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Coffee Waste-Derived Nanoporous Carbons for Hydrogen Storage

Sebastian Stock, Nikolaos Kostoglou, Julian Selinger, Stefan Spirk, Christos Tampaxis, Georgia Charalambopoulou, Theodore Steriotis, Claus Rebholz, Christian Mitterer, and Oskar Paris*



ABSTRACT: Biological waste such as residues from the food and beverage industry provides a valuable and abundant resource to be used as a precursor for the synthesis of activated carbons that can be subsequently employed as adsorbents for, e.g., hydrogen storage. Materials with a large specific surface area and pores of appropriate size are necessary to achieve reasonable hydrogen adsorption capacity. Here, we present the repeatable synthesis of activated carbons from coffee waste, i.e., spent coffee grounds and coffee silver skins, on the basis of two independently synthesized batches. The carbonization process under nitrogen gas flow followed by chemical activation with solid potassium hydroxide results in microporous carbons with bimodal pore size distribution and specific surface area up to 3300 and 2680 m²/g based on



Brunauer–Emmett–Teller and density functional theory methods, respectively. The materials exhibit excellent hydrogen adsorption performance under cryogenic conditions (77 K), reaching high and fully reversible excess gravimetric hydrogen uptake values of up to 5.79 wt % at 37 bar, and total capacities exceeding 9 wt % at 100 bar.

KEYWORDS: coffee waste, activated carbons, nanoporous structures, hydrogen storage, gas sorption analysis, X-ray scattering

1. INTRODUCTION

Replacement of fossil fuels by renewable energy sources is a major milestone to limit CO_2 emissions and to reach climate neutrality, as proposed by the European Commission within the scope of the European Green Deal.¹ One of the most promising options is the use of H₂ as an energy carrier. Besides the high gravimetric energy density of H₂² (lower heating value of 120 kJ/g compared to 50 kJ/g of methane), environmentally clean combustion is a key argument to replace fossil-based fuels by H₂ in industrial processes that require high temperatures, which are difficult to achieve using electrical energy.

While issues with production can be addressed by optimizing the renewable energy production technologies, the storage of H_2 is a significant challenge. Its low volumetric density under ambient conditions makes it hard to store sufficient energy at technically practical volumes. Mobile H_2 storage systems used for the maritime and railway sector as well as fuel cell electric vehicles, including heavy-duty ones, will play an important role in the decarbonization of the transportation sector. However, the challenge in this context is to decrease the volume of the storage tanks to fit pertinent requirements and develop systems that are competitive to the current transportation technologies.

A simple and easy-to-control method to decrease the volume of the storage systems is to exploit the fully reversible physisorption mechanism of H₂ in nanoporous materials.³ This process is associated with fast adsorption and desorption kinetics, thus requiring refilling times comparable to fossil fuel tank systems. However, cryogenic temperatures (<100 K) are required to reach sufficient uptakes, due to the low interaction energies between carbon and H2. Metal-organic-frameworks (MOFs) have certain advantages in cryogenic adsorptive H₂ storage as their pore networks can be accurately engineered and optimized at the molecular scale.⁴ On the other hand, nanoporous carbons come with the major advantage of significantly lower cost, facile synthesis, and thermal/ chemical/mechanical stability. Taking also into account the available infrastructure worldwide, especially since activated carbons have been industrially produced for more than a century, the incorporation of nanoporous carbons in cryocooled storage tanks could be a promising option for future H₂-based transportation.⁵ The global activated carbon market in 2020 demanded around 2.7 million tons and is forecasted to

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Figure 1. Schematic synthesis route from coffee waste to nanoporous carbon.

demand around 3.9 million tons by the year 2026.⁶ The COVID-19 pandemic affected the worldwide economy and did not spare the activated carbon market either, causing volatile prices because of the scarcity of raw materials, such as coconut shells, as well as an increase in demand of suitable coal-based raw materials as a result of higher energy consumption to fuel industry.⁷

In Europe, as of 2019/20, 3.2 million tons of coffee were consumed, accounting to roughly 34% of the worldwide consumption.⁸ Coffee silver skin, a thin tegument of the outer layer of green coffee beans corresponding to about 4.2% of their weight, is obtained as a byproduct during the roasting process.⁹ The annually accumulated coffee waste is mostly disposed together with other bio-based waste, mainly originating from home use, but can also be used for the generation of heat by combustion as it exhibits high levels of calorific value (i.e., a higher heating value of 22.36 MJ/kg).¹⁰ Spent coffee grounds could also directly be used as fertilizers or as feedstock to produce biogas and biodiesel.^{11,12} Moreover, defatted spent coffee grounds were tested as a metal-free catalyst for hydrogen (H₂) gas generation.¹³

The chemical composition of spent coffee grounds and coffee silver skin (SCG and CSS, respectively), with its rather high carbon content (\sim 52%), makes them attractive precursors for activated carbons.¹⁴ Despite possessing similar elemental composition (C, H, N, O), the materials strongly differ in their macromolecular composition. While SCG is rich in hemicelluloses (~40 vs ~17% in CSS), CSS comprises a higher share of cellulose and lignin (i.e., ~24 and ~28%, respectively), compared to SCG (i.e., \sim 12 and \sim 24%, respectively).⁹ This difference has a large impact on the pyrolysis process and the resulting morphology of the obtained carbon.^{15,16} Complexity is added in carbonization as the botanical origin and environmental conditions during growth may alter the chemical and macromolecular composition, affecting carbon porosity and yield.¹⁷ Activation of the carbon precursors is commonly achieved by either physical activation using oxidizing gases (i.e., air, CO2, O2, or H2O steam) at high

temperatures up to 1000 °C or chemically, using strong chemical agents (i.e., acids, bases or salts) or by a combination of both approaches. Spent coffee grounds have been utilized as precursors for the synthesis of activated carbons using different approaches and thoroughly studied in terms of morphological characteristics and pore structure.¹⁸ Coffee-derived activated carbons were reported for various applications such as in electrodes for supercapacitors^{19–26} or batteries,^{27,28} adsorbents for waste water treatment,^{29,30} and the removal of dyes,^{31,32} as electrodes in fuel cells,³³ as well as for hydrogen storage purposes.^{34–38}

Concerning the H₂ adsorption behavior in nanoporous carbons, a recent study employed a machine learning algorithm to evaluate the important structural (and chemical) parameters responsible for the high H₂ uptake in activated carbons using data presented in the literature.³⁹ Kusdhany et al. concluded that the specific surface area (SSA) and the specific pore volume (SPV) have stronger effects than the pore size distribution, whereas an increase in ultra-micropore volume (i.e., for pores in width <0.7 nm) is more effective than increasing the micropore volume (i.e., for pores in width <2nm). Indeed, the accessible surface area (typically approximated by the Brunauer-Emmett-Teller (BET) area) is a measure of the gas-solid interface and thus it determines the extent of the gas-solid interaction and consequently the amount adsorbed. Likewise, pore volume is in principle a measure of the available space for adsorption, but this might be highly misleading as in practice the interplay of pore size and volume is very complex. In brief, smaller pores are characterized by enhanced gas-solid interactions due to the overlapping potential of neighboring atoms of the pore walls.⁴⁰ This leads to increased excess amounts adsorbed at relatively low pressures but due to pore filling, such pores are blocked and practically inactive at higher pressures (no free space for further adsorption). In this respect, despite their lower interaction energy, wider pores are more efficient at higher pressures as they offer more space (increased pore volume) for adsorption and easier desorption. On the other hand, beyond a

certain pore size, the effect of confinement is practically lost and densification is only due to compression. Thus, very wide pores may offer very high pore volume, but this volume is practically just empty space. Overall, in reality, an optimal combination of pore sizes is required to utilize as efficiently as possible the whole practical pressure range (up to 100 bar for cryo-adsorption). In all cases, it should be noted that although excess amounts are measured experimentally, it is the total amount adsorbed that is of interest for a real storage system.

In this study, we demonstrate a simple and repeatable synthesis process using solid potassium hydroxide (KOH) as the activation agent to transform coffee waste, namely, spent coffee grounds and coffee silver skins, into a high added-value product for exploitation in H₂ storage application. The investigation is based on two independently synthesized batches, whereas the reproducibility of the activation process to tailor the pore structure properties was investigated by structural analysis using scanning electron microscopy (SEM), Raman spectroscopy, X-ray diffraction (XRD), small-angle Xray scattering (SAXS), and N_2 gas adsorption/desorption measurements at 77 K. The H₂ storage properties and ultimate performance of the coffee-derived carbons were evaluated in detail by low- and high-pressure H₂ adsorption/desorption studies at cryogenic and room temperature conditions and our findings are compared to previously reported H₂ uptakes of comparably synthesized coffee-derived activated carbons.^{34–3}

2. MATERIALS AND METHODS

2.1. Synthesis Procedure. SCG and CSS (5.0 g each) from Coffee arabica were first dried at 105 °C for 24 h and then heated to 400 °C at 5 °C/min heating rate under N_2 flow and held for 1 h in a horizontal tube furnace (TZF 15/610, Carbolite), evenly distributed in aluminum oxide crucibles. The precarbonized materials were then mixed with solid potassium hydroxide (KOH; Merck, Darmstadt, Germany) in a mass ratio of 1:5. The mixtures were ground by means of a pestle and mortar for several minutes and subsequently heated to 800 °C at 5 °C/min heating rate under 0.5 L/min N₂ flow and held at this temperature for 2 h. Under these conditions, various reactions occur, the most important ones being displayed in Figure 1, leading to partial carbon gasification and thus generating pores. After cooling to room temperature, impurities were removed by washing the materials with 1 M hydrochloric acid (HCl; Merck) and de-ionized water until a pH value of 7 was reached. Finally, a drying step at 105 °C for 24 h was employed to remove residual water. For this study, two independent batches of activated carbons (batches B1 and B2) were synthesized from the same batch of SCG and CSS precursors, respectively. The four resulting samples are hereafter denoted as SCG-B1, SCG-B2, CSS-B1, and CSS-B2.

2.2. Materials Characterization. Scanning electron microscopy (SEM) analysis was performed with a Sigma VP (Zeiss) using an inlens detector and a working distance of around 4-5 mm. The microscope was operated in low-voltage mode, using an acceleration voltage of 700 V.

A Thermo Scientific FlashSmart Elemental Analyzer was used to determine the contents of carbon, hydrogen, nitrogen, sulfur, and oxygen (CHNS/O).²⁶ For all measurements, ~2.5 mg of the carbon powder was put in a tin or silver cup, and 8–10 mg of vanadium pentoxide was added as a catalyst. All measurements were using BBOT (2,5-bis(5-tert-butyl-benzoxazol-2-yl) thiophene) as the standard. While the samples for CHNS analysis were burned in an oxygen atmosphere, a helium flow was used for the pyrolysis to determine the amount of oxygen.

Raman spectra were recorded with a confocal spectrometer equipped with a frequency-doubled Nd-YAG laser emitting at a wavelength (λ) of 532.2 nm (Jobin-Yvon, LABRAM). The scattered light was measured using a Peltier-cooled slow-scan charge-coupled device (CCD) matrix detector. The laser beam (power density of 0.1

mW/ μ m² and spectral resolution of 1.5 cm⁻¹) was focused on the sample by a microscope (Olympus BX 40) fitted with a 50× long working distance objective lens. Raman shifts were recorded in the wavenumber range of 500–3500 cm⁻¹. The uniformity of the spectra was verified by probing different sample areas, and the spectra with the highest signal-to-noise ratio were used for analysis. The intensity ratio of the G- and D-band was used to calculate an in-plane correlation length L_a^{41} using the empirical relationship proposed by Matthews et al.⁴²

$$L_{\rm a} = (-12.6 \text{ nm} + 0.033 \cdot \lambda_{\rm laser}) \cdot \left(\frac{I_{\rm G}}{I_{\rm D}}\right) \tag{1}$$

The D- and 2D-bands were fitted with symmetric Lorentzian functions, whereas the G-band was fitted using the asymmetric Breit–Wigner–Fano (BWF) function.^{43–46} The area of the peaks was obtained by numerical integration of the fitted functions and thus the $I_{\rm G}/I_{\rm D}$ ratios were obtained from the peak area ratio.

Small-angle X-ray scattering (SAXS) measurements were performed using a NanoStar (Bruker AXS) SAXS facility equipped with an X-ray micro-source operating at 45 kV voltage and 0.65 mA current delivering Cu K α radiation (wavelength λ = 0.1549 nm). The SAXS signal was recorded with a Vantec 2000 area detector and azimuthally averaged, leading to the scattered intensity as a function of the scattering vector length ($Q = 4\pi \sin \theta / \lambda$). These 1-D scattering curves were normalized to the corresponding transmission value measured with a glassy carbon standard.⁴⁷ To cover a wide Q-range, SAXS curves were collected for two different sample-detector distances (25 and 65 cm) and then merged. The SAXS signals of microporous activated carbons (see Figure 4c) were approximated as the incoherent sum of three intensity contributions $I_{(Q)} = I_{\text{particle}} + I_{\text{NP}}$ + I_{Fluct} .⁴⁸ The first contribution (I_{particle}) in the low Q regime (Q < 0.2 nm⁻¹) is due to large carbon powder particles and may be approximated by a power law $P \cdot Q^{-\alpha}$, where the exponent α is 4 for perfectly smooth surfaces and is lower for rough surfaces.^{49,50} The second term $(I_{\rm NP})$, dominant at $Q > 0.6 \text{ nm}^{-1}$, originates from the nanopore scattering and contains information on the pore structure. The last part (I_{Fluct}) is associated with density fluctuations of the carbon structure.^{51,52} The SAXS curves of the different samples were fitted in the range 0.8 < Q < 10 nm⁻¹, neglecting I_{particle} to avoid excessive fit parameters, using the Debye–Anderson–Brumberger model (representing I_{NP})⁵³

$$I(Q) = \frac{B \cdot t^{3}}{\left(\frac{1}{t^{2}} + Q^{2}\right)^{2}} + C$$
(2)

Here, *B* is a scaling factor, *t* is the Debye length, and *C* is a constant to account for the assumed three-dimensional density fluctuations (I_{Fluct}) . The Debye length (t) can be used to calculate the average chord length of the carbon phase $\langle l_{\text{carbon}} \rangle$ and the pores $\langle l_{\text{pore}} \rangle$

$$t = \varphi \cdot \langle l_{\text{carbon}} \rangle = (1 - \varphi) \cdot \langle l_{\text{pore}} \rangle \tag{3}$$

with porosity φ

$$\varphi = \frac{\rho_{\rm skel} \cdot V_{\rm QSDFT}}{1 + \rho_{\rm skel} \cdot V_{\rm QSDFT}} \tag{4}$$

calculated using the specific pore volume $V_{\rm QSDFT}$ obtained from gas sorption analysis and the skeletal density $\rho_{\rm skel}$.

X-ray diffraction (XRD) data were collected using a D8 Advance Eco (Bruker AXS) instrument, equipped with an X-ray sealed tube (Cu-anode, 40 kV, 25 mA) and an energy-sensitive detector (LYNXEYE-XE). The recorded angular range (2θ) was $10-130^{\circ}$ with a step size of 0.01° and an exposure time of 1 s/step using a zero-background sample holder. To remove the influence of air scattering, the empty sample holder was measured using the same conditions and the background signal was subtracted from the sample signals. For quantitative analysis, the monotonous background of the XRD profiles was fitted using a power-law function in the form of $A \cdot Q^{-k}$ in the Q-range between 10 and 20 nm⁻¹, followed by a subsequent



Figure 2. SEM images of the CSS (a) and SCG (b) precursor materials before carbonization. The activated carbons obtained from CSS (c, d) and from SCG (e, f) shown at low and high magnifications, respectively.

subtraction of this contribution. The (10) diffraction peaks were then fitted using two BWF functions and the in-plane correlation length was calculated using the Scherrer equation

$$L_{\rm a} = 1.84 \cdot \frac{2\pi}{\Gamma_{(10)}} \tag{5}$$

where $\Gamma_{(10)}$ is the full width at half-maximum of the (10)-reflection.^{54,55} The peak position $Q_{(10)}$ obtained by fitting was used to calculate the in-plane lattice parameter

$$a = \frac{4\pi}{\sqrt{3} \cdot Q_{(10)}} \tag{6}$$

The SAXS and XRD data were merged together but analyzed separately, as shown in Figure 3b.

Low-pressure gas sorption experiments were performed with an Autosorb iQ³ gas sorption analyzer (Anton Paar QuantaTec) using N₂ of ultrahigh purity (99.999%) as adsorbate. The carbon materials (sample mass was ranging between 30 and 60 mg) were outgassed under vacuum (10⁻⁶ mbar) for 24 h at 250 °C. Glass filling rods were placed inside the sample cells to reduce the dead volume of the sample cell, which was automatically evaluated before each run using helium (purity 99.999%) gas. N2 adsorption/desorption isotherms were recorded at 77 K by means of a liquid N₂ Dewar vessel in a relative pressure (P/P_0) range from 10^{-6} to 0.99 in 77 steps for adsorption and 36 steps for desorption. The specific surface area was estimated by the multipoint Brunauer-Emmett-Teller (BET) method following the BET consistency criteria (ISO 9277:2010) (in the P/P_0 range of 0.02–0.2), as well as by the Quenched Solid Density Functional Theory (QSDFT) method using the N_2 -carbon equilibrium transition kernels at 77 K for slit pores.⁵⁶ The specific pore volume and the pore size distribution (PSD) were also calculated using the QSDFT method.

2.3. Hydrogen Storage. Low-pressure H_2 (99.999% purity) adsorption/desorption isotherms were collected with an Autosorb iQ³

gas sorption analyzer (Anton Paar QuantaTec) at 77, 87, and 97 K using 57 adsorption and 20 desorption points starting from 10^{-3} up to 1000 mbar. For the measurements, a liquid nitrogen bath was used in connection with sample heating (CryoSync, Anton Paar QuantaTec). In this work, the excess gravimetric H₂ uptake (n_{ex}) is defined as the mass of adsorbed H₂ (m_{H_2}) divided by the system mass (i.e., $m_{sample} + m_{H_2}$). Using a plot of ln(*P*) vs the gravimetric H₂ uptake it is possible to calculate the heat of adsorption using the virial eq 7, with m being the number of virial coefficients which were set to 5.

$$\ln P = \ln n + \frac{1}{T} \sum_{i=0}^{m} a_{i} n^{i} + \sum_{i=0}^{m} b_{i} n^{i}$$
(7)

The fit was performed from the lowest to the highest uptake common values.⁵⁷ With eq 7, the heat of adsorption as a function of the H₂ uptake can be calculated and additionally allows an estimation of the heat of adsorption at zero coverage (depicted by $Q_{st}^0 = -R \cdot a_0$).

$$Q_{\rm st}(n) = -R \cdot \sum_{i=0}^{m} a_i \cdot n^i \tag{8}$$

High-pressure (0-100 bar) H₂ adsorption/desorption isotherms were recorded using a SETARAM Hy-Energy PCTPro-2000 manometric system and ultrapure (99.999%) H₂ gas. Excess H₂ adsorption isotherms were collected at 77 and 298 K. Approximately 200 mg of each of the carbon materials were loaded in a stainless-steel sample holder and degassed in situ under high vacuum (10^{-6} mbar) at 250 °C for 12 h. Prior to each measurement, the dead volume of the system was determined by performing a series of volume calibrations at ambient temperatures (303 and 298 K) using ultrapure (99.999%) He gas. To avoid possible calibration errors due to helium adsorption at 77 K, the system volume at the experimental temperature was determined using a reference volume calibrations at 303 and 77 K on different quantities of a nonadsorbing material (nonporous glass) at the same sample holder. The main part of the device was always temperature controlled at 303 K with the aid of a specially designed air bath. The sample holder was immersed in either a dewar vessel equipped with a custom-made liquid nitrogen level sensor/auto refill system (ensuring negligible sample temperature and cold volume variations) for the measurements at 77 K or a water/ethylene glycol bath for the measurements at 298 K. For technical applications, the total amount of H₂ in the system (n_{tot}) is of interest, which can be estimated from the excess isotherm (n_{ex}) using⁵⁸

$$n_{\text{tot}} = n_{\text{ex}} + \rho_{\text{bulk}(p,T)} \cdot V_{\text{pore}} = n_{\text{ex}} + \frac{p \cdot V_{\text{pore}}}{(R \cdot T)} \cdot \frac{1}{Z_{(p)}}$$
(9)

where $\rho_{\text{bulk}(p,T)}$ is the bulk H₂ molar density as a function of pressure (p) at a given temperature (T), V_{pore} is the total pore volume (obtained by the QSDFT method in our case), *R* is the universal gas constant, and $Z_{(p)}$ is the compressibility factor of H₂ as a function of pressure at 77 K.⁵⁹

3. RESULTS AND DISCUSSION

3.1. Powder Morphology. The SEM images of the CSS and SCG precursor materials are shown in Figure 2a,b, respectively. SEM images of the activated carbons at different magnifications are shown in Figure 2c,d for the material synthesized from CSS, and in Figure 2e,f for the SCG material. The CSS material displays a cellular structure (containing macropores and large mesopores), which is typical for cellulose-based organic materials. The SCG precursor, on the other hand, being rich in hemicellulose, results upon treatment in a more compact morphology at the macropore level. Although the details may depend on the type of coffee beans and the roasting process, the SEM images of the SCG material in Figure 2e,f are quite similar to previously investigated activated carbons derived from coffee waste.^{18,28}

3.2. Chemical Composition. The representative chemical compositions of CSS and SCG (batch 2 samples) based on the CHNS/O analysis are presented in Table 1. The main

Table 1. Elemental Composition (Excluding Ash) of CSS-B2 and SCG-B2^a

element	carbon (wt %)	oxygen (wt %)	hydrogen (wt %)	nitrogen (wt %)	sulfur (wt %)	
CSS-B2	89.2	6.7	0.2	0.1	n.d.	
SCG-B2	91.7	4.3	0.2	0.1	n.d.	
^a n.d.: not detected.						

difference can be found in the oxygen content of the samples, where CSS shows 6.7 wt % and SCG 4.3 wt %. The hydrogen and nitrogen contents were found to be equal for both materials. Based on this analysis, no prediction can be made regarding the composition of functional surface groups.

3.3. Nanoscale Structural Features. The Raman spectra shown in Figure 3a exhibit three characteristic bands identified as the D-band at 1360 cm⁻¹, the G-band at 1560 cm⁻¹, and the 2D-band (also denoted as G') at 2870 cm⁻¹. The D-band arises from in-plane distortion of the graphene sheets. Hence, it would not be present in a perfect, infinitely extended single-layer graphene, and may be related to the sp³ hybridization of carbon atoms.^{60,61} The G-band originates from in-plane stretching of the sp²-bonds in the aromatic carbon rings. The 2-D band, located at approximately twice the frequency of the D-band, arises from second-order scattering processes, with a broad and featureless 2D-band being characteristic for turbostratic carbons. The intensity ratio I_D/I_G can be used to

calculate the in-plane correlation length L_a and the resulting values are shown in Table 2. L_a values between 2.3–2.8 nm were obtained for all samples, with systematic slightly lower L_a values from the batch 1 samples compared to batch 2.

The merged SAXS and XRD curves of the samples, shown in Figure 3b, are composed of three characteristic contributions in the small-angle regime ($Q < 10 \text{ nm}^{-1}$). In the low Q regime $(<0.5 \text{ nm}^{-1})$, the scattering intensity is dominated by surface scattering from carbon powder particles with rough surface (see Figure 2). The nanopore scattering and the fluctuation contribution are dominant for scattering vectors 0.5 <Q <10 nm⁻¹. While the hump around $Q_{\rm h} \approx 3 \text{ nm}^{-1}$ is characteristic for a typical length scale in the system $(\pi/Q_h \approx 1 \text{ nm})$, the regime at larger Q $(5-10 \text{ nm}^{-1})$ is typical for the surface scattering of the nanopores and should be described by a power-law with exponent -4 for sharp interfaces (Porod's law).⁶² Yet, it is well known that for microporous carbons with sub-nm pore sizes, Porod's law may be invalid because of the difficulty to define a "sharp" interface at this scale.^{48,51} Moreover, the SAXS signal overlaps with scattering from atomistic features of the highly defective "few-layer" graphene structure for this type of carbons. For purely 1D density fluctuations due to turbostratic stacking of graphene sheets, a power law with slope -2 should apply.^{51,63} In contrast, for random 3D fluctuations, this scattering contribution should be a constant (Laue scattering). Moreover, at an even larger Q, the scattering contribution from very small micropores and the (001) stacking reflection of the graphene sheets start to overlap, making SAXS data evaluation even more complex. Therefore, we refrain from the determination of the pore surface area from SAXS and we use eq 2 to obtain an estimate for a characteristic length t of the system. This length parameter is listed in Table 2 together with the chord lengths of the pores and the carbon phase, obtained from t using eqs 3 and 4.

While *t* has no simple explanation, the chord lengths $\langle l_{carbon} \rangle$ and $\langle l_{pore} \rangle$ are directly related to an average size of the carbonand the pore phases, respectively. Table 2 shows that while $\langle l_{
m carbon}
angle$ is similar for all four samples, $\langle l_{
m pore}
angle$ is around 1.1 nm for the CSS samples, while it is considerably smaller (around 0.75 nm) for the SCG samples. It should be noted that $\langle l_{carbon} \rangle$ is around 0.33 nm, which corresponds almost perfectly to the stacking distance of two graphene sheets in graphite $(d_{002} =$ 0.335 nm). This is consistent with the almost absent (002) stacking reflection, manifesting only in a broad shoulder in the XRD data in Figure 3b at scattering angles >10 nm⁻¹.⁵⁵ The weak stacking reflection indicates a highly disordered structure with poor stacking ordering of only very few graphene sheets. For this reason, no further evaluation of the carbon stacking height from the (002)-reflection was possible. In contrast to the stacking reflection, the (10) in-plane reflection is clearly visible around 30 nm⁻¹, indicating some degree of in-plane order. The in-plane correlation length (L_a) obtained from XRD using eq 5 is also listed in Table 2. The L_a values of both samples from the second batch (i.e., 2.6 and 2.4 nm for CSS-B2 and SCG-B2, respectively) are slightly larger compared to the first batch (i.e., 2.2 nm for CSS-B1 and SCG-B1). They follow the same systematic trend as the L_a values obtained from Raman spectroscopy and can therefore be judged reliable. Yet, the estimation of possible systematic errors is difficult for both methods. Since the effects are rather small (in the order of 2 times the distance of neighboring carbon atoms), they will not be discussed further.



Figure 3. (a) Raman spectra of the CSS and SCG materials from the two batches. (b) Merged SAXS and XRD profiles of the carbon materials collected in the Q range of 0.1-10 and 10-60 nm⁻¹, respectively.

Table 2. Summary of Parameters Derived from Structural Analysis Using Raman Spectroscopy, XRD, and SAXS^c

	Raman sh	ift (cm^{-1})							
material	D	G	$L_{a,(Raman)}^{a}$ (nm)	$a_{(10)}^{b}$ (nm)	$L_{a,(XRD)}^{c}$ (nm)	φ^d	t ^e (nm)	$\langle l_{\rm carbon} \rangle^f (\rm nm)$	$\langle l_{\rm pore} \rangle^{\rm g} \ ({\rm nm})$
CSS-B1	1362	1597	2.3	0.24	2.2	0.76	0.28	0.37	1.17
CSS-B2	1352	1592	2.8	0.24	2.6	0.76	0.24	0.32	1.02
SCG-B1	1356	1592	2.4	0.24	2.2	0.71	0.22	0.31	0.77
SCG-B2	1357	1594	2.7	0.24	2.4	0.72	0.21	0.29	0.74

"In-plane correlation length calculated with eq 1 using the area ratio of the Raman G and D bands. ^bIn-plane lattice parameter calculated from XRD using eq 6. ^cIn-plane correlation length obtained from XRD using eq 5. ^dPorosity calculated with eq 4 assuming a skeletal density of 2 g/cm³ for all samples. ^eDebye length obtained from SAXS using eq 2. ^fAverage chord lengths of the carbon phase calculated with eq 3.

3.4. Pore Structure. The N_2 adsorption/desorption isotherms at 77 K for the nanoporous carbon materials are presented in Figure 4a. Figure 4b shows the same data in a semi-logarithmic plot to highlight the low-pressure adsorption behavior. The SCG materials show a fully reversible type I isotherm (combination of I(a) and I(b) types), typical for microporous solids (i.e., with pore widths below 2 nm), according to the classification of the International Union of Pure and Applied Chemistry (IUPAC).⁶⁴ The CSS materials reveal an isotherm shape related rather to type I(b), implying a broader distribution of pores toward the small mesopore range. Moreover, they exhibit minuscule hysteresis loops between the adsorption and desorption branches associated with cavitation phenomena within mesopores (i.e., 2-50 nm), whereas the presence of a further slight increase in N₂ uptake at P/P_0 > 0.95 is caused by adsorption in macropores and external surfaces. All samples exhibit a steep uptake at low relative pressures $(P/P_0 < 10^{-1})$. The SCG samples show a slightly higher uptake at low pressures, suggesting increased microporosity.6

This is confirmed by the analysis of the isotherms based on the QSDFT method, shown in Figure 4c,d, revealing the cumulative and differential pore size distributions of the materials, respectively. The volume-weighted medians of the pore size (d_{50}) , as obtained from the cumulative PSD plots (see Figure 4c), are listed in Table 3 together with the 25th and 75th percentiles. The d_{50} values are around 1 nm for all samples but are somewhat lower for the SCG samples compared to the CSS samples. This trend is generally

consistent with the pore chord lengths from SAXS (see Table 2). The differential PSD plots in Figure 4d exhibit a sharp peak at 0.85 nm for all samples, followed by a broader peak with a maximum located around 1.5 nm. The size distribution of the SCG samples extends only to the micropore limits (2 nm), while the CSS samples reveal a significantly broader distribution extending to small mesopores up to about 2.5 nm. Moreover, the CSS samples also reveal a third (small) pore population between 3.0-4.0 nm, possibly associated with the hysteresis loop. Table 3 summarizes all pore structure parameters of the materials derived from the BET and QSDFT methods. The specific surface area from QSDFT ($\approx 2600 \text{ m}^2$ / g) is similar for all four samples. There is a slightly higher specific surface area for the batch 2 samples, which correlates with the corresponding smaller L_a values obtained from Raman spectroscopy and XRD (Table 2). However, this difference in specific surface area is only about 5%. The micropore volume is very similar for all four samples, while the total pore volume is somewhat larger for the CSS samples due to the mesopore contribution.

3.5. H₂ Adsorption and Storage. The low-pressure (0-1 bar) H₂ adsorption and desorption isotherms, collected at 77, 87, and 97 K, are shown in Figure 5a. All samples show a fully reversible uptake-release behavior and lack a saturation plateau at 1 bar. The H₂ uptake decrease by ~30% and by ~50% by an increase in temperature of 10 and of 20 K, respectively. The uptake at 77 K is similar for all four samples (Table 4). The slightly higher value for SCG-B1 might be attributed to its smallest mean pore size d_{50} (see Table 3), as narrow



Figure 4. (a) N_2 gas adsorption (solid symbols) and desorption (open symbols) isotherms collected at 77 K, (b) adsorption and desorption isotherms plotted semi-logarithmic to highlight the micropore filling at low relative pressures, and (c) cumulative pore volume versus pore width derived by the quenched solid density functional theory (QSDFT) carbon slit-pore model for N_2 adsorption at 77 K. d_{50} is the volume-weighted median of the pore sizes, whereas d_{25} and d_{75} denote the 25th and 75th percentiles of the pore size, respectively, which are exemplarily indicated with dashed and dotted lines for SCG-B2. (d) Differential pore volume versus pore width derived by QSDFT carbon slit-pore model for N_2 adsorption at 77 K.

Table 3. Pore Structure Characteristics from N2 Gas Adsorption at 77 K

material	$S_{\rm BET}^{a} ({\rm m}^2/{\rm g})$	$S_{\rm QSDFT}^{\ b} ({\rm m}^2/{\rm g})$	$V_{\rm QSDFT}^{c} (\rm cm^3/g)$	$V_{\rm Micro}^{\ \ d} ({\rm cm}^3/{\rm g})$	$V_{ m Micro}/V_{ m QSDFT}$	$d_{50} (d_{25} - d_{75})^e (\text{nm})$
CSS-B1	3310	2570	1.6	1.3	0.8	1.4 (0.9–1.9)
CSS-B2	3330	2680	1.6	1.3	0.8	1.3 (0.9–1.8)
SCG-B1	2990	2530	1.2	1.2	1.0	1.1 (0.8–1.5)
SCG-B2	3160	2680	1.3	1.3	1.0	1.1 (0.8–1.5)

^{*a*}Brunauer–Emmet–Teller (BET) area. ^{*b*}Specific surface area (SSA) calculated by the quenched solid density functional theory (QSDFT) method. ^{*c*}Specific pore volume (SPV) derived by the QSDFT method. ^{*d*}Cumulative SPV of pores smaller than 2 nm in width obtained with the QSDFT method. ^{*c*}Volume-weighted median of the pore sizes (d_{50}) and the corresponding 25th and 75th percentiles (d_{25} and d_{75} , respectively), derived from Figure 4c.

micropores act as preferred adsorption sites.^{66,67} From the lowpressure H_2 adsorption isotherms collected at different temperatures, the isosteric heat of adsorption can be calculated (Section 2.2), being similar for all samples (Table 4). Using the virial equation approach, it is possible to deduce the heat of adsorption at low surface coverage, which gives a rough estimate of the mean interaction energy between the carbon surface and a H_2 molecule (Table 4). Again, the values are identical for all four samples within the error margins. Values presented in the literature for standard activated carbons range between 5 and 8 kJ/mol,⁴⁰ with the present samples lying at

the upper limit. Kemp et al. synthesized activated carbon by mixing spent coffee grounds with a 7 M KOH solution (which resulted in a mass ratio of 10:4 after drying at 100 °C) and a subsequent activation step at 700, 800, and 900 °C under argon atmosphere for 1 h. The materials exhibited a BET area of 537, 815, and 1040 m²/g and a H₂ uptake at 1 bar and 77 K of 1.34, 1.53, and 1.75 wt %, respectively.³⁶ More comparably to the samples presented in this work, Gadipelli et al. synthesized activated carbons using spent coffee grounds by mixing precarbonized (at 350, 450, 550, and 650 °C) samples with solid KOH in a ratio of 1:3 in distilled water. Subsequent



Figure 5. (a) Gravimetric H_2 uptake versus pressure up to 1 bar measured at 77, 87, and 97 K, respectively. Full symbols represent the adsorption isotherms, and open symbols represent the desorption isotherms. (b) Isosteric heat of adsorption versus gravimetric uptake calculated using the virial equation.⁵⁷

Table 4. Gravimetric H_2 Uptake at 1 bar and Three Different Cryogenic Temperatures and Isosteric Enthalpies of H_2 Adsorption (Low Surface Coverage and Mean Values) for the CSS and SCG Materials

	gravimetric H ₂ uptake (wt %)				
material	77 K	87 K	97 K	heat of adsorption at low coverage Q ⁰ _{st} (kJ/mol)	$\begin{array}{c} \text{mean heat } \underline{\text{of}} \\ \text{adsorption } \overline{Q_{\text{st}}} \\ (\text{kJ/mol}) \end{array}$
CSS-B1	2.77	2.02	1.39	7.39 ± 0.07	6.37
CSS-B2	2.75	1.85	1.30	7.64 ± 0.11	6.72
SCG- B1	2.81	2.06	1.44	7.63 ± 0.09	6.60
SCG- B2	2.76	1.94	1.34	7.73 ± 0.07	6.80

annealing at 750 °C for 1 h under nitrogen atmosphere led to BET areas of 2232, 2522, 2631, and 2656 m²/g as well as H₂ uptake amounts of 2.9, 2.8, 3.0, and 3.0 wt % at 77 K and 1 bar for the materials obtained from precarbonization at 350, 450, 550 and 650 °C, respectively (Table 5).³⁸ These low-pressure uptakes are quite comparable to the ones presented in this work measured at the same conditions and summarized in Table 6.

High-pressure (0-100 bar) excess H₂ adsorption and desorption isotherms were recorded at 77 and 298 K, as shown in Figure 6a. The isotherms at 77 K follow a Langmuir-type behavior,⁶⁸ with a steep increase of the adsorbed H₂ amount at low pressures, due to the presence of sub-nanometer pores which act as strong adsorption sites.⁴⁰ Maximum excess

Table 5. Maximum Excess H_2 Uptake at 77 and 298 K and Maximum Total H_2 Uptake at 77 K

	maximum exc (wt	ess H ₂ uptake %)	maximum total H ₂ uptak (wt %)		
material	77 K	298 K	77 K		
CSS-B1	5.79 (37 bar)	0.75 (97 bar)	9.17 (100 bar)		
CSS-B2	5.79 (37 bar)	0.68 (99 bar)	9.24 (101 bar)		
SCG-B1	5.44 (35 bar)	0.75 (99 bar)	8.29 (101 bar)		
SCG-B2	5.44 (35 bar)	0.81 (97 bar)	7.98 (100 bar)		

uptakes of about 5.79 wt % were reached at pressures around 37 bar for the CSS samples, and of 5.68 and 5.35 wt % for SCG-B2 and SCG-B1, respectively. To the best of our knowledge, these are the highest reported H₂ uptake values for similarly synthesized materials using spent coffee grounds, as evidenced from Table 6. For pressures exceeding the maximum uptake point, the adsorbed excess amount decreases due to bulk H₂ densification.⁵⁸ Figure 6a also shows the adsorption isotherms collected at 298 K, which demonstrate a Henry-type behavior; i.e., H₂ uptake increases linearly with pressure.⁶⁹ The low H₂ uptake values (<1 wt %) at 298 K and 100 bar for all materials clearly demonstrate the necessity of cryogenic temperatures for practical applications of nanoporous carbons for H₂ storage. The SCG-B1 material showed the highest uptake of 0.81 wt % at 298 K and 100 bar, respectively, which is comparable to previous studies on activated carbon from spent coffee grounds.^{34,35,37} Since H₂ uptake is often directly associated with the available surface area, the H₂ uptake normalized by the QSDFT specific surface area (given in mmol H_2/m^2) is shown in Figure 6b. Looking at the maximum uptake, the CSS materials exhibit a slightly larger area-normalized uptake compared to the corresponding SCG material from the same batch, which might be attributed to the higher pore volume (see Table 3) in the CSS samples, as well as the higher oxygen content (Δ oxygen ~2.4 wt %, see Table 1). In comparison, Akasaka et al. prepared activated carbons from waste coffee beans by the means of steam/ CO_2 carbonization and activation, followed by an activation step using KOH in different ratios. This resulted in carbons exhibiting a narrow pore size distribution (mean pore size between 0.81-1.1 nm) and BET areas ranging between 780 to 2070 m²/g. A maximum H₂ storage capacity of ~4 wt % at 77 K and ~ 35 bar was reported.³⁵ The high-pressure H₂ adsorption measurements provide the excess H₂ uptake, which is the total amount of H₂ adsorbed in the sample volume minus the bulk amount of H₂ within the pore structure.⁶⁸ The total H₂ uptake was calculated from the excess uptake using eq 9, which also takes into consideration the amount of H₂ compressed into the pore volume space.⁵⁸ The H_2 compressibility factor (*Z*), shown in Figure 6c was obtained from the REFPROP software (National Institute of Standards

Table 6. Comparison of Excess Gravimetric H₂ Storage Capacities (C_g) at Different Temperatures (77 and 298 K) and Pressures (1–140 bar) for Coffee-Derived Carbon Materials Reported in the Literature

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temperature (K)	pressure (bar)	$S_{\rm BET}~({\rm m^2/g})$	$V_{\rm tot}~({\rm cm^3/g})$	C _g (wt %)	reference
298	120	780-2070		0.6	34
77/298	40/120	780-2070		2.5-4.0/0.35-0.6	35
77	1	537-1040	0.32-0.64	1.34-1.75	36
298	140	3149	1.67	0.91	37
77	1	2232-2656	0.94-1.13	2.8-3.0	38
77	1	2000-2220	12-16	2.75-2.81	this work
77/298	35/100	2790-3330	1.2-1.0	5.44-5.79/0.68-0.81	uns work



Figure 6. (a) Excess H_2 adsorption and desorption isotherms collected up to 100 bar at 77 and 298 K, (b) excess H_2 adsorption uptake normalized by the (QSDFT) specific surface area, (c) compressibility factor Z vs pressure, and (d) total H_2 uptake as a function of pressure at 77 K.

and Technology (NIST)), which is based on the Leachman equation-of-state for H_2 .⁵⁹ The corresponding adsorption isotherms are shown in Figure 6d. The CSS materials exhibit a higher maximum total uptake of about 9.2 wt % compared to the SCG materials. Again, these differences are attributed to the higher pore volumes of the CSS samples as well as the increased oxygen content.

4. SUMMARY AND CONCLUSIONS

Coffee wastes were used as precursors for the synthesis of nanoporous activated carbons with high surface areas and large pore volumes. The carbon materials were synthesized using precarbonization at 400 $^{\circ}$ C and subsequent combined carbonization and activation at 800 $^{\circ}$ C. The resulting nanoporous carbons show specific surface areas up to 2680

 m^2/g and specific pore volumes up to 1.6 cm³/g based on the QSDFT method, with the majority of the nanopores being smaller than 2 nm. The reproducibility of the carbonization/ activation process to tailor the pore structure was confirmed for two independent batches of samples, using quantitative analysis tools to derive key structural parameters. While the CSS materials exhibit larger pore volumes due to some mesoporosity, the SCG materials exhibit slightly smaller average pore sizes, leading to a quite similar specific surface area. The low- and high-pressure H₂ uptake performance was evaluated at different temperatures showing similar uptake behavior for all samples. Slight differences between the batches can be explained by slight differences in structural parameters, but overall the data are very well reproduced. The small differences between the SCG and the CSS samples might be

attributed to the smaller pore size of SCG dominating at low pressures and the higher oxygen content of CSS might be responsible for the higher uptake at high pressures.³⁹ To the best of our knowledge, the presented coffee waste-derived nanoporous activated carbon materials show the highest H₂ uptake (5.79 wt % at 37 bar and 77 K) reported in the literature so far. For other adsorbents such as MOFs typical uptake values of around 3-7 wt % at 77 K and pressures between 50 and 100 bar were reported.⁴ We emphasize that although uptake values for such systems might be somewhat higher compared to activated carbons from bio-waste, their complex synthesis procedure and therefore their availability for mass applications remains highly limited. As spent coffee ground and coffee silver skins are widely and readily available worldwide, a collection through smart waste management systems may provide a new feedstock for the production of activated carbons for hydrogen storage and other energy storage applications.

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Notes

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