Hierarchically Organized and Anisotropic Porous Carbon Monoliths
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ABSTRACT: Anisotropy is a key factor regarding mechanical or transport properties and thus the functionality of porous materials. However, the ability to deliberately design the pore structure of hierarchically organized porous networks toward anisotropic features is limited. Here, we report two straightforward routes toward hierarchically structured porous carbon monoliths with an anisotropic alignment of the microstructure on the level of macro- and mesopores. One approach is based on nanocasting (NC) of carbon precursors into hierarchical and anisotropic silica hard templates. The second route, a direct synthesis approach based on soft templating (ST), makes use of the flexibility of hierarchically structured resorcinol–formaldehyde gels, which are compressed and simultaneously carbonized in the deformed state. We present structural data of both types of carbon monoliths obtained by electron microscopy, nitrogen adsorption analysis, and SAXS measurements. In addition, we demonstrate how the degree of anisotropy can easily be controlled via the ST route.

INTRODUCTION

Porous carbon materials play an important role in various scientific and industrial fields, ranging from separation science (e.g., filters), medical applications, and thermal insulation to electrodes for electrochemical energy storage.1−5 Their unique combination of properties, such as electrical conductivity, mechanical strength, and heat resistance of carbon combined with a high specific surface area and adjustable porosity/density of the porous networks are some of the reasons for their significant role in everyday life. Especially, the fabrication of monolithic porous carbons draws much attention since macroscopic objects exhibiting complex geometric shapes can be created without the need of an additional binder, which typically impairs the beneficial properties of the pure carbon network.6−8 Not only the control over macroscopic shape but also the deliberate design of morphological features on the micro- and nanoscale is of great importance for influencing the material’s structural and functional properties. The precise adjustment of pore sizes, for instance, can be used to tailor critical characteristics of the resulting material. Small pores (meso- and micropores) provide a high specific surface area and allow for size and shape selectivity, which is beneficial for surface reactions, whereas large pores (macropores) facilitate high flow rates of fluids through the material.9 In particular, the combination of different pore sizes in a hierarchically organized, porous network has been shown to yield unique properties.9,10,11 Another promising structural feature is the anisotropic alignment of pores or microstructural design elements.12−14 Such arrangements often provide high mechanical strength in certain directions, or a direction-dependent mechanical response, and allow for the directed transport of liquids or gases through the material. Although most of the mentioned characteristics (monolithic material, hierarchy, anisotropy, ordered mesopores, etc.) have individually been implemented in porous carbons,13−19 a fabrication strategy simultaneously addressing all these design principles in the same sample is still a challenging task.

Sol−gel processing in combination with soft templating and polymerization-induced phase separation is a feasible technique to create hierarchical porous materials.5−9,16,19 For instance, for the synthesis of hierarchically organized silica monoliths, consisting of a macroporous network of struts, each strut comprising cylindrical mesopores on a 2D hexagonal lattice was recently demonstrated.20−22 While the cylindrical mesopores in each strut are arranged in an anisotropic fashion, the overall macroscopic network is constructed as an isotropic architecture. Very recently, Hasegawa et al. presented a similar synthesis route toward hierarchical porous resorcinol–formaldehyde (RF) and carbon monoliths, which exhibit a microstructure equivalent to the silica monoliths mentioned above.23,24 Koczwar et al. showed that hierarchical porous
carbon can be synthesized by nanocasting of carbon precursors into hierarchical silica, subsequent carbonization, and removal of the hard template by treatment with hydrofluoric acid (HF).\textsuperscript{25,26} Regarding anisotropy, different methods for the alignment of porous structures in monolithic samples have already been demonstrated, ranging from directional freezing or the application of magnetic fields to mechanical methods.\textsuperscript{27–31} The synthesis of hierarchical and anisotropic porous silica monoliths has recently been demonstrated by shear-induced alignment of a preformed gel.\textsuperscript{12} Yet, to the best of our knowledge, the fabrication of hierarchically organized and anisotropic carbon monoliths has not been reported so far.

Here, we present two synthesis routes toward hierarchical and anisotropic carbon monoliths based on (i) nanocasting (NC) into a preformed, anisotropic silica hard template and (ii) the direct synthesis via soft templating (ST) and subsequent carbonization of a flexible RF gel under uniaxial compression. In both cases, the resulting carbon monoliths show anisotropy on the level of the macropores as well as on the mesopore level. Especially, the ST route is a simple and convenient approach to adjust the degree of anisotropy of the porous network and its distribution across the monolith in a desired fashion.

**RESULTS AND DISCUSSION**

Hierarchically structured and anisotropic porous silica monoliths used as hard templates for the synthesis of carbon monoliths via a NC approach can be fabricated by sol–gel processing of condensable silanes in the presence of a preformed lyotropic liquid crystal phase concomitant with the application of external shear forces.\textsuperscript{12} The resulting silica templates consist of cylindrical struts that are aligned in preferential directions corresponding to the direction of the applied shear force (Figure 1a). Each of these struts contains cylindrical mesopores arranged on a 2D hexagonal lattice, which can be used for the infiltration with carbon precursors like resorcinol (R) and formaldehyde (F).\textsuperscript{25} Carbonization yields a silica–carbon composite where the mesopores of the original silica monolith are filled with carbon nanorods (Figure 1b). Removal of the silica template by etching with HF generates a hierarchical and anisotropic carbon network in which the macroscopic morphology of the template is reproduced, whereas the struts are now composed of bundles of carbon nanorods (Figure 1c). These rods are presumably stabilized on the original 2D hexagonal pore lattice due to interconnections originating from micropores in the mesopore walls of the silica template, an effect which was already proposed for the synthesis of so-called CMK-3 material from SBA-15 silica.\textsuperscript{16} The degree and uniformity of anisotropic
alignment in the final carbon structure of NC monoliths strongly depends on the structural characteristics of the corresponding silica template. Likewise, this applies for gradients of anisotropy, which are usually introduced in the hard template by the application of shear forces.\textsuperscript{12} The ST route toward hierarchically structured and anisotropic carbon monoliths starts with the synthesis of flexible RF gels, as described elsewhere.\textsuperscript{24} In short, a similar approach as for the synthesis of the above described silica template covering supramolecular templating and polymerization-induced phase separation is used to create a network of cylindrical RF struts comprising hexagonally arranged mesopores (Figure 1d). Utilizing the mechanical flexibility of the thus synthesized material with a recoverable compressibility against 80–90\% engineering strain,\textsuperscript{32,33} the cylindrical monoliths are compressed to achieve an anisotropic arrangement of the constituting RF struts (Figure 1e). This step is performed in a self-designed compression unit consisting of a metal tube, containing 1 mm sized holes, as support and guidance for the flexible monolith and two flat metal plates to exert pressure (Figure S1). In principle, this setup enables uniaxial compression without any bending or distortion of a cylindrical sample geometry (Figure 2e). However, it also represents a geometric confinement for the monolith and thus creates certain boundary conditions, which also affect the arrangement of the microstructure to some extent, especially in regions close to the metal housing. The related impact on the homogeneity of anisotropic alignment in ST samples is discussed below on the basis of acquired SAXS data. In a last step, carbonization at 850 °C in inert atmosphere is applied, not only to transform the material into carbon but also to switch from the flexibility of the original RF network to a highly rigid carbon structure, which allows for the preservation of the anisotropic arrangement without external forces (Figure 1f). During this fabrication step, the monoliths experience a volumetric shrinkage of about 50\%. The change in flexibility of the porous network occurs in a temperature range between 250 and 450 °C due to the degradation of organic groups (e.g., template molecules),\textsuperscript{24} which can evaporate through the small holes in the surrounding metal tube of the applied setup. First, the flexibility of the strut network even increases at temperatures around 350 °C. In contrast, at higher temperatures of, e.g., 450 °C, the flexibility of the material is already significantly compromised.\textsuperscript{24} Shrinkage of RF gels is a result of carbonization at temperatures above 600 °C and therefore sets in after the loss of flexibility.\textsuperscript{32,33} Despite this significant shrinkage of an already stiffened network, the monolithic structure remains completely intact and no cracks or microfissures can be observed after carbonization. This implies that RF gels with different initial heights can be compressed to the same height in the compression unit and then exhibit very similar dimensions after carbonization since no significant shrinkage is expected before the network is completely rigid. Thus, the impact of shrinkage on the microstructural arrangement as well as the degree of anisotropy can be disregarded.

The resulting macroscopic carbon monoliths from both synthesis routes are shown in Figure 2a,e. In both cases, the porous architectures consist of a macroporous network of struts that are aligned either in shear direction (Figure 2b) or perpendicular to the direction of the applied compression force (Figure 2f) and converge into star-shaped junctions (Figure 2c,g). However, while for the NC approach, each of the struts is built up of hexagonally arranged carbon nanorods (Figure 2d); for the ST route, the struts comprise cylindrical mesopores on a 2D hexagonal lattice (Figure 2h). For comparison, SEM images of the corresponding isotropic carbon networks are provided for both synthesis routes in Figure S2.

Despite these structural similarities between carbon monoliths from the NC and the ST route, major differences become obvious when calculating pore characteristics from nitrogen adsorption/desorption isotherms (Table 1 and Figure S3). It should be noted that, for both synthesis routes, the acquired data do not show any dependence on the degree of microstructural alignment by shear or compression, and thus, all isotherms for isotropic and anisotropic samples originating from the same synthesis route are very similar. The differences between the two synthesis routes are exemplified by comparison of an anisotropic NC sample with a ST sample

### Table 1. Specific Surface Area $S_{\text{BET}}$, Specific External Surface Area $S_{\text{ext}}$, Specific Micropore Volume $V_{\text{micro}}$ and Specific Mesopore Volume $V_{\text{meso}}$ Calculated from Corresponding N$_2$ Adsorption Isotherms (See Figure S3) for Representative Samples from the NC and the ST Approach

| sample | $S_{\text{BET}}$ [m$^2$/g] | $S_{\text{ext}}$ [m$^2$/g] | $V_{\text{micro}}$ [cm$^3$/g] | $V_{\text{meso}}$ [cm$^3$/g] |
|--------|--------------------------|--------------------------|--------------------------|--------------------------|
| NC     | 817                      | 739                      | 0.04                     | 0.65                     |
| ST     | 727                      | 81                       | 0.30                     | 0.07                     |
compressed by 30%. While the specific surface area \( S_{\text{BET}} \) is in the same range for both sample types (817 m\(^2\) g\(^{-1}\) for NC vs 727 m\(^2\) g\(^{-1}\) for ST), the specific external surface area \( S_{\text{ext}} \) (covering essentially the macro- and mesopore surface area) of the NC sample is with 739 m\(^2\) g\(^{-1}\), almost 10 times higher as \( S_{\text{ext}} \) of the ST sample with only 81 m\(^2\) g\(^{-1}\). This latter value is probably solely due to the macropores given the size and geometry of the struts (Figure 2g), suggesting that the ST sample exhibits essentially no open mesopores. This is consistent with the shape of the adsorption isotherm (type I; see Figure S3) and with the very different extent of micro- and mesoporosity calculated for the two sample types. The specific micropore volume \( V_{\text{micro}} \) reaches a value of 0.30 cm\(^3\) g\(^{-1}\) for the ST monolith but only 0.04 cm\(^3\) g\(^{-1}\) for the NC counterpart. In contrast, the specific mesopore volume \( V_{\text{meso}} \) is with 0.65 cm\(^3\) g\(^{-1}\), much higher for NC than for ST with only 0.07 cm\(^3\) g\(^{-1}\). The latter value is quite surprising since an ordered structure of two separated phases with different density inside the struts is clearly visible in TEM images of ST monoliths (compare Figure 2h), and thus, a value for \( V_{\text{meso}} \) closer to the one measured for NC samples should be expected. Similarly, small-angle X-ray scattering (SAXS) of the ST samples shows well-resolved Bragg peaks arising from a 2D hexagonally ordered lattice comparable to the NC samples, suggesting ordered cylindrical mesopores. In the literature, higher values for \( V_{\text{meso}} \) have been obtained by a slightly different heat treatment (300 °C in N\(_2\) atmosphere containing 10% air) prior to carbonization to completely remove the remaining template F127 from the mesopores.\(^{23}\) This suggests that the conducted oxidative heat treatment at 250 °C in air atmosphere does not fully decompose the template but leaves some residues, which are then converted into carbon in the subsequent carbonization step. Consequently, the mesopores of thus prepared ST monoliths may be partially blocked or simply divided into smaller (microporous) units. However, since the main goal of this work was not to achieve high mesoporosity but to demonstrate a method for the creation of anisotropy on the macropore scale, the parameters of the heat treatment were maintained for the following sample series.

To demonstrate that the degree of anisotropy of the porous network can be easily manipulated via the ST route, a series of monolithic samples with varying amounts (17, 24, 30, and 46%) of compression (with respect to the original specimen length) prior to carbonization has been prepared. Results of this experiment at the macropore scale are shown in Figure 3 where the extent of compression is given for each sample relative to the original length of the compressed cylindrical RF monolith. The SEM images show cross sections parallel to the cylinder axis of the monolithic samples, indicating the compression direction from top to bottom of each image (see the sketch in Figure 3). After a compression of 17%, no obvious anisotropic arrangement of the network can be observed by SEM, although the architecture looks slightly disturbed as compared to an isotropic sample (see Figure S2). The sample compressed by 24% already indicates a preferred alignment of the struts perpendicular to the applied force. For the samples with 30 and 46% compression, this effect is further enhanced. Especially for higher degrees of compression, also, a densification of the porous network can be clearly observed, which is also reflected in bulk density of the corresponding monoliths (see Table 2). Noteworthy, even for the highest degree of compression, the monolithic character of the samples is fully preserved.

The SEM investigation shows a clear trend regarding the degree of anisotropy of the individual samples, but one has to keep in mind that these images only show a very small section of the monolithic sample. For this reason, small-angle X-ray scattering (SAXS) measurements were performed to get a more detailed insight of the homogeneity of the micro-structural arrangement.

The analysis of the SAXS patterns collected from the NC and ST samples allows deriving a semiquantitative parameter for the preferred orientation of the struts. The analysis is based on the orientation distribution of 2D hexagonal ordered cylindrical units, i.e., nanorods in the case of NC and (partially filled) cylindrical mesopores in the case of ST, which result in Bragg peaks in the SAXS patterns. For a single strut, the cylindrical units are perfectly parallel to the direction of the strut. Thus, assuming cylindrical symmetry with respect to the compression/shear direction, the azimuthal intensity distribution of the Bragg reflections on a 2D SAXS detector is closely related to the orientation distribution of the struts. To take potential heterogeneities across the sample sections into account, SAXS measurements at several, evenly spaced points were performed (see Figure 4 a,b). A typical 2D SAXS pattern is shown in Figure 4c where the preferred alignment of the struts is indicated by the double-headed blue arrow, which is perpendicular to the observed intensity maximum along the intensity ring from the (10) reflection. Since the preferred strut orientation is parallel to the shear direction (horizontal in Figure 4a) for the NC sample and perpendicular to the compression direction (vertical in Figure 4b) for the ST samples, the intensity maximum is consistently found on the top and the bottom positions of the Debye–Scherer rings.

### Table 2. Bulk Density \( \rho \), Mean Degree of Orientation DPO, and Corresponding Standard Deviation \( \sigma \) for a NC Sample and Four ST Samples with Different Percentage of Compression

| Sample | \( \rho \) [g cm\(^{-3}\)] | DPO | \( \sigma \) |
|--------|------------------|-----|-----|
| NC     | 0.1 – 0.2        | 0.155 | 0.001 |
| ST 17% | 0.14 ± 0.01      | 0.166 | 0.012 |
| ST 24% | 0.14 ± 0.01      | 0.187 | 0.020 |
| ST 30% | 0.17 ± 0.01      | 0.209 | 0.017 |
| ST 46% | 0.20 ± 0.01      | 0.310 | 0.003 |

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However, the degree of preferred orientation represented by the relative height of the intensity maximum with respect to the minimum can vary quite strongly across the samples (see Figure S4), suggesting structural heterogeneity due to, e.g., inhomogeneous deformation of the gels.

To quantify the degree of preferred orientation, the so-called DPO parameter was used, with \( D = \frac{1}{I_I + I_{II}} \) (see Figure 4d).\(^{34}\) However, since the present carbon samples exhibit a high amount of (randomly oriented) micropores, which contribute to the diffuse small-angle scattering below the Bragg peaks, their contribution has to be estimated and subtracted. The detailed analysis is described in the Experimental Section, and the results are summarized in Table 2. Compared to the ST samples, the NC sample shows an overall smaller degree of orientation, but the sample seems to be clearly more homogeneous than the ST samples (Figure S4 and standard deviation \( \sigma \) in Table 2). For the ST sample, there is also a clear trend toward a higher average degree of orientation and also a more homogeneous orientation distribution within the sample with an increasing compression ratio. In the NC sample, the struts are preferentially aligned along the direction of extrusion,\(^{12}\) whereas in the ST samples, the struts are mainly aligned perpendicular to the direction of compression. Due to the different deformation mechanisms, the 3D orientation distribution are however presumably quite different. For the shear aligned NC sample, we expect a preferential uniaxial orientation along the shear direction, while for the compressed ST samples, the strut axes lie preferentially within the plane perpendicular to the compression direction but should be randomly oriented within this plane. Therefore, the absolute values of the DPO parameter are not directly comparable for the two types of samples. A more detailed analysis of the orientation distribution is however beyond the scope of this work.

It can be surmised that the preferred alignment of the struts in the ST samples is mainly due to the local release of strain energy leading to a local densification of the strut network. This can be confirmed by bulk density measurements (Table 2), showing an increase in density from 0.14 g cm\(^{-3}\) for slightly compressed samples to 0.20 g cm\(^{-3}\) for monoliths compressed to about half the original size. Indeed, also, the X-ray transmission images of the ST samples (see Figure 4b and Figure S4) are consistent with increasing densification with increasing ratio of compression (decrease in transmission). This argument seems also to hold true locally for the single samples, i.e., denser regions (lower transmission) is positively correlated with higher degree of orientation (Figure S5). This is in line with theoretical considerations, which also predict a homogenization of a porous body at higher compression ratios just as observed in our experiments (Table 2).\(^{35}\)

**CONCLUSIONS**

Anisotropy featured in hierarchically organized porous carbon monoliths was successfully created via two newly developed synthesis routes. One approach is based on nanocasting (NC) of carbon precursors into a preformed hierarchical and anisotropic porous silica monolith followed by carbonization and removal of the hard template. The second approach, a direct synthesis based on soft templating (ST), starts from hierarchically structured, flexible RF monoliths that are uniaxially compressed and carbonized to freeze the microstructure in the thus achieved anisotropic state.

Carbon monoliths from these two synthesis routes share some common characteristics such as an anisotropically arranged macroporous network of cylindrical struts that in turn contain an anisotropic mesostructure. On the other hand,
there are clear structural differences regarding the nature of the mesostructure (carbon nanorods in NC vs cylindrical mesopores in ST): the amount of microporosity and the accessibility of the mesopores. Also, the macrostructure is different due to the different methods to introduce anisotropy (i.e., uniaxial preferred orientation for NC and preferential planar orientation for ST).

Especially, the ST approach obviously represents a simple method to control the degree of anisotropy of the resulting carbon network. The extent of structural alignment is directly related to the amount of compression prior to carbonization. The homogeneity of the arrangement strongly depends on the total amount of compression. For a high degree of compression, a relatively homogeneous distribution of the anisotropic alignment can be achieved.

**EXPERIMENTAL SECTION**

**Nanocast Carbon.** Hierarchical and anisotropic silica hard templates were synthesized, according to Putz et al.21 In short, wet gel preparation was conducted by adding tetraakis(2-hydroxyethyl)-orthosilicate (an ethylene glycol modified silane; EGMS) to a homogeneous mixture of aqueous P123 (Sigma-Aldrich) in 1 M HCl with a composition by weight (Si/P123/HCl) of 84/30/70. Stirring for 1 min yielded a clear, viscous liquid that was filled into plastic syringes (5 mm diameter, Henke-Sass, Wolf GmbH), which was then sealed and placed in an oven to gel for 1–2 h at 313 K. Subsequently, by pressing the stamp, a shear force was applied, leading to a directed flow of the gel inside the syringe. Within the syringe, on both sides sealed, the gels aged for 7 days at 313 K in the mother liquor. Demolding of the wet gels was followed by a treatment with ethanol (EtOH), petroleum ether (PE), and a mixture of chloro(trimethyl)-silane (TMCS) and PE (TMCS/PE = 10:90 by weight) in the order EtOH-PE-TMCS/PE-PE-EtOH for 24 h each to remove the surfactant and residual ethylene glycol.

The synthesis of carbon monoliths was conducted following the procedure described by Koczvara et al.22 The above described wet silica monoliths were infiltrated at room temperature with an aqueous solution of resorcinol (R), formaldehyde (F), and sodium carbonate (SC) with a molar ratio of R/F/SC/H₂O = 1.5/1.0/0.003/15, stored at 80 °C for 24 h for polymerization and subsequently carbonized at 850 °C (holding time, 1 h) in argon atmosphere. After cooling to room temperature, the silica–carbon composite was immersed in 20% orthosilicate (an ethylene glycol modifi

**Soft-Templated Carbon.** Hierarchical and anisotropic, flexible RF gels were synthesized according to Hasegawa et al.23 In a typical one-pot synthesis, 3.0 g of F127, 3.0 mL of 1,3,5-trimethylbenzene (TMB), and 3.0 mL of benzyl alcohol (BrOH) were added to a mixture of 60 mL of triethylene glycol (TEG) and 16 mL of 1 M HCl aq in a plastic vessel followed by stirring at room temperature to obtain a homogeneous solution. Then, 2.2 g of resorcinol was dissolved in the resulting solution, and 6.0 mL of formaldehyde solution (37 wt % in H₂O) was subsequently added. After stirring for 30 min at room temperature, the sol was kept at 60 °C for 48 h for gelation and aging. The obtained wet gels were subjected to solvent exchange with 2-propanol followed by evaporative drying under ambient pressure. The thus synthesized flexible RF monoliths were uniaxially compressed by means of a self-designed compression unit (see Figure S1) made of stainless steel. By the use of various cylindrical side tubes with a different length (7–20 mm) and six threaded bars with screw nuts, a range of 10–50% uniform compression could be realized. In this state, the compression unit with the compressed RF sample was placed into a tube furnace. The compressed gels were calcined at 250 °C for 30 min in air (heating rate, 1 K min⁻¹). Carbonization of the compressed gels was performed at 850 °C for 1 h in argon atmosphere (heating rate, 1 K min⁻¹).

**Reproducibility and Uniformity.** In general, the described synthesis routes are stable and the presented morphologies as well as the general trends regarding the degree of anisotropy can easily be reproduced. However, two major aspects regarding reproducibility and structural uniformity have to be considered:

a) The applied sol–gel synthesis routes are very sensitive to parameter changes (e.g., pH value, temperature, drying conditions, etc.), and slight deviations can lead to noticeable differences (e.g., different aspect ratios in strut length/width) between samples from different batches.22,24 Even conditions, such as room temperature or humidity, may have an influence. For this reason, only samples from one batch were taken for the investigation of the influence of the amount on compression on the degree of anisotropy. Within one batch of samples (even with different degrees of anisotropy), pore characteristics (apart from anisotropy) are very similar, e.g., the variation of the specific surface area $S_{BET}$ is in the range of ±5% within one batch.

b) Typically, anisotropic samples do not possess a completely uniform microstructure but exhibit gradients in anisotropy arising from the mechanical forces that have been applied for the rearrangement of the porous network. For cylindrical samples arranged by shear (NC samples), regions close to the cylinder axis are usually less aligned as compared to areas close to the cylinder surface.22 For samples arranged by compression (ST samples), there is also a clear difference between bulk and surface regions. However, the exact influence of the confining compression unit has still to be further investigated. The resulting lack of uniformity implies that the data acquired by different characterization methods have to be treated with care. While techniques that allow for probing a large sample volume, such as nitrogen sorption analyses, give reproducible results with variations in the range of ±5%, methods that are more localized to smaller sample volumes, such as, e.g., electron microscopy, show larger differences. Accordingly, single SAXS measurements on different positions of a given carbon sample and the evaluation of the corresponding DPO parameter yield quite different results, as demonstrated in the Supporting Information. The reason for this is the inherent structural irregularity of the samples combined with the limited sampling area of one single SAXS measurement. However, if several SAXS measurements across a large sample area are performed and an average DPO is calculated (as realized in the present work), then we expect this value to be a quite stable indicator of the trend of the preferred orientation, which we expect to hold also for samples with a comparable synthesis history.

**Electron Microscopy.** Scanning electron microscopy (SEM) micrographs were recorded using a ZEISS FE-SEM ULTRA PLUS, applying its in-lens secondary electron detector at an accelerating voltage of 2 kV. Transmission electron microscopy (TEM) was performed with a JEOL JEM-F200 cold field emission transmission electron microscope at a accelerating voltage of 200 kV. Micrographs were recorded with a TVIPS TemCam-F216 (2x2k) CMOS camera.

**Nitrogen Adsorption Analysis.** Nitrogen adsorption analysis was performed at 77 K using a Micrometrics ASAP 2420 instrument. Prior to analysis, samples were degassed for 12 h at 300 °C. The adsorption isotherms were evaluated in terms of the combined specific micro- and mesopore volume ($V_{micro} + V_{meso}$) by applying the Gurvich rule. The specific surface area $S_{BET}$ was determined by the BET method,37 and the external surface area $S_{ext}$ was obtained by the t-method4 using a reference isotherm for carbon black.

**Small-Angle X-Ray Scattering (SAXS).** The SAXS experiments were conducted using a laboratory instrument (NanoStar, Bruker AXS, Karlsruhe) equipped with two 300 μm scatterless pinholes (Scatex) and a 2D detector (Vantec 2000). The sample to detector distance was 70.5 cm, which defines the q-range ($q = 4\sin(\theta)/\lambda$, where $\theta$ is the scattering angle and $\lambda$ is the wavelength of the X-ray).

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with $\theta$ being half the scattering angle and $\lambda=0.1542\ \text{nm}$ being the X-ray wavelength) from 0.2 to 3.15 nm$^{-1}$. The samples with a thickness of about 3 mm were cut from the center of the monoliths parallel to the cylinder axis. The bulk density $\rho$ was determined from the mass and the geometric dimensions of these samples.

For the rectangular-shaped ST samples, nine measurement positions arranged in a rectangular grid were chosen (see Figure 4 and Figure S4), while for the extruded NC samples, a variable number of evenly spaced measurement positions were selected (see Figure 4) from scanning X-ray transmission images performed with steps of 0.3 mm. In line with earlier studies on extruded hierarchical silica monoliths, the DPO parameter was chosen to determine the degree of preferred orientation of the struts constituting the macroporous structure, but due to the strong isotropic diffuse scattering from micropores in the carbon materials, the data analysis was slightly adapted, as compared to ref 1.2. The intensities at the left and right borders of the (10) peak were subtracted from the 2D pattern for each azimuthal angle. This leaves the (10) peak separated from the diffuse scattering from disordered meso- and micropores, and its azimuthal pattern was used to calculate the DPO parameter, as described in the main text.

**ASSOCIATED CONTENT**

### Supporting Information

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acs.chemmater.0c00302](https://pubs.acs.org/doi/10.1021/acs.chemmater.0c00302).

Photograph and schematic drawing of compression unit, SEM images, $N_2$ adsorption/desorption isotherms, X-ray transmission images, and azimuthal profiles (PDF)

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**Notes**

The authors declare no competing financial interest.

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