Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Biotemplated carbide-derived Carbons with Hierarchical Pore Structure for the Adsorption of Mercury

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Cultivation and Treatment of Diatoms

Thalassiosira pseudonana (*T. pseudonana*) has been isolated from the North Sea in June 2004 by Prof. Manfred Sumper (Regensburg). Cultivation was performed in a 20 L polycarbonate vessel (Nalgene) with artificial seawater (ASW) medium prepared according to the protocol of Harrison *et al.*[1]. Diatoms grew in 20 L of sterile filtrated (0.2 lm, Kleenpak) ASW medium for 2 weeks. A RUMED 1301 light thermostat (18 °C, 12 h/12 h day/night cycle, ca. 1000 lux) provided constant growing conditions. Adjustment of the rising pH to 8.0 – 8.2 was carried out with 2.5 M HCl. The cells were harvested by centrifugation of the culture medium (Heraeus biofuge primo, swinging bucket rotor, 1000 RCF). Cell wall extraction follows the protocol described by Hedrich *et al.*[2]. In order to remove physically bound organic material from the cell walls, an aqueous buffer containing ethylenediaminetetraacetic acid (EDTA) (0.1 M) and sodiumdodecylsulfate (SDS) (2 %) at pH 8 was used. The harvested cells were suspended in 20 mL buffer solution and heated to 95°C for 10 min. This treatment was repeated three times. Finally, the biosilica was washed at least three times with Milli-Q water. In all steps, the biosilica was separated from the supernatants via centrifugation (Heraeus biofuge primo, swinging bucket rotor, 4000 RCF, 10 min). After extraction, the samples were freeze-dried. To further remove organic material from the biosilica, a calcination was performed in a muffle furnace (Nabertherm) for 5 h at 550°C under static air atmosphere.

Parameters of CDC Process

100 mg of vacuum dried *T. pseudonana* biosilica was infiltrated with different amounts (0.06 mL – low, 0.10 mL – medium and 0.17 mL – high) of the liquid polycarbosilane SMP-10 (Starfire Systems) in a mortar followed by pyrolysis in a tube furnace at 800°C for 2 h with a heating rate of 60 K h^{-1} under flowing argon atmosphere. After cooling to room temperature, the materials were washed with 150 mL HF solution (H_2O:EtOH:37%HF in H_2O = 1:1:1) over night, filtrated and washed with EtOH. The

obtained silicon carbide (SiC) materials were treated with hot chlorine gas at 800°C for 3 h. A final hydrogen treatment at 600°C for 1 h was performed to remove residual chlorine and chlorides[3].

Characterization

Nitrogen physisorption isotherms were measured at -196°C on a Quadrasorb apparatus (Quantachrome Instruments). Specific surface areas (SSA) were calculated using the multipoint BET equation (p/p_0 = 0.05 – 0.2 for the TP-SiC materials, p/p_0 = 0.01 – 0.1 for the TP-CDC materials). Total pore volumes were calculated at p/p_0 = 0.99. Pore size distributions (PSDs) were calculated using the quenched solid density functional theory (QSDFT) method for nitrogen at -196°C on carbon with slit/cylindrical/spherical pore geometry from the adsorption branch and non-local density functional theory (NLDFT) with cylindrical pore geometry for the diatom biosilica. Micropore volumes were estimated at the cumulative pore volumes at a diameter of 2 nm.

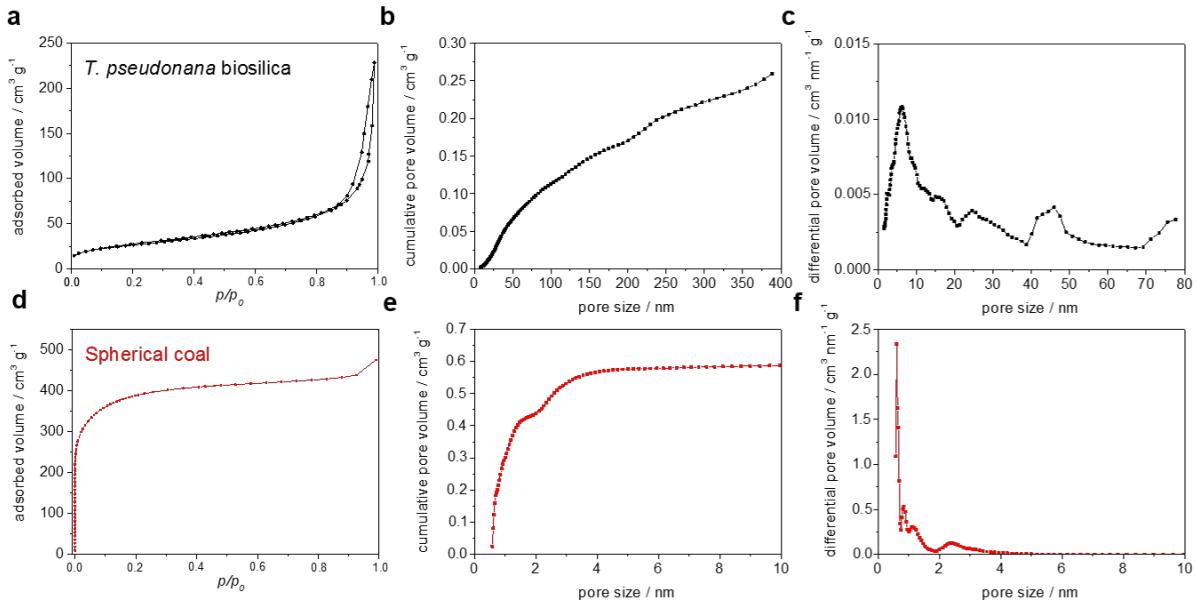
SEM analyses were performed on a Zeiss DSM 982 Gemini field-emission scanning electron microscope. Droplets of water suspensions of the samples were placed on alumina sample holders.

TG was performed on a Netzsch STA 409CD (Netzsch, Germany) under synthetic air with a heating rate of 5 K h^{-1}.

Mercury Adsorption

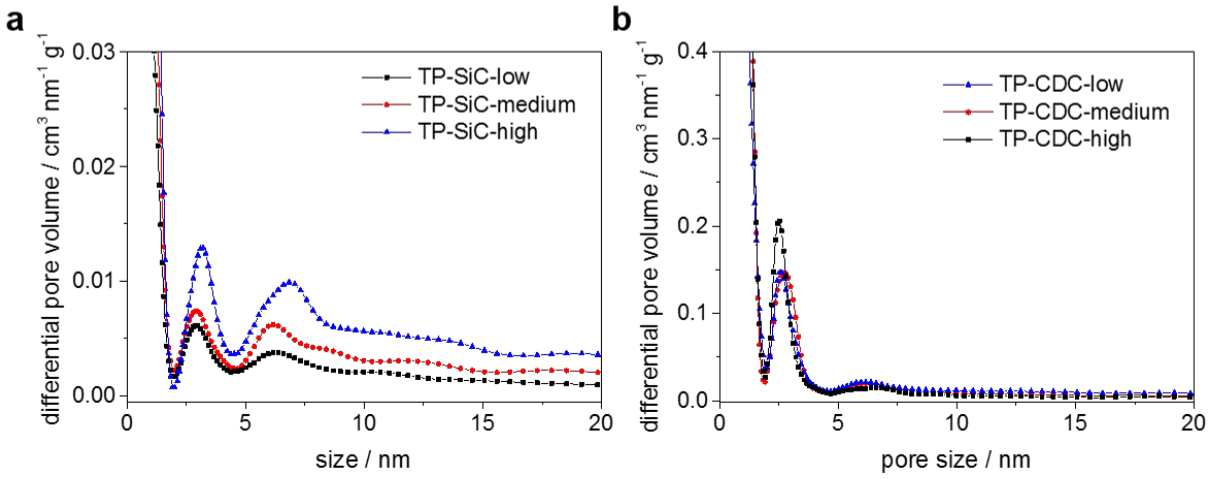
The adsorption of mercury was performed with 250 mL of a 100 mg L^{-1} Hg^{2+} solution with 10 mg of the carbon material under continuous stirring for 3 h (pH 6.5). For the isotherm measurements, different Hg^{2+} initial concentrations of 10, 50, 100, 200, 400 and 800 mg L^{-1} were used (pH 6.5). Samples were taken at different times and filtered through a 0.22 µm PVDF syringe filter (Rotilabo). The concentration of Hg^{+} was determined photometrically using UV-VIS measurements. Therefore 50 µl of the sample were mixed with 1 mL potassium iodide/ potassium hydroxyphthalate solution (20 g L^{-1} each) and shacked for 1 h. Then, 2.95 mL H_2O and 1 mL Rhodamin-6G were added, shaked and the solution was measured after 30 s using a UV/VIS (UV-3100PC Spectrophotometer, VWR). The recyclability was tested by filtering and washing the material with Milli Q water through a nylon mesh (1 µm pore size) followed by drying over night.

S1 – N_2-Isotherms of TP Biosilica and Spherical Coal



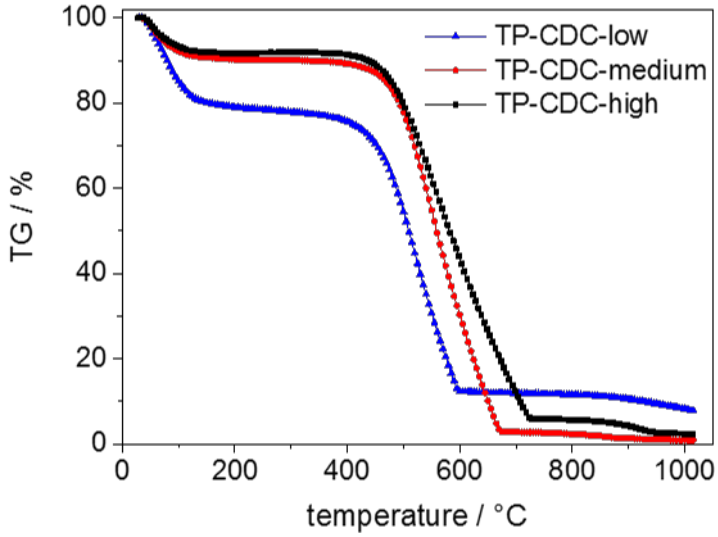
S1: N_2-physisorption isotherms (-196 °C), cumulative pore size distributions and differential pore size distributions of *T. pseudonana* biosilica (a, b, c) and spherical coal (d, e, f).

S2 – Differential Pore Size Distributions



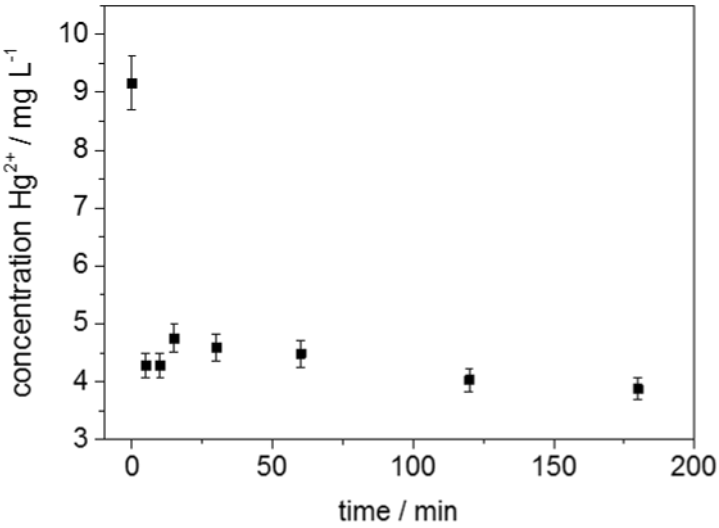
S2: Differential QSDFT pore size distribution of TP-SiC (a) and TP-CDC (b) materials.

S3 – TG Data of TP-CDC Materials



S3: Thermogravimetric analysis curve of TP-CDC materials under synthetic air, heating rate: 5 K min^{-1}..

S4 – Kinetic Study of TP-CDC Material at 10 mg L^{-1} Hg^{2+} Initial Concentration



S4: Hg^{2+} adsorption of TP-CDC-high over time at a Hg^{2+} initial concentration of 10 mg L^{-1}.

T 1 – Composition of the TP-SiC Materials Measured with EDX

Sample	C-Content / %	Si-Content / %
TP-SiC-0.06	88 ± 3.9	12 ± 3.9
TP-SiC-0.10	76 ± 6.9	24 ± 6.9
TP-SiC-0.17	75 ± 6.3	25 ± 6.3

T 2 – Q_e Values of the Different Hg^{2+} Equilibrium Concentrations

Equilibrium concentration C_e / mg L^{-1}	***Adsorbed amount Q_e / mg g^{-1}***
3.9	132
23.9	833
54.6	957
110.1	1610
253.2	3063
491.5	7166

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1 P. J. Harrison, R. E. Waters, F. J. R. A. Taylor, *J. Phycol*., 1980, **16**, 28.

2 R. Hedrich, S. Machill, E. Brunner, *Carbohydr. Res.*, 2013, **365,** 52.

3 M. Oschatz, L. Borchardt, M. Thommes, K. A. Cychosz, I. Senkovska, N. Klein, R. Frind, M. Leistner, V. Presser, Y. Gogotsi, S. Kaskel, *Angew. Chem. Int. Ed.*, 2012, **51**, 7577.