Creating Directionality in Nanoporous Carbon Materials: Adjustable Combinations of Structural and Chemical Gradients

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The properties of porous materials benefit from hierarchical porosity. A less noted element of hierarchy is the occurrence of directionality in functional gradient materials. A sharp boundary is replaced by a transition from one feature to the next. The number of cases known for porous materials with either structural or chemical gradients is small. A method capable of generating combinations of structural and chemical gradients in one material does not exist. Such a method is presented with a focus on silver and nitrogen containing carbon materials because of the potential of this system for electrocatalytic CO₂ reduction. A structural gradient results from controlled separation using ultracentrifugation of a binary mixture of template particles in a resorcinol-formaldehyde (RF) sol as carbon precursor. A new level of complexity can be reached, if the surfaces of the template particles are chemically modified. Although the template is removed during carbonization, the modification (Ag, N) becomes integrated into the material. Understanding how modified and unmodified large and small particles sediment in the RF sol enables almost infinite variability of combinations: chemically graded but structurally homogeneous materials and vice versa. Ultimately, a material containing one structural gradient and two chemical gradients with opposing directions is introduced.

1. Introduction

Numerous applications rely on the introduction of porosity to a certain solid. Porous materials are known for a huge variety of matrix materials ranging from ceramics to metallic and polymeric. Nanostructured carbon holds an outstanding position among these materials, especially because of its role and promises in future energy-related technologies. It is an important question, how properties change or improve by the existence of multiple pore types. Sun et al. or Parlett et al. have extensively reviewed the state of the art for the so-called hierarchically structured porous materials in 2016 and 2013, respectively. A powerful strategy for the design of porous solids is the use of templates. Whenever two different templates do not fuse but remain dispersed separately, this can lead to bimodal pore systems. However, the distribution of the two types of templates is statistical, and this results in a homogeneous distribution of differently sized pores. The next level of complexity is realized by hierarchical materials, which are characterized by a graded porosity, represented by a defined distribution of different pore sizes on a microstructural level.

The generation of graded porosity has been addressed in the literature for materials with very large pores (>10 µm) and for applications like gel electrophoresis. For instance, Zhou et al. presented polymers with graded porosity by a refined foaming procedure using supercritical CO₂. An impressive study was published by Stubenrauch and co-workers in 2017. Zhang and co-workers utilized centrifugation methods applied on a polydisperse oil in water emulsion, followed by polymerization of water-soluble monomers. The emulsion droplets acted as templates and as a result, polymeric bodies with gradient porosity could be achieved. Microfluidic techniques were used to control the distribution of differently sized voids in polystyrene foams. Luo et al. presented an impressive study in 2015. The authors describe a macroporous hydrogel composed of N-isopropylacrylamide prepared by hydrothermal synthesis. It could be shown that the gradient in porosity resulted in programmable locomotion. Inorganic materials with graded porosity have been created by anisotropic sintering, freeze-casting, or gel-casting processes. Sailor and co-workers showed that electrochemical etching of silicon is suitable for producing graded porosity, and the materials were then used for size-exclusion chromatography. Holtappels et al. indicated that gradient porosity can be beneficial for the performance of electrode materials. A nice paper demonstrating the benefits of a gradient pore structure in the solid-oxide fuel cell was published by Brandon and Brett in 2006. The literature on carbon characterized by graded porosity is extremely small. The paper published by Wiesner and co-workers in 2015 is worth mentioning. Using a special block copolymer that concurrently served as a carbon precursor and structure-directing agent by anisotropic microphase separation the formation of graded porosity was induced.

The majority of cases discussed above involve very large pores, often with ill-defined shape, broad size dispersity, and low porosities. Although the advantages of materials with graded porosity in the size range <1 µm or even <100 nm are evident for energy-related applications and electrochemistry chromatography, or poromechanics, for instance.
the experimental realization is extremely difficult and represents an open scientific gap.\textsuperscript{[22,23]}

Gradient porous materials represent a family among the superordinate class of the so-called functional gradient materials. A second family in this class is given by solids possessing surface chemical gradients.\textsuperscript{[24]} A powerful strategy to introduce chemical gradients is the application of organosilane surface modification strategy,\textsuperscript{[25]} and a typical feature is to observe how the gradient influences the wettability of surfaces. A nice overview was given by Lin and co-workers in 2017.\textsuperscript{[26]} Porous materials equipped with functional chemical gradients could find applications in chromatography, for instance.\textsuperscript{[27]} The analysis of the existing literature shows,\textsuperscript{[5,28]} even porous materials with chemical gradients are rare, but those with a combination of a structural and a chemical gradient do not exist to the best of our knowledge. Here, we present the synthesis of porous carbon materials possessing combined structural and (chemical) functional gradients (see Figure 1).

2. Results and Discussion

Our approach is based on a paper published in 2016.\textsuperscript{[29]} A bimodal dispersion of colloidal polystyrene (PS) particles was used as template particles. The controlled fractionation of those particles by ultracentrifugation was performed in presence of a resorcinol–aldehyde gel as carbon precursor. The resulting carbon material was characterized by a gradient in porosity and was used as binder-free electrode for a lithium–oxygen battery. In addition to combining PS of different sizes, we can now modify the surfaces of the particles chemically (Figure 1a). Our aim is, if done properly, the surface-bound species will remain in the material after carbonization, leading to an additional functional chemical gradient. Ultimately, chemical and structural gradient properties can be adjusted independently. The paper is structured as follows. First, we quickly recap the generation of pure carbon materials with absence of any gradient. We then present a carbon material containing a chemical but no structural gradient. Then, the chemical gradient is combined with a structural gradient as well. The material of highest complexity comprises chemical gradients combined with a structural gradient. This way, all cases of the matrix shown in Figure 1b will be realized.

2.1. Porous Carbon with Structural Gradient Only

Depending on the size of the used PS pores ranging from 20 to 500 nm, the corresponding structural gradient material can be generated (see Figure S1 in the Supporting Information) in analogy to ref. \textsuperscript{[29]}. It is of course also possible to prepare a material with a monomodal pore system (see Figure S2 in the Supporting Information). The materials are named according to the templates, which were used for their preparation. For instance, PS288/588 is representative for a structurally graded material prepared by template particles with 288 and 588 nm size. It should be noted that the pores are always smaller than the size of the respective template because of the contraction of the material during the carbonization process.

2.2. Porous Carbon Materials with Chemical Gradient Only

For the first carbon material possessing a functional gradient, we used sulfonate-stabilized PS modified with silver (Ag)
prepared according to a method published by Lee et al.\textsuperscript{[30]} The size of the template particles was 480 nm (PS480) (see Figure S3 in the Supporting Information). Ag nanoparticles with sizes of 10–20 nm are attached to the surface of the template particles, as confirmed by transmission electron microscopy (TEM) and powder-X-ray diffraction (PXRD). According to thermogravimetric analysis (TGA), the mass fraction of Ag in these particles is 1.2 wt%. Compared to unmodified PS particles, the mass is now slightly higher, which is sufficient for controlling the separation of equally sized template particles by ultracentrifugation (UZ) in a mixture of bare PS and similarly sized PS modified with Ag. If successful, we expect a carbon material with homogeneous and monomodal distribution of pores, but with a gradient of Ag particles, which are now attached to the matrix (Figure 2).

The structure of the material was analyzed by scanning electron microscopy (SEM), and the concentration of Ag in the material was investigated using energy-dispersive X-ray spectroscopy (EDX). The pore structure remains homogeneous over the entire monolith with pores size $= 376 \pm 35$ nm. At the bottom, there is no Ag detectable, while at the top, the concentration of Ag increases (Figure 2h). One can identify bright spots attached to the surfaces in SEM images of those zones (Figure 2a). We assign these features to the presence of Ag nanoparticles. Final proof comes from TEM and PXRD measurements shown in Figure S4 (Supporting Information). The process proves to be very versatile. Similar materials can be prepared with a different pore size ($180 \pm 18$ nm) if, for instance, smaller template particles such as Ag@PS288 are used in combination with unmodified PS, as shown in Figure S5 (Supporting Information).

2.3. Porous Carbon with Chemical and Structural Gradients

The generation of carbon materials with a structural gradient overlayed by a functional chemical gradient is now straightforward. We show this for small unmodified template particles PS137 and larger Ag-modified Ag@PS480. SEM images of the resulting carbon material are given in Figure 3. The controlled separation of the template particles works very well due to not only their mass but also their size differing significantly. Only small pores are present at the start of the gradient ($x = 0$). An increasing fraction of pores appears the more one progresses in the gradient ($\rightarrow x = 1$). For a more quantitative analysis of the SEM data concerning the structural gradient,
we have applied a machine learning tool (trainable WEKA segmentation,[31] embedded in Fiji)[32] for image analysis (see also Figure S6 in the Supporting Information). As a result, the smaller pores are fractioned in a certain segment along the gradient ($\chi_{\text{small pores}}$), which is also shown in Figure 3 for demonstrating the existence of the structural gradient.

While no Ag particles are observable in the small pores ($x = 0$), their high density can be clearly identified in the SEM images for $x = 1$ (Figure 3). The gradient in the density of the Ag nanoparticles was analyzed as before by recording EDX spectra of the different regions. The position-dependent EDX data confirm the conclusions drawn from TEM. Precise control over the features of the material is given by choice of different template particles. For proof of concept, the case with PS288 and Ag@PS480 is also presented in Figure S7 (Supporting Information).

When a corresponding mixture of template particles was used, e.g., Ag@PS288 and PS480 (Figure S8, Supporting Information), a material can be realized with Ag present in the small pores. Whereas, the change in mass due to the attachment of the Ag particles was beneficial for the preparation of a structurally ungraded Ag-graded material (see above), now the opposite is the case. The higher mass of the Ag@PS288 causes a very similar sedimentation behavior to PS480 during the UZ procedure. The resulting structural gradient is only weak.

For the sake of completeness, a carbon material with a structural gradient but not regarding the Ag content can be prepared by using Ag@PS288 and Ag@480 as template particles (Figure S9, Supporting Information).

The next important question is, whether the described method is applicable for the modification of the carbon matrix rather than surface functionalization, as discussed in the previous paragraphs. In particular, the introduction of heteroelements as substituents into carbon is highly interesting because of the expected electronic effects (e.g., doping). As a proof of concept, we identify nitrogen-doped carbon materials as our target because it has aroused large attention for numerous applications.[33] The required template particles were prepared according to the method published by Wu et al. on PS with a shell of polyaniline (PA).[34] Analytical data for the polyaniline-polystyrene (PAPS) particles used here are given in Figure 5 (Supporting Information). The thickness of the PA shell is of the order of ~20 nm according to TEM data. In contrast to the PS particles which decompose without residue, the PAPS particles show a remaining mass of 9.1% consisting of nitrogen-doped carbon after thermal decomposition. Thus, we expect a nitrogen doping of the porous carbon matrix during carbonization, when we use PAPS as template particles for the generation of the pores (Figure 4). Consequently, PAPS522 was used together with PS288 as template particles, aiming at a carbon material with gradients in porosity and nitrogen doping. Again, SEM images (Figure 4a) prove that the generation of a structural gradient works almost perfectly. The chemical gradient is confirmed by EDX data taken from the different positions along the gradient (Figure 4b). According to X-ray photoelectron spectroscopy (XPS, Figure 4c), nitrogen is included in the carbon matrix, as suspected. We can identify N atoms that have been incorporated with coordination number (CN = 2; pyridine-like) and CN = 3 (graphitic) (Figure 4d). In addition, there is a small fraction of oxidized nitrogen species present. The amount of nitrogen determined by XPS (2.1 wt%) confirms the value received by EDX measurements (Figure 4b). The XPS

![Figure 3.](image-url)

**Figure 3.** a) SEM images (top; scale bars = 1 µm) of a carbon material with a structural and functional gradient (silver) prepared using PS137 and Ag@PS480 as template particles. b) Correlation of the Ag content and $\chi_{\text{small pores}}$ with the rel. position in the gradient $x$ (the corresponding positions are illustrated in Figure S13a in the Supporting Information).
signal in the C1s spectrum (284.4 eV; not shown) is in agreement with the presence of mainly sp²-hybridized, turbostatic carbon. In-line with our finding, the combination of Ag@PS480 and PAPS522 particles leads to a material with almost homogeneous distribution of pores, Ag and N because of their very similar sedimentation behavior in the RF sol; data shown in Figure S11 (Supporting Information).

Next, we want to check some of the functional properties of materials, as shown in Figure 4, which are influenced by the combination of the structural and the functional gradients. In the field of porous materials, it is well-known, the pore size largely influences the adsorption behavior. The correlation of vapor pressure and pore size is described by Kelvin equation, for instance. The phenomena can be documented by measuring gas-adsorption isotherms. Compared to materials, which contain only one pore size, the gradient materials show a gas uptake over the entire pressure range, meaning that the adsorption process is spatially selective (Figure 5a,b).

The special feature of the material shown in Figure 4 is, thus, the affinity of the material toward gases follows the structural gradient. In addition, several researcher have noted the high potential of porous, nitrogen-doped carbon materials for carbon-captured applications. Therefore, the CO₂ uptake characteristics was investigated (Figure 5c). Compared to nitrogen-doped carbon reported in the literature,[35–37] the capacities we find for our material is very good, and it can be expected that it also follows the structural gradient. CO₂ capture of nitrogen-doped materials is interesting, because of the added functionality of carbon as an electrode in electrocatalysis or photocatalysis.[1,38–43]

We found during the I–V curves, proper electric contacting is a demanding task, which is why we observed inconclusive results for the electrochemical reduction of CO₂, for instance, in aqueous solution, which cannot be reported yet and require much more careful experiments.
2.4. Porous Carbon with Double Chemical Gradient

The final task is to bring all strategies mentioned until this point together for preparing a carbon material with unprecedented complexity. For the realization of a structural gradient combined with a chemical gradient, the structure of the material can be adjusted by the selection of differently sized template particles. Ultimately, it was possible to create materials characterized by a double gradient (Ag and N). This combination was selected by purpose.

Ag-containing porous carbon\(^{[51]}\) and N-containing carbon materials\(^{[36]}\) have not only attracted interest (separately) because of their properties in the electrocatalytic \(\text{CO}_2\) conversion and carbon capture applications\(^{[52]}\), but the combination has been shown to provide high selectivities regarding the formation of \(\text{C}_2\) products such as ethanol.\(^{[53]}\) Dinh et al. describe in a groundbreaking paper in 2018\(^{[54]}\) that it is very important to control the concentration of \(\text{CO}_2\) at the catalytically active positions, what seems to be possible with our material in principle. In addition, we demonstrated, there is also an energy gradient created by the controlled doping. Therefore, we believe our gradient materials can be used in the future for studying cooperativity in much more detail and find (in one material) the ideal structure – Ag content–N content combination. In addition, considering the additional structural gradient, one can expect to design mass transport and gas adsorption in the material. However, the necessary, thorough electrocatalytic studies have to be described in a separate paper.

In the future, our method will prove to be even more versatile, because PS colloids cannot only be modified by Ag or polyaniline as described here, but many different hybrid systems exist.

3. Conclusion

The use of chemically modified template particles has been proven to be extremely versatile for the preparation of porous carbon materials containing a defined chemical combined with a structural gradient. The structure of the material can be adjusted by the selection of differently sized template particles. Ultimately, it was possible to create materials characterized by a double gradient (Ag and N). This combination was selected by purpose. Ag-containing porous carbon\(^{[51]}\) and N-containing carbon materials\(^{[36]}\) have not only attracted interest (separately) because of their properties in the electrocatalytic \(\text{CO}_2\) conversion and carbon capture applications\(^{[52]}\), but the combination has been shown to provide high selectivities regarding the formation of \(\text{C}_2\) products such as ethanol.\(^{[53]}\) Dinh et al. describe in a groundbreaking paper in 2018\(^{[54]}\) that it is very important to control the concentration of \(\text{CO}_2\) at the catalytically active positions, what seems to be possible with our material in principle. In addition, we demonstrated, there is also an energy gradient created by the controlled doping. Therefore, we believe our gradient materials can be used in the future for studying cooperativity in much more detail and find (in one material) the ideal structure – Ag content–N content combination. In addition, considering the additional structural gradient, one can expect to design mass transport and gas adsorption in the material. However, the necessary, thorough electrocatalytic studies have to be described in a separate paper.

In the future, our method will prove to be even more versatile, because PS colloids cannot only be modified by Ag or polyaniline as described here, but many different hybrid systems exist.

4. Experimental Section

Materials: Sodium styrene sulfonate (NaSS, >90%), sodium carbonate (Na\(_2\)CO\(_3\), >99.8%), polyvinylpyrrolidone (PVP) K-30, ammonium persulfate (>97%), and potassium persulfate (KPS, >99%) were purchased from Sigma-Aldrich. Sodium sulfite (Na\(_2\)SO\(_3\), >97%), sodium bicarbonate (NaHCO\(_3\), >99.7%), resorcinol (>99%), and styrene (>99%) were purchased from Merck. Aniline (>99.8%) was purchased from ACROS organics. Silver nitrate (>99.9%) was purchased from abcr. Aqueous formaldehyde solution (37 wt%) was purchased from Roth. Styrene was distilled in vacuum at 40 °C before use to remove the polymerization inhibitor; all other chemicals were used as received. Deoxygenated Milli-Q grade water was used for all experiments.

Preparation of Template Particles: Sulfonated PS nanoparticles of different sizes were synthesized by emulsifier free emulsion copolymerization of styrene and NaSS. After synthesis, the nanoparticle dispersions were purified by dialysis against water. The particles were further functionalized with either silver nanoparticles using a polyol process\(^{[55]}\) or a polyaniline shell by oxidative polymerization,\(^{[34]}\) as both reported elsewhere. Detailed synthetic procedures are given in the Supporting Information.

Preparation of Sulfonated Polystyrene Nanoparticles: Spherical polystyrene nanoparticles were synthesized by emulsifier free emulsion copolymerization of styrene and NaSS. After synthesis, the nanoparticle dispersions were purified by dialysis against water. The particles were further functionalized with either silver nanoparticles using a polyol process\(^{[55]}\) or a polyaniline shell by oxidative polymerization,\(^{[34]}\) as both reported elsewhere. Detailed synthetic procedures are given in the Supporting Information.

Figure 5. a) Nitrogen physisorption isotherm (adsorption and desorption branches) of a material with combined structural and chemical (N) gradients. b) Correlation to spatial filling of pores with the adsorbent. c) Carbon capture application (\(\text{CO}_2\) uptake) of the material. d) Proposed energy gradient structure of the electrode created by spatially controlled nitrogen doping.
under stirring (350 rpm) for 10 min, NaSS solution (10 mL, 0.194 mol L⁻¹) was added. After a further equilibration for 5 min, KPS solution (5 mL, 0.019 mol L⁻¹) was added, followed by the addition of KPS solution (5 mL, 0.312 mol L⁻¹) after an additional equilibration time of 10 min. The reaction was heated to 80 °C using an oil bath under continuous stirring. After 3 h, the resulting milky dispersion was cooled to room temperature and filtrated. PS488 and PS522 were prepared by a seeded growth approach. A dispersion of purified particles (PS288 25 mL, 7.9 wt% polystyrene) containing Na₂SO₃ (1.49 mmol) was mixed with water (80 mL). Styrene (11.6 and 14.4 mL, respectively) was added, the reaction was equilibrated for 20 min under stirring. The reaction was initiated by the addition of KPS (5 mL, 0.053 mol L⁻¹) and heating the reaction to 60 °C inside an oil bath. After 18 h, the resulting milky dispersion was cooled to room temperature and filtrated. P538 was synthesized using a procedure reported by Howe and co-workers. A three-necked flask containing NaSS solution (300 mL, 16.2 mmol L⁻¹) was heated to 80 °C inside an oil bath. After equilibration for 10 min, 2 mL styrene was quickly added followed by the addition of KPS solution (10 mL, 370 mmol L⁻¹) to achieve the formation of seeding particles. These seeds were grown to 38 nm by addition of further styrene monomer (11 mL) with a speed of 2 mL h⁻¹. After 18 h, the resulting milky dispersion was cooled to room temperature and filtrated.

Synthesis of Ag@Polystyrene Nanoparticles: Silver-functionalized polystyrene nanoparticles were prepared as reported elsewhere. Purified sulfonated polystyrene nanoparticle dispersion (20 mL, 7.9 wt% polystyrene) containing PVP K-30 (2 g) and AgNO₃ (0.942 mmol) was mixed with ethylene glycol (88 g) and equilibrated for 30 min. The reaction was heated to 90 °C for 12 h, cooled to room temperature, and mixed with ethanol (volume ratio: 50:50). The Ag@polystyrene nanoparticles were collected by centrifugation, washed 3 times with water, and stored in dispersion.

Synthesis of PAPS Nanoparticles: PAPS core–shell particles were synthesized as described elsewhere. Aqueous aniline suspension (10 mL, 0.644 mol L⁻¹) was added to a dispersion of purified particles (PS522, 40 mL, 9.0 wt% polystyrene). This suspension was homogenized for 30 min by ultrasonication. The reaction vessel was then cooled to 0 °C and ammonium persulfate solution (20 mL, 0.322 mol L⁻¹) was quickly added, resulting in a brown color. Subsequently, hydrochloric acid (12.9 mL, 0.5 mol L⁻¹) was dropwise added (0.3 mL min⁻¹), resulting in a deep green color. The reaction was allowed to continue for 5 h at 0 °C and further stirred at room temperature for 12 h. The resulting nanoparticles were collected by centrifugation, washed 3 times with water, and stored in dispersion.

Synthesis of Carbon Materials: A RF sol was prepared by mixing resorcinol (3.77 g) with aqueous formaldehyde solution (37 wt%, 10 mL). PS–RF composites were prepared in a Beckman Optima L-70 ultracentrifuge (Beckman Instruments) equipped with a swinging-bucket rotor (SW 55 Ti, Beckman Instruments) by mixing RF solution (1.8 mL), PS dispersions (1 mL total, for detailed parameters, see Table S1 in the Supporting Information), and sodium carbonate solution (75 µL, 1.51 mol L⁻¹) in polyallomer (13 × 51 mm) centrifuge tubes. The resulting precursor was then centrifuged at 40 °C, 20 000–30 000 rpm, and for typically 12 h. Due to the lower density of polystyrene nanoparticles as compared to RF, the centrifugal force led to a flotation of the nanoparticles. The following gelation of the RF sol during the centrifugation led to a fixation of the formed structure, resulting in a RF–PS composite. This composite was then separated from the remaining sample and aged at 85 °C for 3 days followed by drying at 85 °C for 1 day. Afterward, the PS–RF composite was calcined at 900 °C for 3 h (heating ramp 5 °C min⁻¹) in a flow of N₂ to carbonize the RF and at the same time remove the polystyrene template, yielding a monolithic porous carbon material, while the additional surface functionalities were incorporated into the porous carbon.
Material Characterization—TEM: Samples for TEM analysis were prepared by drop casting diluted dispersions onto carbon coated copper grids. After evaporation of the solvent, high resolution (HR)-TEM images were acquired with a JEOL JEM 2200FS at an accelerating voltage of 200 kV and a Zeiss Libra120 at an accelerating voltage of 120 kV.

Material Characterization—SEM and EDX: For SEM imaging, monolithic carbon samples were cut into two pieces along the direction of the centrifugal force. Images were then acquired at several positions along the resulting cross-section using a Zeiss field-emission (FE)-SEM Auriga Crossbeam operating at 3–15 kV. EDX data were recorded at the same positions using an Oxford Instruments X-MaxN 20 mm² Silicon Drift Detector mounted onto the microscope.

Material Characterization—PXRD: X-ray diffractions were performed with a Bruker AXS D8 Advance diffractometer using Cu-Kα radiation.

Material Characterization—TGA: TGA measurements were performed using a Netzsch STA 429 F3 Jupiter. XPS measurements were performed by Tascon GmbH, Sulzbach, Germany. PESA spectra were recorded using a Riken Keiki AC-2 Photoelectron Spectrometer. Fourier-transform infrared (FT-IR) spectra were obtained with a Perkin-Elmer instrument.

Material Characterization—TriStar II 3020. Adsorption isotherms were determined using a Micromeritics ASAP 2020. Equilibration intervals of 60 s were used. Adsorption isotherms were corrected by additional blank tube measurements.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
aerogels, functional gradient materials, hierarchical porosity, surface modification, templates

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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