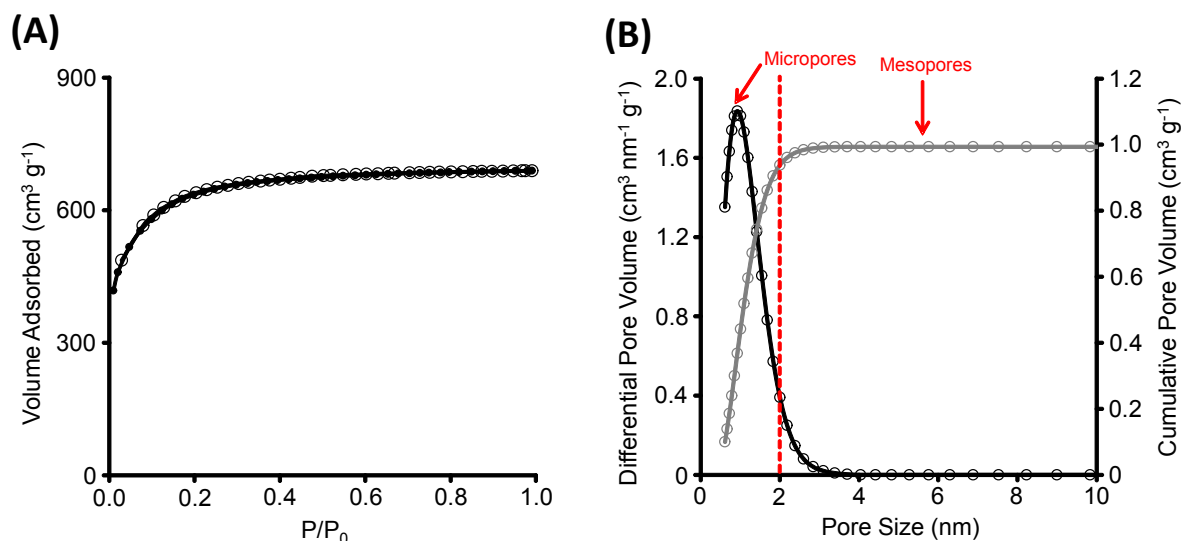


Fig. S6. Nitrogen adsorption/desorption (filled symbols/empty symbols) isotherm of the microporous CDC reference material measured at -196 °C (A) and corresponding cumulative (grey) and differential (black) QSDFT pore size distributions (nitrogen on carbon with slit pores) obtained from the equilibrium kernel (B).

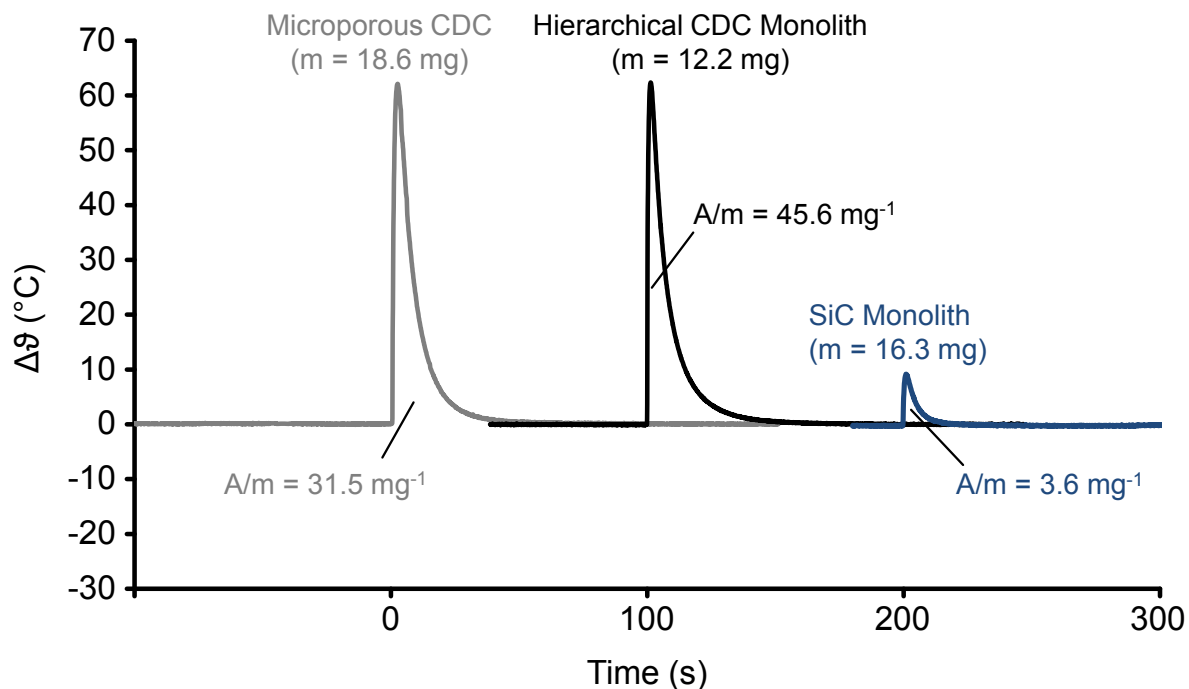


Fig. S7. Thermal response measurements of *n*-butane adsorption (1 bar, 25 °C) in fully activated hierarchical CDC-Ms (black, horizontally shifted by 100 s), SiC monoliths (blue, horizontally shifted by 200 s), and a fully activated microporous CDC (grey) in higher magnification.

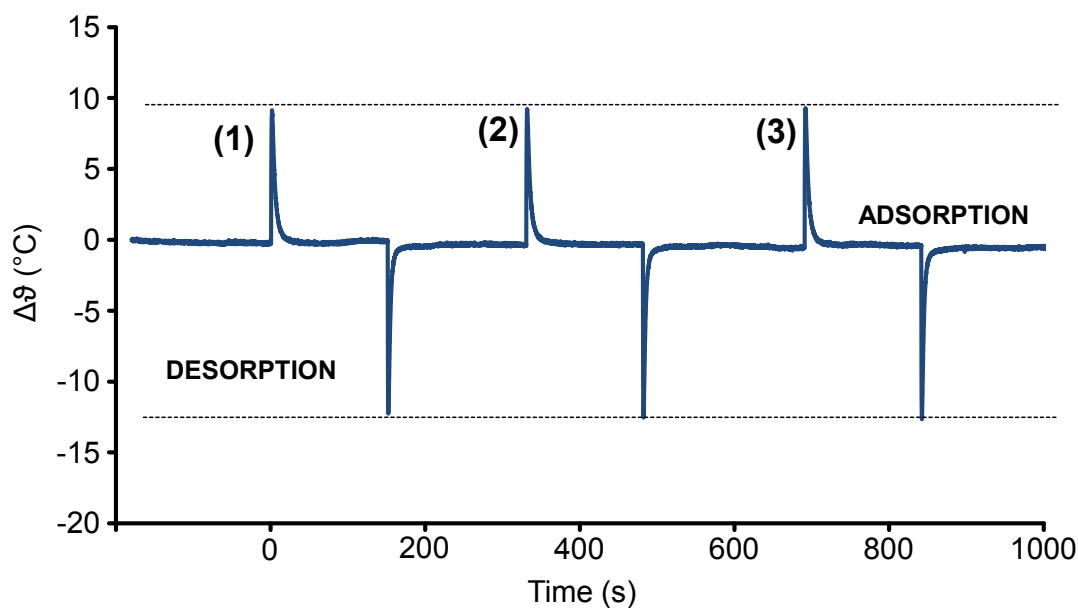


Fig. S8. Thermal response measurements of *n*-butane adsorption (1 bar, 25 °C) in activated SiC monoliths (1) and after desorption times of 120 s (2) and 150 s (3).

Supplementary Table

Table S1. Summary of the textural parameters of the materials in different synthesis stages obtained by nitrogen physisorption measurements at -196 °C.

Material	Specific Surface Area (BET) [m ² /g]	Total Pore Volume [cm ³ /g]	Micropore Volume [cm ³ /g]	Average Pore Size(s) [nm]
SiO ₂ monolith ^{a)}	680	1.01	0.002	7.3
SiC monolith ^{b)}	365	0.38	0.03	4.8
CDC monolith ^{b)}	2662	2.28	0.6	1.0/6.5
Microporous CDC ^{c)}	2342	1.07	0.94	0.9-1.0

^{a)} Pore size distribution obtained using the NLDFT method (nitrogen on silica with cylindrical pores at -196 °C, adsorption branch kernel)

^{b)} Pore size distribution obtained using the QSDFT method (nitrogen on carbon with slit/cylindrical pores at -196 °C, adsorption branch kernel)

^{c)} Pore size distribution obtained using the QSDFT method (nitrogen on carbon with slit pores at -196 °C, equilibrium branch kernel)

Experimental Details

Synthesis Procedure for Silica Monoliths: Monolithic silica rods were obtained by a synthesis procedure given in literature.¹ Typical conditions are as follows. A feed solution containing 1.1 g poly(ethylene glycol) ($10.000 \text{ g mol}^{-1}$), 0.9 g urea, 5.6 mL tetramethyl orthosilicate (Merck KGaA) and 10 mL acetic acid (0.01 M) was stored in a polypropylene plastic tube and then the gelation occurred in a water bath at room temperature for a day. The resultant gel was subjected to further hydrothermal treatment by raising the temperature slowly over a period of 12 h up to 95°C , and then kept for 15 h to form mesopores with the ammonia generated through the hydrolysis of urea. The obtained alkogels were then washed with methanol for 3 days, replacing the solvent daily. Calcination was carried out by raising the temperature to 330°C for 15 h, keeping the temperature at 330°C for 10 h, and cooling down afterwards over 15 h.

Synthesis Procedure for CDC-Ms: 0.93 g of the silica monolith was transferred into a 25 ml Schlenk tube together with a 3:1 (by weight) mixture of liquid allylhydridopolycarbosilane (PCS) (SMP-10, Starfire Systems) and *para*-divinylbenzene (Aldrich, 80%, mixture of isomers) completely covering the pieces. The mixture was evacuated for 24 h at room temperature. The PCS loaded monoliths were then dried at 80°C for 12 h under air. Subsequently, the sample was pyrolyzed under constant argon flow in a horizontal tubular furnace at 800°C for 2 h (heating rate of 30 K h^{-1}), resulting in a monolithic SiO_2/SiC composite. The template was removed using a mixture of deionized water, ethanol (96 %, AHK Berkel) and hydrofluoric acid (40 % in water, Merck KGaA) (125 mL each). After 24 h, the obtained monolithic SiC was washed with ethanol several times and dried overnight at 80°C . For the high-temperature chlorine treatment, approximately 2 g SiC was transferred to a quartz boat in a quartz tube inside a horizontal tubular furnace and heated with 450 K h^{-1} under an argon flow of 150 ml min^{-1} to 800°C . Once the temperature was reached, the gas flow was changed to 80 ml min^{-1} chlorine and 70 ml min^{-1} argon. After 3 h the gas flow was changed to 150 ml min^{-1} of argon and the furnace was cooled down to 600°C in one hour. Removal of residual chlorine species was carried out using a post reductive treatment under hydrogen flow (80 ml min^{-1}) at 600°C for one hour. The sample was cooled down to room temperature under argon.

Synthesis Procedure for Microporous CDC: Pyrolysis and high-temperature chlorine treatment of the microporous reference samples was performed under similar conditions as for

the CDC-Ms, but at a maximum temperature of 700 °C. Pure SMP-10 was used as polymeric precursor for the CDC synthesis.

Structural Characterization of CDC-Ms: Prior to all adsorption measurements the samples were degassed under vacuum for at least 5 h at 150 °C. Nitrogen physisorption (-196 °C measurements were performed using a Quantachrome Quadrasorb apparatus (Quantachrome Instruments, Boynton Beach, USA). Low pressure nitrogen physisorption (-196 °C) isotherms (data presented in Fig. S4) were conducted using an Autosorb 1C apparatus (Quantachrome Instruments, Boynton Beach, USA). Specific surface areas were calculated according to the Brunauer-Emmett-Teller (BET) equation in a range from 0.05 – 0.20 P/P_0 . Total pore volumes were calculated at $P/P_0 = 0.99$. Pore size distributions were calculated from the nitrogen physisorption isotherms using the quenched solid density functional theory (QSDFT, nitrogen on carbon or silica at -196 °C). The specific kernels are given in the corresponding figure captions.

Scanning electron microscopy (SEM) measurements were performed using a DSM982 (Zeiss, Germany). The same instrument (calibrated with a copper standard) was used for the energy-dispersive X-ray spectroscopy (EDX) analyses. Elemental analyses are an average value of 3 – 5 measurements at a magnification of 5000. The thermogravimetric analyses (TGA) were performed using a STA 409 PC LUX (Netzsch) with a heating rate of 5 K min⁻¹ under oxidizing conditions (synthetic air).

Mercury intrusion porosimetry: Measurements were carried out with Pascal 140/440 porosimeters (Thermo Fisher Scientific, Rodano, Italy) in a pressure range from 0 – 400 MPa. Results were calculated using Washburn's equation with a mercury surface tension of 0.48 N m⁻¹ and a contact angle of intruded mercury of $\theta = 140^\circ$, utilizing the software Sol.I.D. of the instrument.

Thermal Response Measurements: The thermal response of the samples was measured using the previously described optical calorimeter setup (InfraSORP Technology by Fraunhofer/Rubotherm).²⁻⁴ Samples were placed in the sample cell and purged with nitrogen until a constant sample temperature was observed. When the sample was at constant temperature, it was exposed to a flow of 70 ml min⁻¹ (25 °C, 1013 kPa) *n*-butane using a mass flow controller for 90s causing a temperature increase of the sample detected by the optical calorimeter due to the adsorption of the hydrocarbon molecules ((1) in Fig. 5). Then, nitrogen was passed by the sample cell to remove *n*-butane from the lines for 90s. Subsequently, the

nitrogen flow was subjected to the sample cell for the duration of 120s initializing desorption of *n*-butane from the carbons leading to a decrease of the temperature. In a subsequent cycle, *n*-butane was adsorbed again on the partially desorbed samples ((2) in Fig. 5), lines were flushed with nitrogen for 90s, and the hydrocarbon was desorbed under nitrogen flow for 180s followed by the repeated adsorption of *n*-butane ((3) in Fig. 5). The peak areas of the thermal response curve were calculated using Origin 9 software.

References

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- [2] M. Leistner, W. Grählert and S. Kaskel, *Chem. Ing. Tech.*, 2013, **85**, 747.
- [3] P. Wollmann, M. Leistner, W. Grählert, O. Throl, F. Dreisbach and S. Kaskel, *Microporous Mesoporous Mater.*, 2012, **149**, 86.
- [4] P. Wollmann, M. Leistner, U. Stoeck, R. Grünker, K. Gedrich, N. Klein, O. Throl, W. Grählert, I. Senkovska, F. Dreisbach and S. Kaskel, *Chem. Commun.*, 2011, **47**, 5151.